David Jou
José Casas-Vázquez
Georgy Lebon

Extended Irreversible Thermodynamics

Fourth Edition

Springer

Extended Irreversible Thermodynamics

David Jou • José Casas-Vázquez • Georgy Lebon

Extended Irreversible Thermodynamics

Fourth Edition

Springer

David Jou
Autonomous University of Barcelona
Bellaterra, Catalonia
Spain

José Casas-Vázquez
Autonomous University of Barcelona
Bellaterra, Catalonia
Spain

Georgy Lebon
University of Liège
Belgium

ISBN 978-90-481-3073-3 e-ISBN 978-90-481-3074-0
DOI 10.1007/978-90-481-3074-0
Springer New York Dordrecht Heidelberg London

Library of Congress Control Number: 2009941949

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Preface to the Fourth Edition

The fast progress in many areas of research related to non-equilibrium thermodynamics has prompted us to write a fourth edition of this book. Like in the previous editions, our main concern is to open the subject to the widest audience, including students, teachers, and researchers in physics, chemistry, engineering, biology, and materials sciences. Our objective is to present a general view on several open problems arising in non-equilibrium situations, and to afford a wide perspective of applications illustrating their practical outcomes and consequences. A better comprehension of the foundations is generally correlated to an increase of the range of applications, implying mutual feedback and cross fertilization. Truly, thermodynamic methods are widely used in many areas of science but, surprisingly, the active dynamism of thermodynamics as a field on its own is not sufficiently perceived outside a relatively reduced number of specialized researchers.

Extended irreversible thermodynamics (EIT) goes beyond the classical formalisms based on the local equilibrium hypothesis; it was also referred to in an earlier publication by the authors (Lebon et al. 1992) as a *thermodynamics of the third type*, as it provides a bridge between classical irreversible thermodynamics and rational thermodynamics, enlarging at the same time their respective range of application. The salient feature of the theory is that the fluxes are incorporated into the set of basic variables. The urge and interest of elevating the fluxes to a central role is illustrated by our everyday experience, the fluxes of people, of goods, of money, of energy, of pollutants, of information, are among the main protagonists of our epoch of globalization. Lowering or exceeding some critical values of the fluxes may be determinant in the survival or collapse of our economical and (or) social system as it has been dramatically illustrated by financial and economical crises. Fluxes are not only essential in social sciences, but also in biology: complex and delicate networks of fluxes of matter, energy and information are basic to life. Thus, paying a special attention to the fluxes seems in tune with science and society of our time. This does not mean that they are the only possible choice for describing systems beyond local-equilibrium, but certainly they are a logical and appealing possibility, worth of exploration.

Our aim in this new edition is to update the previous versions by including new materials and new applications to parallel the vertiginous developments of modern technology. To enhance the pedagogical value of the book, we have increased the number of applications, and figures comparing theory and experimental results.

In comparison with the third edition, the present one has been extensively remodelled. Several fundamental chapters have been restructured and rooted on intuitive physics rather than on lengthy mathematical expressions. Fundamental questions as the definition of temperature, entropy, fluctuations of the fluxes, and the nature of boundary conditions are now becoming clearer than some years ago, and have deserved a new presentation. More explicitly, a new chapter 10 on heat transport at micro- and nano-scales is included; Chaps. 2, 11, 13 and 15 have been revisited in depth, and several new sections have been added throughout the book. Some particular subjects or mathematical developments which can be omitted in a first reading have been collected in boxes. Other aspects treated with detail in the authors' other books *Understanding non-equilibrium thermodynamics* (Springer 2008) and *Thermodynamics of fluids under flow* (Springer 2000) have been suppressed in this new edition. Some misprints in the previous edition have been corrected, and the set of proposed problems has been slightly enlarged and updated.

The present edition has benefited from the precious technical help of Drs. V. Méndez and V. Ortega-Cejas. We are indebted to Dr. P. Galenko for his contribution to Sect. 13.7 and for promoting the Russian translation of our book (*Rasshirenaia Neobratimaia Thermodinamika*, published by Reguliarnaia Kaoticheskaia Dinamika, Moscow-Itzvhesk, 2007). Fruitful discussions with many other colleagues, among which the late Prof. A.M. Anile, are gratefully acknowledged in the prefaces of the previous editions. David Jou and José Casas-Vázquez have benefitted from the Grants BFM2000–0351-C03–01, BFM2003–06033, FIS2006–12296-C02–01 of the Spanish Ministry of Education and Science, and 1999SGR00095, 2001SGR00186 and 2005SGR00087 of the DGR of the Generalitat of Catalonia, Georgy Lebon acknowledges partial financial support from the ESA Prodex Belgium Program.

Bellaterra, Barcelona
Liège
July 2009

David Jou
José Casas-Vázquez
Georgy Lebon

Preface to the Third Edition

In writing this third edition, we proceeded having in mind two main objectives: pedagogy and physics. One of our essential concerns is indeed to open the subject to a large audience of scientists with a diversity of interests. This is the reason we have emphasized the pedagogical aspects, starting with the simplest situations before treating more complex problems. Our aim is to show that thermodynamics is not restricted to the study of purely thermal phenomena but that it largely covers many different areas, going from continuum mechanics to statistical physics, from nuclear collisions to cosmology, by passing, for instance, through chemistry, rheology and biology.

Our second objective is to stress the physical aspects in their broadest sense, i.e. trying to clarify the foundations and relating the theoretical results with experimental data and applications, rather than introducing formal and lengthy developments. Important sections of the book are devoted to the discussion of fundamental notions, such as the selection of basic variables, the definition of entropy, temperature, pressure, and chemical potential outside equilibrium and the statement of the second law. We feel that these crucial questions deserve special attention when they cross the borders of classical theories. We have included new original results and opened the door to new extensions and applications.

For the student or the researcher it may be stimulating to go beyond the classical theories and to discover a domain of new ideas, new applications, and new problems. This is what extended irreversible thermodynamics (EIT) offers nowadays: it does not pretend to solve all the problems raised in continuum physics and statistical mechanics, but it can be viewed as an emergent new global framework of non-equilibrium thermodynamics and a rapidly advancing frontier with new applications being treated and fundamental questions being asked and tentatively clarified.

This edition has been extensively remodelled compared to the first two. We have gone from 12 to 18 chapters as a result of splitting some of the former chapters into shorter ones and focusing better on the foundations and on the introduction to the basic ideas of the latest developments. As for the two preceding editions, we have clearly separated the structure of the book into three parts, namely the general theory (Part I), microscopic foundations (Part II), and selected applications (Part III). Amongst the most visible changes, we have split the general presentation of EIT into two chapters: Chap. 2 devoted to establishing the transport equations and dynamical aspects, and Chap. 3 in which we introduce the non-equilibrium equations of state emphasizing the meaning of entropy and temperature in non-equilibrium states. Comparison with the rational version of extended thermodynamics has been made more explicit. Chapter 4 shows an overview of Hamiltonian formulations, which have developed in recent years into a promising domain.

The microscopic foundations are discussed in Chaps. 5–9, with two new chapters concerning information theory and computer simulations. Both topics were already present in the former editions as subsections of other chapters, but recent developments have justified a renewed and updated presentation.

Applications cover half of the book: nine chapters from the total 18. They show that the exploration of new theoretical grounds is both an intellectual challenge and a source of new practical possibilities. Since contemporary technology strives towards higher speed, power, and miniaturization, the transport equations must incorporate memory, non-local, and non-linear effects. Compared to the generalised transport equations incorporating the aforementioned effects, EIT plays a role similar to that played by classical irreversible thermodynamics with respect to the classical transport equations. Diffusion and electrical phenomena, treated in a single chapter in the previous editions, are the subject of two different, updated chapters; the relativistic formulation has also been split into two different chapters, one devoted to the foundations and the other to cosmological applications. Finally, let us mention that a wide overview of the literature on EIT as well as the solutions to the proposed problems can be found on the http://telemaco.uab.es website.

This book, in its successive editions, has widely benefited from the fruitful suggestions and comments by colleagues, including M. Anile, J. Camacho, M. Criado-Sancho, L.S. García-Colín, M. Grmela, P.T. Landsberg, R. Luzzi, W. Muschik, D. Pavón, M. Torrisi, A. Valenti and many others. We acknowledge the financial support of the DGICyT of the Spanish Ministry of Education and Culture under Grant Nos. PB90–0676 and PB94–0718, of the DGR of the Generalitat of Catalonia, under Grant Nos. 1997SGR 00378 and 2000SGR 00095, of the Belgian Ministry of Scientific Policy under PAI Grant Nos. 21, 29 and IV 6, and a grant from the European Union in the framework of the Program of Human Capital and Mobility (European Thermodynamic Network ERB-CHR XCT 920 007).

Bellaterra, Barcelona
Liège
March 2001

David Jou
José Casas-Vázquez
Georgy Lebon

Preface to the First Edition

Classical irreversible thermodynamics, as developed by Onsager, Prigogine and many other authors, is based on the local-equilibrium hypothesis. Out of equilibrium, any system is assumed to depend locally on the same set of variables as when it is in equilibrium. This leads to a formal thermodynamic structure identical to that of equilibrium: intensive parameters such as temperature, pressure and chemical potentials are well-defined quantities keeping their usual meaning, thermodynamic potentials are derived as Legendre transformations and all equilibrium thermodynamic relations retain their validity. The theory based on this hypothesis has turned out to be very useful and has collected a number of successes in many practical situations.

However, the recent decade has witnessed a surge of interest in going beyond the classical formulation. There are several reasons for this. One of them is the development of experimental methods able to deal with the response of systems to high-frequency and short-wavelength perturbations, such as ultrasound propagation and light and neutron scattering. The observed results have led to generalisations of the classical hydrodynamical theories, by including memory functions or generalised transport coefficients depending on the frequency and the wavevector. This field has generated impressive progress in non-equilibrium statistical mechanics, but for the moment it has not brought about a parallel development in non-equilibrium thermodynamics. An extension of thermodynamics compatible with generalised hydrodynamics therefore appears to be a natural subject of research.

An additional reason has fostered an interest in generalising the classical transport equations, like Fourier's law for heat conduction, Fick's law for diffusion, and Newton's law for viscous flow. It is well known that after introducing these relations in the balance equations, one is led to parabolic partial-differential equations which imply that perturbations propagate with infinite speed. This behaviour is incompatible with experimental evidence and it is also disturbing from a theoretical point of view, because collective molecular effects should be expected to propagate at finite velocity, not only in a relativistic framework, but even from a non-relativistic point of view. This unpleasant property can be avoided by taking into account the finite nonvanishing relaxation time of the respective fluxes, e.g. heat flux, diffusion flux, momentum flux, sometimes generically called dissipative fluxes. The subsequent equations are however not compatible with the classical non-equilibrium thermodynamics, since they lead in some circumstances to negative entropy production. Thus, a thermodynamic theory compatible with these phenomena is highly desirable, because it may provide new insights into the meaning and definition of fundamental thermodynamic quantities, as entropy and temperature, and may clarify the limits of validity of the local-equilibrium hypothesis and of the usual formulations of the second law out of equilibrium.

The former problems are not merely academic. It has been observed in several systems that the dissipative fluxes are characterized by long relaxation times. Typical examples are polymeric fluids, heat and electric conductors at low temperature, superconductors, and so on. An accurate understanding of these systems may thus be important not only from a theoretical point of view, but also for practical purposes. In real situations, these systems are out of equilibrium. Accordingly, there is an urgent need for a non-equilibrium thermodynamic theory able, on the one hand, to cope with the effects of long relaxation times and, on the other, to complement other formalisms based on the use of internal variables.

There are other reasons for the present study. One should be aware that classical irreversible thermodynamics is not the only non-equilibrium thermodynamic theory: other theories, in particular the so-called rational thermodynamics, have achieved some valuable results. To reconcile the classical and the rational points of view, it would be of interest to have a theory able to provide a sufficiently wide ground for discussion, thus making their common points evident and their main differences understandable. Extended irreversible thermodynamics is a promising candidate.

Extended irreversible thermodynamics received a strong impetus in the past decade. Besides the classical thermodynamic variables, this theory introduces as new independent variables the dissipative fluxes and aims to obtain for them evolution equations compatible with the second law of thermodynamics. The central quantity is a generalised non-equilibrium entropy, depending on both the conserved variables and the fluxes, which sheds new light on the content of the second law. This generalised theory is corroborated from a microscopic point of view by the kinetic theory, non-equilibrium information theory and other formulations of non-equilibrium statistical mechanics.

The purpose of this book is to provide an introduction to the foundations of extended irreversible thermodynamics, to discuss the main results and to present some of its applications. After more than twenty years of research and several hundreds of papers published by many groups in several countries we feel such a book is sorely needed. Guided by the aim to be as illustrative and pedagogical as possible, a relatively simple formulation of the theory is presented, but this is nevertheless more than sufficient for the description of several phenomena not accessible to the classical theory. The various topics treated in this book range from thermal waves and phonon hydrodynamics to material and electrical transport, from ultrasound propagation and generalised hydrodynamics to rheology, from kinetic theory to cosmology. Of course, other formulations of extended thermodynamics and other kinds of applications are possible. They are likely to arise in the near future. We hope that this book will be useful in providing a general view of present achievements and in stimulating future research.

We are very pleased to acknowledge many stimulating discussions with our colleagues Carlos Pérez-García, Josep-Enric Llebot, Diego Pavón, José-Miguel Rubí and Joseph Lambermont for more than fifteen years of joint research, and also with many other colleagues from the different groups which have devoted their attention to extended irreversible thermodynamics. We also acknowledge the financial support of the Comisión Asesora para la Investigación Científica y Técnica of the Spanish Government during the years 1979–1986 under grants 3913/79 and 2389/83, and of the Dirección General de Investigación Científica y Técnica of the Spanish Ministry of Education, under grants PB86–0287, PB89–0290, and PB90–0676. The collaboration between our groups in Bellaterra and Liège has been made economically possible because of the NATO grant 0355/83.

Bellaterra, Barcelona
Liège
March 1993

David Jou
José Casas-Vázquez
Georgy Lebon

Contents

Part I General Theory

Part II Microscopic Foundations

Part III Selected Applications

Part I
General Theory

Chapter 1
Classical, Rational and Hamiltonian Formulations of Non-equilibrium Thermodynamics

The nineteenth century was the golden age for classical thermodynamics: as this theory concerns essentially systems at equilibrium, we shall refer to it as equilibrium thermodynamics. It was developed by a pleiad of exceptionally brilliant scientists as Carnot, Mayer, Joule, Helmholtz, Clausius, Lord Kelvin, Maxwell, Boltzmann, Gibbs, Planck, Duhem, etc.

Equilibrium thermodynamics is based on two major statements:

1. The energy of the universe is constant (first law).
2. The entropy of the universe never decreases (second law).

Only in the first half of the twentieth century it was felt necessary to go beyond the equilibrium approach. Lars Onsager published two seminal and pioneering papers on non-equilibrium thermodynamics in the Physical Review in 1931 (Onsager 1931). The merit of Onsager was recognized by the Nobel Foundation, which awarded him the Nobel Prize for chemistry in 1968. Other fundamental contributions to non-equilibrium thermodynamics are due to Eckart, Meixner and Prigogine (Nobel Prize for chemistry in 1977). The formalism proposed by Onsager, Eckart, Meixner, and Prigogine is usually referred to as classical irreversible thermodynamics (CIT). This theory has seen an extraordinary expansion since the 1940s and has been widely applied in physics, biophysics, chemistry and engineering science. Excellent papers and monographs on the subject are those of Eckart (1940), Meixner and Reik (1959), Prigogine (1961), and de Groot and Mazur (1962). Other useful contributions are Denbigh (1950), Haase (1969), Gyarmati (1970), Woods (1975), Lavenda (1979), Kreuzer (1981), Kjelstrup and Bedeaux (2008), Lebon et al. (2008b) among many others.

In this chapter, a broad outline of classical non-relativistic irreversible thermodynamics is presented. Although CIT has been able to describe a large number of non-equilibrium processes in complete agreement with experiment, it suffers from some limitations: several phenomena do not comply with the framework of CIT. Efforts have been made to enlarge the range of application of CIT and these emerge in the formulation of a new theory, called by its authors rational thermodynamics (RT). This formalism, mainly developed by Coleman (1964), Truesdell (1968, 1984) and Noll (1974), has significantly contributed to the advancement of the knowledge

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_1,

of continuum thermodynamics, and it is our opinion that this subject deserves a place in this review section.

In parallel to the above approaches, a Hamiltonian structure of non-equilibrium thermodynamics has also been developed. It was originally proposed as a generalization of the Poisson bracket formalism (Grmela 1984) and more recently Grmela and Öttinger (1997) have arrived at a new framework known as GENERIC (General Equation for the Non-Equilibrium Reversible–Irreversible Coupling) (see also Öttinger 2005). The main merit is to impose restrictions on the reversible part of the evolution equations while the previous formalisms, in particular CIT and RT, place solely restrictions on the irreversible part. In GENERIC, the evolution equations are expressed in terms of two potentials, energy and entropy, generalizing Landau's potential (Landau and Lifshitz 1985) widely used in mechanics and fluid dynamics. GENERIC has been extensively applied to the modelling of the flow properties of rheological fluids. The main ideas underlying this theory are briefly presented in the last section of the present chapter.

1.1 The General Balance Laws of Continuum Physics

This section is preparatory to all the other sections and will concern the establishment of the general balance laws of mass, momentum, and energy. Here, for the sake of simplicity, relativistic effects are not considered. We consider a portion of matter of mass M occupying a volume V limited by a boundary Σ. We suppose that the continuum hypothesis holds and that for any extensive quantity B one has

$$\lim_{\Delta M \to 0} \frac{\Delta B}{\Delta M} = b, \qquad \lim_{\Delta M \to 0} \frac{\Delta B}{\Delta V} = \rho b \quad \text{or} \quad B = \int_V \rho b \mathrm{d}V,$$

where ρ is the total mass density and b the specific value of B referred to per unit mass.

The most general form of the balance equation for any quantity b is given by

$$\int_{V(t)} \frac{\partial}{\partial t}(\rho b)\mathrm{d}V = -\int_{\Sigma(t)} \boldsymbol{J}^b \cdot \boldsymbol{n}\mathrm{d}\Sigma + \int_{V(t)} \sigma^b \mathrm{d}V, \tag{1.1}$$

where $\partial/\partial t$ is the local or Eulerian time derivative, a middot means the scalar product, $\boldsymbol{J}^b$ represents the quantity B flowing per unit area and unit time through the boundary Σ, $\boldsymbol{n}$ is the positive unit normal to Σ, oriented by convention in the outward direction of the volume V, and σ^b is the rate of production (>0) or destruction (<0) per unit volume of the quantity B. The flux $\boldsymbol{J}^b$ is a vector (or tensor) if b is a scalar (or vector), and σ^b has the same tensorial rank as b. Assuming that (1.1) is valid for any volume V and that the integrands are continuous functions of position, one obtains the following local form of the balance equation:

$$\frac{\partial}{\partial t}(\rho b) = -\nabla \cdot \boldsymbol{J}^b + \sigma^b, \tag{1.2}$$

after use is made of Gauss' theorem,

$$\int \boldsymbol{J}^b \cdot \boldsymbol{n} \mathrm{d}\Sigma = \int \nabla \cdot \boldsymbol{J}^b \mathrm{d}V,$$

where ∇ denotes the nabla operator. When σ^b is zero, the quantity b is said to be conserved.

If the integrands in (1.1) are not continuous, there exist discontinuities inside the volume taking for example the form of a surface. By imposing balance laws on a volume surrounding the discontinuity surface and letting the volume go to zero, one obtains the so-called jump conditions. Under rather general conditions (Truesdell and Toupin 1960), it is possible to show that relation (1.2) leads to the jump condition

$$-[\rho v_n b] + [\boldsymbol{n} \cdot \boldsymbol{J}^b] = \sigma^b_\Sigma. \tag{1.3}$$

Brackets denote the jump of the corresponding quantity across the discontinuity; v_n is the normal speed of displacement of the surface with respect to the material and σ^b_Σ the rate of production per unit area. On a material discontinuity surface one has $v_n = 0$. Obviously, the production term σ^b_Σ vanishes for a conserved quantity. For a detailed examination of the thermodynamics of surfaces see Kjelstrup and Bedeaux (2008).

An elegant and quick derivation of the balance equations of mass, momentum and energy can be achieved by starting from the first law of thermodynamics and imposing the principle of Galilean invariance. Other criteria of invariance, like Euclidean invariance are also common in continuum physics.

1.1.1 The One-Component System

The first law of thermodynamics, which expresses the balance of total energy, takes for an electrically neutral system the form

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{\mathrm{d}W}{\mathrm{d}t} + \frac{\mathrm{d}Q}{\mathrm{d}t}, \tag{1.4}$$

with $E = U + K$; E is the total energy, equal to the sum of the internal energy U and the kinetic energy K, W is the work performed by the body forces per unit mass $\boldsymbol{F}$ and the contact forces $\boldsymbol{T}$, and Q is the heat exchanged with the outside world through the boundary. More explicitly, U, K, $\mathrm{d}Q/\mathrm{d}t$, and $\mathrm{d}W/\mathrm{d}t$ are given by

$$U = \int_{V(t)} \rho u \mathrm{d}V, \quad K = \frac{1}{2} \int_{V(t)} \rho \boldsymbol{v} \cdot \boldsymbol{v} \mathrm{d}V, \tag{1.5a}$$

$$\frac{dQ}{\mathrm{d}t} = -\int_{\Sigma(t)} \boldsymbol{q} \cdot \boldsymbol{n} \mathrm{d}\Sigma, \quad \frac{\mathrm{d}W}{\mathrm{d}t} = -\int_{\Sigma(t)} \boldsymbol{T} \cdot \boldsymbol{v} \mathrm{d}\Sigma + \int_{V(t)} \rho \boldsymbol{F} \cdot \boldsymbol{v} \mathrm{d}V, \tag{1.5b}$$

where $\boldsymbol{T}$ is related to the pressure tensor $\mathbf{P}$ by means of Cauchy's relation $\boldsymbol{T} = -\mathbf{P}\cdot\boldsymbol{n}$. The notation in (1.5a and b) is classical: u is the specific internal energy, $\boldsymbol{v}$ the velocity field, and $\boldsymbol{q}$ the heat flux vector. We now make use of the Reynolds transport theorem, which, for an arbitrary quantity b, can be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{V(t)} b\mathrm{d}V = \int_{V(t)} \frac{\partial b}{\partial t}\mathrm{d}V + \int_{\Sigma(t)} b\boldsymbol{v}\cdot\boldsymbol{n}\mathrm{d}\Sigma.$$

After substitutions of expressions (1.5) in the first law (1.4), one is led to the local form of the energy balance

$$\rho(\dot{u}+\boldsymbol{v}\cdot\dot{\boldsymbol{v}})+\left(u+\frac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v}\right)(\dot{\rho}+\rho\nabla\cdot\boldsymbol{v}) = -\nabla\cdot\boldsymbol{q}-\mathbf{P}^T : \nabla\boldsymbol{v}-\boldsymbol{v}\cdot(\nabla\cdot\mathbf{P})+\rho\boldsymbol{F}\cdot\boldsymbol{v}, \quad (1.6)$$

where superscript T means transposition, an upper dot stands for the material or Lagrangian time derivative (i.e., $\mathrm{d}/\mathrm{d}t = \partial/\partial t + \boldsymbol{v}\cdot\nabla$) and a colon the double scalar product

$$\mathbf{A} : \mathbf{B} = \sum_{i,j} A_{ij}B_{ji}.$$

A short summary of basic concepts in tensorial calculus may be found in Appendix A.

According to the Galileo principle, (1.6) must be invariant with respect to the transformation $\boldsymbol{v} \to \boldsymbol{v} + \boldsymbol{v}_0$, where $\boldsymbol{v}_0$ is a constant and uniform velocity. After substitution in (1.6) of $\boldsymbol{v}$ by $\boldsymbol{v} + \boldsymbol{v}_0$ and subtraction of (1.6), one obtains

$$\tfrac{1}{2}\boldsymbol{v}_0\cdot\boldsymbol{v}_0(\dot{\rho}+\rho\nabla\cdot\boldsymbol{v}) + \boldsymbol{v}_0\cdot[(\dot{\rho}+\rho\nabla\cdot\boldsymbol{v})\boldsymbol{v}+\rho\dot{\boldsymbol{v}}+\nabla\cdot\mathbf{P}-\rho\boldsymbol{F}] = 0. \quad (1.7)$$

This relation could be invariant with respect to $\boldsymbol{v}_0$ on condition that the following equations are satisfied:

$$\dot{\rho} = -\rho\nabla\cdot\boldsymbol{v}, \quad (1.8)$$

$$\rho\dot{\boldsymbol{v}} = -\nabla\cdot\mathbf{P} + \rho\boldsymbol{F}. \quad (1.9)$$

With these results in mind, (1.6) reduces to

$$\rho\dot{u} = -\nabla\cdot\boldsymbol{q} - \mathbf{P}^T : \nabla\boldsymbol{v}. \quad (1.10)$$

It is also convenient to express the balance of mass (1.8) in terms of the specific volume $v\ (= 1/\rho)$; this leads to

$$\rho\dot{v} = \nabla\cdot\boldsymbol{v}. \quad (1.11)$$

Relations (1.8–1.10) are the laws of balance of mass, momentum, and internal energy respectively, written in the Lagrange representation; the balance of mass is also known as the continuity equation.

Table 1.1 Fluxes and supply terms (sources)

Quantity, b	Flux, $\boldsymbol{J}^b$	Source, σ^b
Mass	$\rho\boldsymbol{v}$	0
Momentum	$\mathbf{P}+\rho\boldsymbol{v}\boldsymbol{v}$	$\rho\boldsymbol{F}$
Internal energy	$\boldsymbol{q}+\rho u\boldsymbol{v}$	$-\mathbf{P}^T : \nabla\boldsymbol{v}$

In terms of the local time derivative (Euler representation), Eqs. (1.8–1.10) take the form

$$\frac{\partial\rho}{\partial t} = -\nabla\cdot(\rho\boldsymbol{v}), \tag{1.12}$$

$$\frac{\partial(\rho\boldsymbol{v})}{\partial t} = -\nabla\cdot(\mathbf{P}+\rho\boldsymbol{v}\boldsymbol{v})+\rho\boldsymbol{F}, \tag{1.13}$$

$$\frac{\partial(\rho u)}{\partial t} = -\nabla\cdot(\boldsymbol{q}+\rho u\boldsymbol{v})-\mathbf{P}^T : \nabla\boldsymbol{v}, \tag{1.14}$$

where $\boldsymbol{v}\boldsymbol{v}$ is a dyadic product. Expressions (1.12–1.14) are useful because they allow one to identify the various fluxes and supply terms corresponding respectively to the mass, momentum, and energy, as shown in Table 1.1.

Clearly the mass is conserved. The quantities $\mathbf{P}$ and $\rho\boldsymbol{v}\boldsymbol{v}$ are the conductive and convective transport of momentum respectively; if no external (or body) force is acting on the system, momentum is conserved. Similarly, $\boldsymbol{q}$ describes the transport of internal energy due to conduction, while $\rho u\boldsymbol{v}$ is the contribution arising from convection; the term $-\mathbf{P}^T : \nabla\boldsymbol{v}$ represents the internal energy supply.

Addition of (1.13), after scalar multiplication by $\boldsymbol{v}$, and (1.14) yields the balance equation of total energy:

$$\frac{\partial}{\partial t}\left[\rho\left(u+\tfrac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v}\right)\right] = -\nabla\cdot\left[\boldsymbol{q}+\rho\left(u+\tfrac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v}\right)\boldsymbol{v}+\mathbf{P}\cdot\boldsymbol{v}\right]+\rho\boldsymbol{F}\cdot\boldsymbol{v}, \tag{1.15}$$

from which it follows that in the absence of external force the total energy is conserved.

For later use, we split the velocity gradient (a tensor) into a symmetric and an antisymmetric part

$$\nabla\boldsymbol{v} = \mathbf{V}+\mathbf{W}, \tag{1.16}$$

with

$$\mathbf{V} = \tfrac{1}{2}\left[\nabla\boldsymbol{v}+(\nabla\boldsymbol{v})^T\right], \mathbf{W} = \tfrac{1}{2}\left[\nabla\boldsymbol{v}-(\nabla\boldsymbol{v})^T\right],$$

or, in Cartesian coordinates,

$$V_{ij} = \frac{1}{2}\left(\frac{\partial v_j}{\partial x_i}+\frac{\partial v_i}{\partial x_j}\right), W_{ij} = \frac{1}{2}\left(\frac{\partial v_j}{\partial x_i}-\frac{\partial v_i}{\partial x_j}\right).$$

The rate of deformation tensor $\mathbf{V}$ may be further decomposed as

$$\mathbf{V} = \tfrac{1}{3}(\nabla \cdot \boldsymbol{v})\mathbf{U} + \overset{0}{\mathbf{V}}, \tag{1.17}$$

where $\mathbf{U}$ is the identity tensor and $\overset{0}{\mathbf{V}}$ the deviatoric traceless tensor.

Without loss of generality, the pressure tensor can be decomposed into an equilibrium part p and a viscous part $\mathbf{P}^v$:

$$\mathbf{P} = p\mathbf{U} + \mathbf{P}^v. \tag{1.18}$$

Further, the viscous pressure tensor $\mathbf{P}^v$ can be split into a scalar bulk viscous pressure p^v and a traceless deviator $\overset{0}{\mathbf{P}}{}^v$ according to

$$\mathbf{P}^v = p^v\mathbf{U} + \overset{0}{\mathbf{P}}{}^v, \tag{1.19}$$

with

$$p^v = \tfrac{1}{3}\mathrm{Tr}\,\mathbf{P}^v.$$

In the absence of intrinsic rotational motions and external couples, conservation of the angular momentum implies the symmetry of the pressure tensor (de Groot and Mazur 1962): $\mathbf{P} = \mathbf{P}^T$. Along this book, tensor $\mathbf{P}$ is assumed to be symmetric. For a hint of the physical meaning of the antisymmetric part of $\mathbf{P}$ see Problem 1.5.

1.1.2 The Multicomponent Mixture

Let us consider a system containing N different constituents labelled $k = 1, 2, \ldots, N$, with mass density ρ_k, among which take place n chemical reactions. It is assumed that every point in space is occupied simultaneously by particles of all the constituents. The balance equations of mass, momentum, and energy of the individual constituents are derived in many books and papers (e.g. De Groot and Mazur 1962; Woods 1975; Truesdell 1984) and we just list the results:

$$\frac{\partial \rho_k}{\partial t} = -\nabla \cdot (\rho_k \boldsymbol{v}_k) + \rho \sum_{l=1}^{n} \nu_{kl}\dot{\xi}_l \qquad (k = 1, 2, \ldots, N), \tag{1.20}$$

$$\frac{\partial}{\partial t}(\rho_k \boldsymbol{v}_k) = -\nabla \cdot (\mathbf{P}_k + \rho_k \boldsymbol{v}_k \boldsymbol{v}_k) + \rho_k \boldsymbol{F}_k + \Gamma_k \qquad (k = 1, 2, \ldots, N), \tag{1.21}$$

$$\begin{aligned}\frac{\partial}{\partial t}\left[\rho_k\left(u_k + \tfrac{1}{2}\boldsymbol{v}_k \cdot \boldsymbol{v}_k\right)\right] = {} & -\nabla \cdot \left[\boldsymbol{q}_k + \rho_k\left(u_k + \tfrac{1}{2}\boldsymbol{v}_k \cdot \boldsymbol{v}_k\right)\boldsymbol{v}_k + \mathbf{P}_k \cdot \boldsymbol{v}_k\right] \\ & + \rho_k \boldsymbol{F}_k \cdot \boldsymbol{v}_k + e_k. \qquad (k = 1, 2, \ldots, N)\end{aligned} \tag{1.22}$$

In (1.20), the term $\nu_{kl}\dot{\xi}_l$ represents the rate of production of constituent k in the lth chemical reaction, ν_{kl} is the stoichiometric coefficient of constituent k in the chemical reaction l times the ratio of the molecular mass of k and a constant mass, say the total mass of the reactants (ν_{kl} is positive for products of the reaction and negative for reactants), and ξ_l is the rate of advancement of reaction l. In (1.21) and (1.22), $\boldsymbol{F}_k$ is the specific body force acting on constituent k, and the quantities $\mathbf{P}_k$, $\boldsymbol{q}_k$, u_k denote respectively the partial pressure tensor, heat flux, and internal energy corresponding to component k. The production terms Γ_k in the momentum law (1.21) and e_k in (1.22) play similar roles as the mass production due to chemical reactions in (1.20): the productions Γ_k and e_k of momentum and energy contain contributions due to the interaction forces and the exchange of momentum and energy between the various components, respectively.

Let us define the total density ρ and the centre-of-mass velocity $\boldsymbol{v}$ by

$$\rho = \sum_{k=1}^{N} \rho_k \tag{1.23}$$

and

$$\rho \boldsymbol{v} = \sum_{k=1}^{N} \rho_k \boldsymbol{v}_k. \tag{1.24}$$

By mass fraction of the constituent k is meant the ratio

$$c_k = \frac{\rho_k}{\rho}, \tag{1.25}$$

with, obviously, $\sum_{k=1}^{N} c_k = 1$.

It is customary to introduce the diffusion velocity $\boldsymbol{w}_k$ and diffusion flux $\boldsymbol{J}_k$ as:

$$\boldsymbol{w}_k = \boldsymbol{v}_k - \boldsymbol{v}, \tag{1.26a}$$

$$\boldsymbol{J}_k = \rho_k(\boldsymbol{v}_k - \boldsymbol{v}), \tag{1.26b}$$

with the property

$$\sum_{k=1}^{N} \boldsymbol{J}_k = 0. \tag{1.27}$$

Bearing in mind these definitions, the balance law for the mass fraction takes the form

$$\rho \dot{c}_k = -\nabla \cdot \boldsymbol{J}_k + \rho \sum_{l=1}^{n} \nu_{kl} \dot{\xi}_l. \tag{1.28}$$

The balance equations (1.12), (1.13), and (1.15) for the total mass, momentum, and energy must be satisfied, and this requirement is reflected in the following constraint equations:

$$\sum_{k=1}^{N} \nu_{kl} = 0 \qquad (l = 1, 2, \ldots, n), \tag{1.29a}$$

$$\sum_{k=1}^{N} (\mathbf{P}_k + \rho_k \boldsymbol{w}_k \boldsymbol{w}_k) = \mathbf{P}, \qquad \sum_{k=1}^{N} \rho_k \boldsymbol{F}_k = \rho \boldsymbol{F}, \qquad \sum_{k=1}^{N} \Gamma_k = 0, \tag{1.29b}$$

$$\sum_{k=1}^{N} \rho_k \left(u_k + \frac{1}{2} \boldsymbol{w}_k \cdot \boldsymbol{w}_k \right) = \rho u, \quad \sum_{k=1}^{N} \left[\boldsymbol{q}_k + \rho \boldsymbol{w}_k (u_k + \tfrac{1}{2} \boldsymbol{w}_k \cdot \boldsymbol{w}_k) + \mathbf{P}_k \cdot \boldsymbol{w}_k \right] = \boldsymbol{q}, \tag{1.29c}$$

$$\sum_{k=1}^{N} e_k = 0. \tag{1.29d}$$

Equation (1.29a) expresses the conservation of mass in each chemical reaction. Equation (1.29b and c) indicate that the sum of the partial pressure tensors, internal energies, and heat fluxes represent only partial contributions to the total pressure tensor, internal energy, and heat flux respectively.

1.1.3 Charged Systems

In this subsection, we shall reformulate the balance equations for a mixture of N charged components subject to an electromagnetic field. Denoting by z_k the charge per unit mass of constituent k, the total charge per unit mass is given by

$$\rho z = \sum_{k=1}^{N} \rho_k z_k. \tag{1.30}$$

The current density is defined by

$$\boldsymbol{I} = \sum_{k=1}^{N} \rho_k z_k \boldsymbol{v}_k, \tag{1.31}$$

which can be cast into

$$\boldsymbol{I} = \sum_{k=1}^{N} \rho_k z_k (\boldsymbol{v}_k - \boldsymbol{v}) + \sum_{k=1}^{N} \rho_k z_k \boldsymbol{v}. \tag{1.32}$$

Defining the conduction current by

$$\boldsymbol{i} = \sum_{k=1}^{N} \rho_k z_k (\boldsymbol{v}_k - \boldsymbol{v}) = \sum_{k=1}^{N} z_k \boldsymbol{J}_k \tag{1.33}$$

and using expression (1.30), we find that (1.31) becomes

$$\boldsymbol{I} = \boldsymbol{i} + \rho z \boldsymbol{v}, \tag{1.34}$$

where $\rho z \boldsymbol{v}$ is the convection current.

We now assume, for simplicity, that the components are chemically inert and that polarization effects are negligible. The charge conservation law is directly derived from the mass fraction balance law (1.28). After multiplying (1.28) by z_k and adding up all the N constituents one obtains

$$\rho \dot{z} = -\nabla \cdot \boldsymbol{i}, \tag{1.35}$$

or, equivalently,

$$\frac{\partial}{\partial t}(\rho z) = -\nabla \cdot \boldsymbol{I}. \tag{1.36}$$

The laws of momentum and energy are obtained by using the same procedure as in Subsect. 1.1.1. The only difference with the above developments is expression $\mathrm{d}W/\mathrm{d}t$, which now contains an additional term arising from the presence of electrical forces and is given by

$$\frac{\mathrm{d}W_{\mathrm{el}}}{\mathrm{d}t} = \int_{V(t)} \sum_{k=1}^{N} \rho_k \boldsymbol{F}_k \cdot \boldsymbol{v}_k \mathrm{d}V, \tag{1.37}$$

where W_{el} is the work performed by electromagnetic forces and $\boldsymbol{F}_k$ stands for the Lorentz force acting per unit mass of constituent k,

$$\boldsymbol{F}_k = z_k(\boldsymbol{E} + \boldsymbol{v}_k \times \boldsymbol{\mathcal{B}}), \tag{1.38}$$

$\boldsymbol{E}$ being the electrical field and $\boldsymbol{\mathcal{B}}$ the magnetic induction. It is a simple exercise to show that (1.37) can be rewritten as

$$\frac{\mathrm{d}W_{\mathrm{el}}}{\mathrm{d}t} = \int_{V(t)} \sum_{K=1}^{N} [\rho_k z_k(\boldsymbol{E} + \boldsymbol{v}_k \times \boldsymbol{\mathcal{B}}) \cdot \boldsymbol{v} + \boldsymbol{i} \cdot (\boldsymbol{v} \times \boldsymbol{\mathcal{B}})] \, \mathrm{d}V. \tag{1.39}$$

Denoting by U_t the sum of the total internal energy and the diffusion energy,

$$U_t = U + \tfrac{1}{2} \int_{V(t)} \sum_{K=1}^{N} \rho_k \boldsymbol{w}_k \cdot \boldsymbol{w}_k \mathrm{d}V, \tag{1.40}$$

one can write the balance of total energy (1.4) as

$$\frac{\mathrm{d}U_t}{\mathrm{d}t}+\frac{\mathrm{d}K}{\mathrm{d}t}=\frac{\mathrm{d}Q}{\mathrm{d}t}+\frac{\mathrm{d}W_{mec}}{\mathrm{d}t}+\frac{\mathrm{d}W_{el}}{\mathrm{d}t}, \tag{1.41}$$

where K is the kinetic energy of the centre of mass,

$$K=\tfrac{1}{2}\int_{V(t)}\rho\boldsymbol{v}\cdot\boldsymbol{v}\mathrm{d}V, \tag{1.42}$$

and $\mathrm{d}W_{mec}/\mathrm{d}t$ is the power developed by the mechanical forces,

$$\frac{\mathrm{d}W_{\mathrm{mec}}}{\mathrm{d}t}=-\int_{V(t)}[\nabla\cdot(\boldsymbol{v}\cdot\mathrm{P})-\rho\boldsymbol{F}\cdot\boldsymbol{v}]\mathrm{d}V,$$

where (1.13) and (1.14) have been used.

It is readily checked that (1.41) is locally given by

$$\begin{aligned}\rho\dot{u}_t+\rho\boldsymbol{v}\cdot\dot{\boldsymbol{v}}=-\nabla\cdot\boldsymbol{q}+&\left[\rho\boldsymbol{F}-\nabla\cdot\mathbf{P}+\sum_{k=1}^{N}\rho_k z_k(\boldsymbol{E}+\boldsymbol{v}_k\times\boldsymbol{\mathcal{B}})\right]\cdot\boldsymbol{v}\\ &+\boldsymbol{i}\cdot(\boldsymbol{E}+\boldsymbol{v}\times\boldsymbol{\mathcal{B}})-P:\nabla\boldsymbol{v}.\end{aligned} \tag{1.43}$$

Let $\boldsymbol{\varepsilon}$ be the Galilean invariant quantity

$$\boldsymbol{\varepsilon}=\boldsymbol{E}+\boldsymbol{v}\times\boldsymbol{\mathcal{B}} \tag{1.44}$$

representing the electric field measured in a moving reference frame with velocity $\boldsymbol{v}$. In terms of $\boldsymbol{\varepsilon}$, (1.43) becomes

$$(-\rho\dot{\boldsymbol{v}}+\rho\boldsymbol{F}-\nabla\cdot\mathbf{P}+\rho z\boldsymbol{\varepsilon}+\boldsymbol{i}\times\boldsymbol{\mathcal{B}})\cdot\boldsymbol{v}=\rho\dot{u}_t+\nabla\cdot\boldsymbol{q}+\mathbf{P}:\nabla\boldsymbol{v}-\boldsymbol{\varepsilon}\cdot\boldsymbol{i}. \tag{1.45}$$

The invariance with respect to the Galilean transformations results in the following balance equations for momentum and internal energy:

$$\rho\dot{\boldsymbol{v}}=-\nabla\cdot\mathbf{P}+\rho\boldsymbol{F}+\rho z\boldsymbol{\varepsilon}+\boldsymbol{i}\times\boldsymbol{\mathcal{B}}, \tag{1.46}$$

$$\rho\dot{u}_t=-\nabla\cdot\boldsymbol{q}-\mathbf{P}:\nabla\boldsymbol{v}+\boldsymbol{\varepsilon}\cdot\boldsymbol{i}. \tag{1.47}$$

In addition to the mechanical forces, the momentum balance (1.46) contains extra contributions coming from the Lorentz force $\rho z\boldsymbol{\varepsilon}$ and the Laplace force $\boldsymbol{i}\times\boldsymbol{\mathcal{B}}$ acting on current $\boldsymbol{i}$. In the energy law, the supplementary contribution $\boldsymbol{\varepsilon}\cdot\boldsymbol{i}$ is identified as the rate of dissipated energy.

1.2 The Law of Balance of Entropy

In analogy with equilibrium thermodynamics, it is assumed that outside equilibrium there exists an extensive quantity S, called entropy, which is a sole function of the state variables. In general, the rate of change of S can be written as the sum of two terms:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\mathrm{d}^e S}{\mathrm{d}t} + \frac{\mathrm{d}^i S}{\mathrm{d}t}, \tag{1.48}$$

where $\mathrm{d}^e S/\mathrm{d}t$ is the rate of entropy exchanged with the surroundings, which may be zero, positive, or negative, and $\mathrm{d}^i S/\mathrm{d}t$ derives from processes occurring inside the system. According to the second law of thermodynamics, $\mathrm{d}^i S/\mathrm{d}t$ is a non-negative quantity:

$$\frac{\mathrm{d}^i S}{\mathrm{d}t} \geq 0. \tag{1.49}$$

$\mathrm{d}^i S/\mathrm{d}t$ is zero at equilibrium or for reversible transformations and positive for irreversible processes.

Without loss of generality, we can define a local specific entropy s, a local entropy flux $\boldsymbol{J}^s$, and a local rate of production σ^s, respectively:

$$S = \int_{V(t)} \rho s \mathrm{d}V, \tag{1.50a}$$

$$\frac{\mathrm{d}^e S}{\mathrm{d}t} = -\int_{\Sigma(t)} \boldsymbol{J}^s \cdot \boldsymbol{n} \mathrm{d}\Sigma, \tag{1.50b}$$

$$\frac{\mathrm{d}^i S}{\mathrm{d}t} = \int_{V(t)} \sigma^s \mathrm{d}V. \tag{1.50c}$$

After replacing (1.50a–c) in (1.48) and making use of the Gauss and Reynolds theorems, one obtains the local Lagrangian form of the entropy balance:

$$\rho \dot{s} = -\nabla \cdot \boldsymbol{J}^s + \sigma^s, \tag{1.51}$$

and, in Eulerian form, one has

$$\frac{\partial}{\partial t}(\rho s) = -\nabla \cdot (\boldsymbol{J}^s + \rho s \boldsymbol{v}) + \sigma^s, \tag{1.52}$$

with

$$\sigma^s \geq 0 \tag{1.53}$$

in either case. Inequality (1.53) goes beyond the usual formulation of the second law in equilibrium thermodynamics, where only the global increase of entropy between two equilibrium states in an isolated system is considered. Here it is assumed that the statement (1.53) holds at any position in space and any instant of time, for whatever the evolution of the system.

One of the main objectives of non-equilibrium thermodynamics is to express σ^s as a function of the quantities characterizing the irreversible processes. This is important because it displays the sources of irreversibility occurring in a process. Moreover, it will be shown later that the very form of the local rate of entropy production may serve as a guide to determine the constitutive relations describing the dynamical response of the system to external or internal solicitation.

1.3 Classical Irreversible Thermodynamics

This section is devoted to the derivation and discussion of the main results of classical irreversible thermodynamics (CIT). Here we only examine the macroscopic aspects, but it must be realized that these are deeply rooted in the microscopic point of view. The reader interested in a detailed analysis is referred to the authoritative treatises mentioned in the introduction. The range of application of CIT comprises those systems satisfying the hypothesis of local equilibrium, which is analysed in full in the next subsection.

1.3.1 The Local-Equilibrium Hypothesis

The fundamental hypothesis underlying CIT is that of local equilibrium. It postulates that the local and instantaneous relations between the thermal and mechanical properties of a physical system are the same as for a uniform system at equilibrium. It is assumed that the system under study can be mentally split into a series of cells sufficiently large to allow them to be treated as macroscopic thermodynamic subsystems, but sufficiently small that equilibrium is very close to being realized in each cell.

The local-equilibrium hypothesis implies that

1. All the variables defined in equilibrium thermodynamics remain significant. Variables such as the temperature and the entropy are rigorously and unambiguously defined just as they are in equilibrium. In each cell, these quantities remain uniform but they take different values from cell to cell; they are also allowed to change in the course of time in such a way that they depend continuously on the space and time coordinates $(\boldsymbol{r}, t)$.
2. The relationships in equilibrium thermodynamics between state variables remain valid outside equilibrium provided that they are stated locally at each instant of time. Thus, the entropy outside equilibrium will depend on the same state variables as at equilibrium.

For an N-component fluid, the specific entropy s will be a function of the specific internal energy u, the specific volume v, and the mass fractions c_k of the different components, i.e. $s(\boldsymbol{r}, t) = s[u(\boldsymbol{r}, t), v(\boldsymbol{r}, t), c_k(\boldsymbol{r}, t)]$ and in differential form,

$$\mathrm{d}s = \left(\frac{\partial s}{\partial u}\right)_{v,c_k} \mathrm{d}u + \left(\frac{\partial s}{\partial v}\right)_{u,c_k} \mathrm{d}v + \sum_{k=1}^{N} \left(\frac{\partial s}{\partial c_k}\right)_{u,v,c_{k'}} \mathrm{d}c_k \qquad (\text{for } k' \neq k). \tag{1.54}$$

Defining, as in equilibrium thermodynamics, the absolute temperature T, the pressure p, and the chemical potential μ_k by

$$T^{-1} = \left(\frac{\partial s}{\partial u}\right)_{v,c_k}, \qquad T^{-1}p = \left(\frac{\partial s}{\partial v}\right)_{u,c_k}, \qquad T^{-1}\mu_k = -\left(\frac{\partial s}{\partial c_k}\right)_{u,v,c_{k'}}, \tag{1.55}$$

respectively, one obtains from (1.54) the local form of the Gibbs equation, namely

$$T\mathrm{d}s = \mathrm{d}u + p\mathrm{d}v - \sum_{k=1}^{N} \mu_k \mathrm{d}c_k. \tag{1.56}$$

This equation is fundamental for finding out the rate of entropy production, as shown in the next subsection. Note that (1.56) is written in the centre-of-mass reference frame, since equilibrium thermodynamics cannot cope with convective phenomena. A simple procedure allowing one to determine the form of the Gibbs equation for a wide variety of systems (one-component fluids, mixtures, electromagnetic systems) was proposed by Lambermont and Lebon (1973).

3. A third consequence of the local-equilibrium hypothesis is that it permits one, from the concavity property of entropy, to derive locally the thermodynamic conditions of stability, such as the positiveness of the specific heat and the isothermal compressibility.

A precise limitation of the domain of validity of CIT cannot be obtained from the macroscopic formalism itself: it requires either a wider macroscopic theory or a microscopic theory like the kinetic theory of gases. Starting from the Chapman–Enskog development, Prigogine (1949) has shown that the hypothesis of local equilibrium is satisfactory provided that the distribution function is limited to the first-order term. Explicit conditions under which the local-equilibrium hypothesis holds are established in Chap. 4.

1.3.2 Entropy Production and Entropy Flux

Our objective is to explicitly calculate the entropy flux and entropy production in a system in which different irreversible processes are under way. Consider a mixture of N charged components among which n chemical reactions may take place. In terms of time derivatives, the Gibbs equation (1.56) can be written as

$$T\dot{s} = \dot{u} + p\dot{v} - \sum_{k=1}^{N} \mu_k \dot{c}_k. \tag{1.57}$$

By multiplying (1.57) by ρ and replacing $\dot{u}$, $\dot{v}$, and $\dot{c}_k$ by their values determined from the energy balance equation (1.47), the total mass conservation equation (1.11), and the mass fraction balance equation (1.28) respectively, we obtain the following expression for the rate of change of the entropy:

$$\rho\dot{s} = -\frac{1}{T}\nabla\cdot\boldsymbol{q} - \frac{1}{T}\mathbf{P}^v : \nabla\boldsymbol{v} + \frac{1}{T}\sum_{k=1}^{N}\mu_k\nabla\cdot\boldsymbol{J}_k + \frac{\rho}{T}\sum_{l=1}^{n}\mathcal{A}_l\dot{\xi}_l + \frac{1}{T}\boldsymbol{\varepsilon}\cdot\boldsymbol{i}. \tag{1.58}$$

In establishing (1.58), it was assumed that the external forces applied to each species $k = 1, \ldots, N$ are all identical and that the time derivative of the diffusion velocities $\boldsymbol{w}_k$ may be neglected, which is a hypothesis frequently used in CIT. Otherwise, (1.58) would contain a supplementary contribution of the form $-\sum_k \boldsymbol{J}_k\cdot\dot{\boldsymbol{w}}_k$ (de Groot and Mazur 1962). The quantity $\mathcal{A}_l$ is the affinity of the lth chemical reaction, defined by

$$\mathcal{A}_l = -\sum_{k=1}^{N}\nu_{kl}\mu_k \qquad (l = 1, 2, \ldots, n). \tag{1.59}$$

By using the decomposition (1.19) of the pressure tensor, and rewriting the divergence terms, (1.58) may be also rearranged as follows:

$$\begin{aligned}\rho\dot{s} = {} & -\nabla\cdot\left[\frac{1}{T}\left(\boldsymbol{q} - \sum_{k=1}^{N}\mu_k\boldsymbol{J}_k\right)\right] + \boldsymbol{q}\cdot\nabla\left(\frac{1}{T}\right) - \sum_{k=1}^{N}\boldsymbol{J}_k\cdot\nabla\left(\frac{\mu_k}{T}\right)\\ & -\frac{1}{T}p^v\nabla\cdot\boldsymbol{v} - \frac{1}{T}\overset{0}{\mathbf{P}}{}^v : \overset{0}{\mathbf{V}} + \frac{\rho}{T}\sum_{l=1}^{n}\mathcal{A}_l\dot{\xi}_l + \frac{1}{T}\boldsymbol{\varepsilon}\cdot\boldsymbol{i}.\end{aligned} \tag{1.60}$$

A comparison of this expression and the general balance equation of entropy (1.51) reveals that $\boldsymbol{J}^s$ and σ^s are respectively given by

$$\boldsymbol{J}^s = \frac{1}{T}\left(\boldsymbol{q} - \sum_{k=1}^{N}\mu_k\boldsymbol{J}_k\right) \tag{1.61}$$

and

$$\sigma^s = \boldsymbol{q}\cdot\nabla\left(\frac{1}{T}\right) - \sum_{k=1}^{N}\boldsymbol{J}_k\cdot\nabla\left(\frac{\mu_k}{T}\right) - \frac{1}{T}p^v\nabla\cdot\boldsymbol{v} - \frac{1}{T}\overset{0}{\mathbf{P}}{}^v : \overset{0}{\mathbf{V}} + \frac{\rho}{T}\sum_{l=1}^{n}\mathcal{A}_l\dot{\xi}_l + \frac{1}{T}\boldsymbol{\varepsilon}\cdot\boldsymbol{i} \tag{1.62}$$

Expression (1.61) shows that the entropy flux splits into two parts: the first is connected with heat conduction and the second arises from the diffusion of matter. From (1.62) it is concluded that six different effects contribute to the rate of entropy

Table 1.2 Independent fluxes and forces

Flux: J_α	$\boldsymbol{q}$	$\boldsymbol{J}_k$	p^v	$\overset{0}{\mathbf{P}}{}^v$	$\rho\dot{\xi}_l$	$\boldsymbol{i}$
Force: X_α	∇T^{-1}	$-\nabla\left(T^{-1}\mu_k\right)$	$-T^{-1}\nabla\cdot\boldsymbol{v}$	$-T^{-1}\overset{0}{\mathbf{V}}$	$T^{-1}\mathcal{A}_l$	$T^{-1}\varepsilon$

production: the first is related to heat conduction, the second to matter flow, the third and fourth to mechanical viscous dissipation, the fifth is due to chemical reactions, and the sixth to electric currents. Relation (1.62) for σ^s is a sum of products of two factors called respectively thermodynamic flux J_α and thermodynamic force X_α (explicit expressions of these quantities are given in Table 1.2). In terms of them the rate of entropy production presents the bilinear structure

$$\sigma^s = \sum_\alpha J_\alpha X_\alpha. \tag{1.63}$$

The fluxes J_α and forces X_α in (1.63) are not necessarily scalar quantities: they represent vectorial and tensorial quantities as well. Each individual flux and force has the property of vanishing at equilibrium. It must be stressed that the decomposition into thermodynamic fluxes and forces is arbitrary to a certain extent: one could, for instance, include the factor $1/T$ in the flux instead of in the force. Likewise, one could permute the definitions of fluxes and forces. However, these various choices are not crucial and have no direct consequences for the interpretation of the final results.

Nevertheless, as shown by Meixner (1943), it is essential to select independent fluxes and independent forces as well. This can be achieved in particular by choosing the quantities of Table 1.2. This splitting is quite natural, since it meets the requirements of cause and effect: the cause is provided by the driving thermodynamic force, which elicits the effect manifested through the conjugated flux.

1.3.3 Linear Constitutive Equations

The fluxes are unknown quantities, in contrast to the forces, which are known functions of the state variables or (and) their gradients. It has been found experimentally that fluxes and forces are interwoven. In general, a given flux does not only depend on its own conjugated force but may depend on the whole set of forces acting on the system. Furthermore, the flux may depend on all the thermodynamic state variables T, p and c_k as well:

$$J_\alpha = J_\alpha(X_1, X_2, \ldots, X_\alpha, \ldots; T, p, c_k). \tag{1.64}$$

A relation like (1.64) between fluxes and forces is called a phenomenological or constitutive equation: it expresses specific properties of the material involved in an irreversible process. After expansion of (1.64) around the equilibrium values $J_{\alpha,\text{eq}} = 0$ and $X_{\alpha,\text{eq}} = 0$, one has

$$J_\alpha = \sum_\beta (\partial J_\alpha/\partial X_\beta)_{\text{eq}} X_\beta + \mathcal{O}(X_\beta X_\gamma) + \ldots \tag{1.65}$$

Neglecting the second-order and subsequent terms and setting

$$L_{\alpha\beta} = (\partial J_\alpha/\partial X_\beta)_{\text{eq}}, \tag{1.66}$$

we find that (1.65) reduces to

$$J_\alpha = \sum_\beta L_{\alpha\beta} X_\beta. \tag{1.67}$$

The $L_{\alpha\beta}$ quantities are called phenomenological coefficients and depend generally on T, p, and c_k. The constitutive equations (1.67), together with the balance equations of mass, momentum, and energy, constitute a closed set of equations which can be solved when initial and boundary conditions are specified. Experimental evidence and theoretical considerations in statistical mechanics have confirmed that a wide class of phenomena can be described by means of linear flux–force relations. This is true in particular for transport processes where the macroscopic gradients vary on a much larger scale than the mean free path.

It must be realized that the symmetry properties of the material have an influence on the form of the constitutive equations. For instance, in isotropic systems, some couplings between fluxes and forces are forbidden. As a consequence of the representation theorem of isotropic tensors (Truesdell and Noll 1965), it can be shown that fluxes and forces of different tensorial rank do not couple so far as linear relations are involved. For example, a temperature gradient cannot give rise to a viscous pressure in a linear description. The independence of processes of different tensorial rank is often referred to as the 'Curie principle' in the CIT literature. As Truesdell (1984) acidly observes, it is redundant to invoke the name of Curie and the term 'principle' to establish a result which comes directly from tensor algebra.

For isotropic systems, the most general linear constitutive relations between the fluxes and forces of Table 1.2 are

$$\boldsymbol{q} = L_{qq}\nabla\left(\frac{1}{T}\right) - \sum_{k=1}^{N} L_{qk}\nabla\left(\frac{\mu_k}{T}\right) + L_{qe}\frac{\boldsymbol{\varepsilon}}{T}, \tag{1.68a}$$

$$\boldsymbol{J}_k = L_{kq}\nabla\left(\frac{1}{T}\right) - \sum_{j=1}^{N} L_{kj}\nabla\left(\frac{\mu_j}{T}\right) + L_{ke}\frac{\boldsymbol{\varepsilon}}{T} \quad (k = 1, 2, \ldots, N), \tag{1.68b}$$

$$\boldsymbol{i} = L_{eq}\nabla\left(\frac{1}{T}\right) - \sum_{k=1}^{N} L_{ek}\nabla\left(\frac{\mu_k}{T}\right) + L_{ee}\frac{\boldsymbol{\varepsilon}}{T}, \tag{1.68c}$$

$$\rho\dot{\xi}_j = \frac{l_{jv}}{T}\nabla\cdot\boldsymbol{v} + \sum_{l=1}^{n} l_{jl}\frac{\mathcal{A}_l}{T} \quad (j = 1, 2, \ldots, n), \tag{1.68d}$$

$$p^v = -\frac{l_{vv}}{T}\nabla \cdot \boldsymbol{v} + \sum_{l=1}^{n} l_{vl}\frac{\mathcal{A}_l}{T}, \tag{1.68e}$$

$$\overset{0}{\mathbf{P}}{}^v = -\frac{L}{T}\overset{0}{\mathbf{V}}. \tag{1.68f}$$

In these relations, all the phenomenological coefficients are scalar quantities. The phenomenological coefficients L_{qq}, L_{kj}, L_{ee}, l_{vv}, and L are related to the usual transport coefficients of thermal conductivity λ, diffusion D_{kj}, electrical resistivity r_e, bulk viscosity ζ, and shear viscosity η by

$$L_{qq} = \lambda T^2,\ D_{kj} = \frac{1}{T}\sum_{r=1}^{N} L_{kr}\left(\frac{\partial \mu_r}{\partial c_j}\right)_{T,p,c_{j'}},\ L_{ee} = \frac{T}{r_e},\ l_{vv} = \zeta T,\ L = 2\eta T. \tag{1.69}$$

By using the identifications (1.69) and omitting in (1.68a, e and f) the coupling coefficients, one recovers the Fourier and Newton–Stokes laws:

$$\boldsymbol{q} = -\lambda \nabla T \text{ (Fourier's law)}, \tag{1.70}$$

$$p^v = -\zeta\, \nabla \cdot \boldsymbol{v} \text{ (Stokes' law)}, \tag{1.71}$$

$$\overset{0}{\mathbf{P}}{}^v = -2\eta \overset{0}{\mathbf{V}} \text{ (Newton's law)}. \tag{1.72}$$

The Ohm and Fick laws are obtained by introducing supplementary constraints; for instance, the classical expression for Fick's law,

$$\boldsymbol{J}_k = -\sum_{j=1}^{N} D_{kj}\nabla c_j, \tag{1.73}$$

demands that one works at constant temperature and pressure, and Ohm's law

$$\boldsymbol{i} = \frac{1}{r_e}\boldsymbol{E}, \tag{1.74}$$

is derived from (1.68c), provided that the magnetic induction and all couplings are ignored. It is worthwhile pointing out that (1.68d) predicts a linear relation between the rate of advancement of a chemical reaction and the affinities. Such a linear law is unrealistic, since it is only correct in a very narrow domain around the equilibrium. It is indeed known from chemical kinetics that in a multicomponent incompressible system ($\nabla \cdot \boldsymbol{v} = 0$) in which just one chemical reaction takes place, one has

$$\rho\dot{\xi} = l\left[1 - exp\left(-\frac{\mathcal{A}}{RT}\right)\right], \tag{1.75}$$

where the coefficient l is a function of the temperature and mass fractions. The derivation of expression (1.75) is outlined in Problem 1.2. It is only in the limiting case $\mathcal{A} \ll RT$ that (1.75) reduces to

$$\rho\dot{\xi} = \frac{l}{RT}\mathcal{A}, \tag{1.76}$$

from which it may be concluded that the linear relation (1.68d) between $\dot{\xi}$ and $\mathcal{A}$ is only satisfied in the close vicinity of equilibrium.

1.3.4 Constraints on the Phenomenological Coefficients

The linear flux–force relations are the simplest constitutive equations which guarantee the semi-positiveness of the rate of entropy production. Indeed, by substitution of (1.67) into (1.63), one gets

$$\sigma^s = \sum_{\alpha\beta} L_{\alpha\beta} X_\alpha X_\beta \geq 0. \tag{1.77}$$

By writing (1.77) in the form

$$\sigma^s = \sum_{\alpha} L_{\alpha\alpha} X_\alpha X_\alpha + \sum_{\alpha,\beta\neq\alpha} \tfrac{1}{2}\left(L_{\alpha\beta} + L_{\beta\alpha}\right) X_\alpha X_\beta, \tag{1.78}$$

it can be seen that the necessary and sufficient conditions for $\sigma^s \geq 0$ to be held are that the determinant of the symmetric part of $L_{\alpha\beta}$ and all its principal minors are positive; in particular, necessary but not sufficient conditions are

$$L_{\alpha\alpha} \geq 0, \tag{1.79a}$$

$$L_{\alpha\alpha} L_{\beta\beta} \geq \tfrac{1}{4}\left(L_{\alpha\beta} + L_{\beta\alpha}\right)^2. \tag{1.79b}$$

As a consequence of (1.79a), it is seen that the heat conductivity λ, the bulk and shear viscosity coefficients ζ and η, and the electrical resistivity r_e are all semi-positive definite quantities.

1.3.5 The Onsager–Casimir Reciprocal Relations

Another important kind of constraint on the coefficients $L_{\alpha\beta}$ concerns their symmetry property and was established by Onsager (1931). Under the three conditions that (a) the fluxes are identified as time rates of state variables a_α, (b) the forces X_α are identified as the derivatives of the entropy with respect to the state variables a_α, and (c) there exists between these so-defined fluxes and forces linear constitutive relations of the form

$$\dot{a}_\alpha = \sum_\beta L_{\alpha\beta} X_\beta, \tag{1.80}$$

the coefficients $L_{\alpha\beta}$ obey the reciprocal relations

$$L_{\alpha\beta} = L_{\beta\alpha}. \tag{1.81}$$

This result is a consequence of the time-reversal invariance of the microscopic dynamics demanding that the particles retrace their former path when the velocities are reversed, as it is shown in Sect. 5.6. The Onsager reciprocal relations (1.81) are very useful in studying coupled phenomena, such as thermodiffusion, thermoelectricity, and thermoelectromagnetic effects. The Onsager original derivation was only valid for state variables that are even under microscopic time-reversal. An extension to variables with odd parities was carried out by Casimir (1945), who demonstrated that in full generality

$$L_{\alpha\beta} = \varepsilon_\alpha \varepsilon_\beta L_{\beta\alpha}, \tag{1.82}$$

where ε_α, ε_β are equal to $+1$ or -1 depending on whether the corresponding state variable is even or odd under time-reversal.

If an external magnetic induction $\boldsymbol{\mathcal{B}}$ is acting, one must not only reverse the velocities but also the magnetic field if it is desired that the particles retrace their former path: this is a consequence of the expression of the Lorentz force (1.38). The same reasoning can be applied for processes taking place in non-inertial frames rotating with an angular velocity $\boldsymbol{\omega}$. It follows from the form of the Coriolis force that, in this case, the velocity of particles $\boldsymbol{v}$ and $\boldsymbol{\omega}$ must be reversed. The reciprocal relations (1.82) have now to be replaced by the following expression:

$$L_{\alpha\beta}(\boldsymbol{\mathcal{B}}, \boldsymbol{\omega}) = \varepsilon_\alpha \varepsilon_\beta L_{\beta\alpha}(-\boldsymbol{\mathcal{B}}, -\boldsymbol{\omega}). \tag{1.83}$$

It must be mentioned that the validity of the Onsager–Casimir relations has been challenged by some people working in continuum thermodynamics (Truesdell 1984). In this respect, we wish to make the following comments.

Although various proofs of the Onsager reciprocal relations have been proposed so far, all of them are based on microscopic theories: statistical mechanics of fluctuations or kinetic theory. Nevertheless, the Onsager relations are generally accepted to be correct at the macroscopic level, even when the thermodynamic fluxes cannot be expressed in the form of time derivatives of state variables. Typical quantities that do not meet this condition are the heat flux vector and the viscous pressure tensor.

A crucial point in the derivation of Onsager's relations is that the regressions of fluctuations are assumed to follow the same linear dynamical laws as the macroscopic equations. This assertion is questionable because, quoting Truesdell (1984), '… not even the form of the constitutive equation is derived from the molecular theory, rather the molecular theory, so-called, is forced into agreement with preconceived phenomenological ideas'.

These criticisms have been the motivation behind submitting the Onsager–Casimir relations to severe experimental scrutiny. Careful experimental tests have been performed, especially in thermodiffusion and thermoelectricity. They do confirm the symmetry property of the coefficients $L_{\alpha\beta}$ within reasonable limits of experimental errors (Miller 1960). In spite of these encouraging observations, it is our opinion that, unless a complete macroscopic proof of the Onsager relations is proposed, one should regard them as postulates at the macroscopic level.

Finally we summarize that the main points underlying CIT are:

- The local-equilibrium hypothesis that allows one to write the Gibbs equation locally for any time
- The existence of a non-negative rate of entropy production
- The existence of linear constitutive laws
- The Onsager–Casimir reciprocal relations

1.3.6 Limitations

The classical description has been undoubtedly useful, and has led to an impressive production of scientific work. Nevertheless, it presents some drawbacks like the mentioned below.

1. It is based on the local-equilibrium hypothesis, which breakdowns for a wide class of phenomena involving short time and small space scales at which the velocity distribution of particles cannot be described by a Maxwell distribution function. It is conceivable, indeed, that other variables, not found in equilibrium, may influence the thermodynamic equations in non-equilibrium situations. To illustrate this observation, we mention an old example quoted by O. Reynolds (1885). He pointed out that when a leather bag is filled with marbles, topped up with water, and then twisted, the marble density decreases when the rate of shear is increased, at constant temperature and pressure. This means that, in contradiction with the local-equilibrium assumption, the density does not only depend on temperature and pressure but also on the shearing rate.
2. Statistical and kinetic analyses show that the local-equilibrium hypothesis is only consistent with linear and instantaneous relations between fluxes and forces. In many problems, the assumption of linear and stationary constitutive relations is too stringent. This is particularly true in chemistry, as mentioned above, and in rheology as well.
3. The linear steady constitutive equations are not satisfactory at high frequencies and short wavelengths, as manifested in experiments on sound absorption and dispersion in dilute gases. The dispersion relation obtained from CIT is in agreement with experimental observations at low frequencies only.
4. The classical Fourier law of heat conduction leads, when introduced into the energy conservation law, to a partial differential parabolic equation for the temperature. This implies that disturbances propagate with boundless speed. This

unpleasant physical property is also observed with other quantities, such as concentration and viscous signals.

5. In the so-called generalised hydrodynamics, the transport coefficients in the Stokes–Navier–Fourier constitutive equations are frequency and wavelength dependent, as confirmed by neutron scattering techniques. Such a result is at variance with the local-equilibrium assumption assessing that the transport coefficients are frequency and wavelength independent.
6. In nanotechnology, the size of the devices is comparable to the mean free path of the particles or even smaller; in these situations, local equilibrium is not achieved and generalized transport equations describing non-local, ballistic effects must be used instead of the classical transport equations, which are valid in the diffusive regime, where collisions amongst particles are dominant.

1.4 Rational Thermodynamics

This formalism was essentially developed by Coleman (1964), Truesdell (1984), and Noll (1974) and follows a line of thought drastically different from CIT. Its main objective is to provide a method for deriving constitutive equations. The basic hypotheses underlying rational thermodynamics can be summarized as follows.

1. Absolute temperature and entropy are considered primitive concepts. They are introduced a priori in order to ensure the coherence of the theory and do not have a precise physical interpretation.
2. It is assumed that materials have a memory, i.e. the behaviour of a system at a given instant of time is determined not only by the values of the characteristic parameters at the present time, but also by their past history. The local-equilibrium hypothesis is no longer assumed, since the knowledge of the values of the parameters at the present time is not enough to specify unambiguously the behaviour of the system.
3. The general expressions previously formulated for the balance of mass, momentum, and energy are however retained. Nevertheless, there are two essential nuances. The first is the introduction of a specific rate of energy supply r in the balance of internal energy, which in local form is written as

$$\rho \dot{u} = -\nabla \cdot \boldsymbol{q} - \mathbf{P} : \nabla v + \rho r; \tag{1.84}$$

   r is generally referred to as the power supplied or lost by radiation. The second crucial point is that the body forces $\boldsymbol{F}$ and the radiation term r are not given a priori as a function of position and time but are computed from the laws of momentum and internal energy respectively.
4. Another capital point is the mathematical formulation of the second law of thermodynamics, which serves essentially as a restriction on the form of the constitutive equations. The starting relation is the Clausius–Planck inequality, which states that between two equilibrium states A and B one has

$$\Delta S \geq \int_A^B \frac{đQ}{T}. \tag{1.85}$$

In rational thermodynamics, inequality (1.85) is written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{V(t)} \rho s \mathrm{d}V \geq -\int_{\Sigma(t)} \frac{1}{T}\boldsymbol{q}\cdot\boldsymbol{n}\mathrm{d}\Sigma + \int_{V(t)} \rho\frac{r}{T}\mathrm{d}V, \tag{1.86}$$

or, in local form, as

$$\rho\dot{s} + \nabla\cdot\frac{\boldsymbol{q}}{T} - \rho\frac{r}{T} \geq 0. \tag{1.87}$$

By introducing the Helmholtz free energy ϕ $(= u - Ts)$ and eliminating r between the energy balance equation (1.84) and the inequality (1.87) leads to

$$-\rho\left(\dot{\phi} + s\dot{T}\right) - \mathbf{P} : \mathbf{V} - \frac{1}{T}\boldsymbol{q}\cdot\nabla T \geq 0. \tag{1.88}$$

This inequality, established here for a one-component uncharged system, is either known as the *Clausius–Duhem* or the *fundamental inequality.*

An important problem is certainly the selection of the constitutive independent variables. This choice is subordinated to the type of material one deals with. In hydrodynamics, it is customary to take as variables the density, velocity, and temperature fields. It is also known that the balance laws and Clausius–Duhem inequality introduce complementary variables, such as the internal energy, the heat flux, the pressure tensor, and the entropy. The latter are expressed in terms of the former by means of constitutive equations. By an *admissible process* is meant a solution of the balance laws when the constitutive relations are taken into account and the Clausius–Duhem inequality holds.

1.4.1 The Basic Axioms of Rational Thermodynamics

Before deriving the constitutive equations, let us briefly examine the main principles they must meet. A word of caution is required about the use and abuse of the term 'principle' in rational thermodynamics. In most cases, this term is employed to designate merely convenient assumptions.

1.4.1.1 The Principle of Equipresence

This principle asserts that if a variable is present in one constitutive equation, it will be a priori present in all the constitutive equations. However, the condition for the final presence or absence of independent variables in a constitutive relation derives from the Clausius–Duhem inequality.

1.4.1.2 The Principle of Memory or Heredity

According to this principle the present effects are dictated not only by present causes but by past causes as well. Consequently, the set of independent variables is no longer formed by the variables at the present time but by their whole history. If Φ is an arbitrary variable, e.g. v, $\boldsymbol{v}$ and T, we shall denote its history up to time t by

$$\Phi^t = \Phi\left(t - t'\right) \qquad \left(0 < t' < \infty\right). \tag{1.89}$$

The principles of equipresence and memory when applied to hydrodynamics assert that

$$\left.\begin{array}{c} u(\mathrm{or}\ \phi) \\ s \\ \boldsymbol{q} \\ \mathbf{P} \end{array}\right\} \text{ at } (\boldsymbol{r}, t) \text{ are functionals of } \left\{\begin{array}{l} v^t \\ \boldsymbol{v}^t \\ T^t \end{array}\right. . \tag{1.90}$$

Of course, the choice of the dependent and independent variables is not unique. One could for instance permute the roles of u and T, but, since the usual attitude in rational thermodynamics is to select T as the independent quantity, here we shall follow this point of view.

1.4.1.3 The Principle of Local Action

This principle establishes that the behaviour of a material point should only be influenced by its immediate neighbourhood. Otherwise stated, the values of the constitutive equation at a given point are insensitive to what happens at distant points; accordingly, in a first-order theory, second-order and higher-order space derivatives should be omitted.

1.4.1.4 The Principle of Material Frame-Indifference

As a preliminary to the formulation of this principle of frame indifference, it is useful to introduce the notion of objectivity. Consider two reference frames (or observers) moving with respect to each other arbitrarily. Let $\boldsymbol{r}$ be the position vector of a material point at time t in one of the reference frames (say an inertial one) and $\boldsymbol{r}^*$ its position vector at the same time in the other frame (say a non-inertial one). We impose that the relation between $\boldsymbol{r}$ and $\boldsymbol{r}^*$ be such that the distance between two arbitrary points in the body and the angle between two directions are preserved. The most general transformation law that satisfies these requirements is the one given by the Euclidean transformation

$$\boldsymbol{r}^* = \mathbf{Q}(t) \cdot \boldsymbol{r} + \boldsymbol{c}(t), \tag{1.91}$$

where $\mathbf{Q}(t)$ is a real, proper orthogonal, time-dependent tensor

$$\mathbf{Q}\cdot\mathbf{Q}^T = \mathbf{Q}^T\mathbf{Q} = \mathbf{U}, \qquad \det\mathbf{Q} = 1, \tag{1.92}$$

and $\boldsymbol{c}(t)$ is the distance between the origins of the two frames. In this book we have not considered the more general transformation det $\mathbf{Q} = \pm 1$, which includes symmetry under reflection and a possible translation in time $t^* = t - \tau$, with τ being a real constant. The general transformation $\det\mathbf{Q} = \pm 1$ has been introduced and fully discussed in specific works on rational thermodynamics (Coleman 1964; Truesdell 1984; Noll 1974; Truesdell and Toupin 1960) to which the reader is referred for further details. When the Euclidean group (1.91) acts on a tensor of rank n ($n = 0, 1, 2, \ldots$), the latter is said to be objective, if it transforms according to

$$A^*_{ij\cdots k} = Q_{i\alpha}Q_{j\beta}\cdots Q_{k\gamma}A_{\alpha\beta\cdots\gamma}. \tag{1.93}$$

For tensors of rank zero (scalar), rank one (vector), and rank two, one has

$$a^* = a \qquad \text{(objective scalar)}, \tag{1.94a}$$
$$\boldsymbol{a}^* = \mathbf{Q}\cdot\boldsymbol{a} \qquad \text{(objective vector)}, \tag{1.94b}$$
$$\mathbf{A}^* = \mathbf{Q}\cdot\mathbf{A}\cdot\mathbf{Q}^T \qquad \text{(objective tensor)}, \tag{1.94c}$$

respectively. According to (1.94a), a scalar is objective if it keeps the same value in all moving reference frames. The velocity vector is not objective because it transforms like

$$\boldsymbol{v}^* = \mathbf{Q}\cdot\boldsymbol{v} + \dot{\mathbf{Q}}\cdot\boldsymbol{v} + \dot{\boldsymbol{c}}, \tag{1.95}$$

which is not of the form (1.94b). Similarly, the acceleration $\dot{\boldsymbol{v}}$ is not objective either. It can also be shown that the symmetric and antisymmetric parts of the velocity gradient transform like

$$\mathbf{V}^* = \mathbf{Q}\cdot\mathbf{V}\cdot\mathbf{Q}^T, \tag{1.96a}$$
$$\mathbf{W}^* = \mathbf{Q}\cdot\mathbf{V}\cdot\mathbf{Q}^T - \dot{\mathbf{Q}}\cdot\mathbf{Q}^T. \tag{1.96b}$$

Thus $\mathbf{V}$ is objective and $\mathbf{W}$ is not. The term responsible for the non-objective character of $\mathbf{W}$ is the angular velocity $\boldsymbol{\Omega} = \dot{\mathbf{Q}}\cdot\mathbf{Q}^T$ of the moving frame with respect to the inertial one.

It can also be seen that the material time derivatives of objective vectors and tensors are not objective because they transform like

$$\dot{\boldsymbol{a}}^* = \mathbf{Q}\cdot\dot{\boldsymbol{a}} + \dot{\mathbf{Q}}\cdot\boldsymbol{a}, \tag{1.97a}$$
$$\dot{\mathbf{A}}^* = \mathbf{Q}\cdot\dot{\mathbf{A}}\cdot\mathbf{Q}^T + \dot{\mathbf{Q}}\cdot\mathbf{A}\cdot\mathbf{Q}^T + \mathbf{Q}\cdot\mathbf{A}\cdot\dot{\mathbf{Q}}^T. \tag{1.97b}$$

The failure of the objectivity of the material time derivatives of vectors and tensors arises obviously from the time-dependence of the orthogonal tensor $\mathbf{Q}(t)$.

This has motivated the search for objective time derivatives. The answer is not unique and several objective time derivatives satisfying (1.94b and c) have been proposed. Among the most frequently used, let us mention the Jaumann or co-rotational derivative:

$$\mathrm{D}_J \boldsymbol{a} = \dot{\boldsymbol{a}} + \mathbf{W} \cdot \boldsymbol{a}, \tag{1.98a}$$

$$\mathrm{D}_J \mathbf{A} = \dot{\mathbf{A}} + \mathbf{W} \cdot \mathbf{A} - \mathbf{A} \cdot \mathbf{W}, \tag{1.98b}$$

the covariant or lower convected derivative:

$$\mathrm{D}_{\downarrow} \boldsymbol{a} = \dot{\boldsymbol{a}} + (\nabla \boldsymbol{v}) \cdot \boldsymbol{a}, \tag{1.99a}$$

$$\mathrm{D}_{\downarrow} \mathbf{A} = \dot{\mathbf{A}} + (\nabla \boldsymbol{v}) \cdot \mathbf{A} + \mathbf{A} \cdot (\nabla \boldsymbol{v})^T, \tag{1.99b}$$

and the contravariant or upper convected derivative:

$$\mathrm{D}^{\uparrow} \boldsymbol{a} = \dot{\boldsymbol{a}} - (\nabla \boldsymbol{v})^T \cdot \boldsymbol{a}, \tag{1.100a}$$

$$\mathrm{D}^{\uparrow} \mathbf{A} = \dot{\mathbf{A}} - (\nabla \boldsymbol{v})^T \cdot \mathbf{A} - \mathbf{A} \cdot (\nabla \boldsymbol{v}). \tag{1.100b}$$

The Jaumann's derivative has a simple physical interpretation, since it is the derivative measured by an observer whose frame of reference is carried by the medium and rotates with it; upper and lower convected derivatives correspond to non-orthogonal time-dependent reference frames deforming with the medium and moving with it. From a pure continuum mechanics standpoint, there is no preference for any of the above objective time derivatives. However, it may happen that the formulation of some particular class of constitutive equations becomes more simple and elegant when one particular objective derivative is selected. The Jaumann's upper and lower convective derivatives are of wide use in rheology (see Chap. 15)

We are now in a position to formulate the principle of material frame indifference. Generally stated, this principle demands that the constitutive equations be independent of the observer. This statement implies two requirements. First, the constitutive equations should be objective, i.e. form-invariant under arbitrary time-dependent rotations and translations of the reference frames as expressed by the Euclidean transformations (1.91). This statement amounts to the requirement that the form of the constitutive relations is left unaffected by the superposition of any arbitrary rigid body motion. Second, the constitutive equations should be independent of the frame, in particular its angular velocity. To give an example, Newton's equation of motion is form invariant, but at the same time it depends on the frame through the inertial forces; therefore, it fulfills the first requirement but not the second one.

Of course, before examining the effect of a change of frame on a constitutive equation, it is necessary to specify how the basic variables such as temperature, energy, entropy, heat flux, pressure tensor, etc. behave under such a transformation. Since these quantities have an intrinsic meaning, they are expected to be objective and at the same time frame independent. It is thus taken for granted that

u,s,ϕ, ... are objective scalars.
$\boldsymbol{q}$ is an objective vector.
$\mathbf{P}$ is an objective tensor of order two.

1.4.2 Constitutive Equations

We proceed further with the establishment of the constitutive equations. For simplicity, we consider a particular thermomechanical material, namely the Stokesian fluid. It is characterized by the absence of memory and described by the following set of constitutive equations:

$$\varphi = \varphi(v, \boldsymbol{v}, T, \nabla\boldsymbol{v}, \nabla T), \tag{1.101}$$

where φ stands for any constitutive dependent variable. The absence of memory allows us to express the dependence of φ by means of ordinary functions instead of functionals. In explicit form, the constitutive relations (1.101) will be given by

$$\phi = \phi(v, T, \mathbf{V}, \nabla T), \tag{1.102a}$$
$$s = s(v, T, \mathbf{V}, \nabla T), \tag{1.102b}$$
$$\boldsymbol{q} = \boldsymbol{q}(v, T, \mathbf{V}, \nabla T), \tag{1.102c}$$
$$\mathbf{P} = \mathbf{P}(v, T, \mathbf{V}, \nabla T). \tag{1.102d}$$

By formulating (1.102a–d), the axiom of equipresence was used. In these equations, the non-objective velocity $\boldsymbol{v}$ has been eliminated and the velocity gradient $\nabla\boldsymbol{v}$ replaced by its objective symmetric part $\mathbf{V}$ to ensure material frame-indifference.

A further constraint is imposed by the second law of thermodynamics. This is achieved by substituting the constitutive laws (1.102a–d) in the Clausius–Duhem inequality (1.88). Using the chain differentiation rule for calculating $\dot{\phi}$, inequality (1.88) reads

$$-\rho\left(\frac{\partial\phi}{\partial T}+s\right)\dot{T}-\rho\frac{\partial\phi}{\partial\mathbf{V}}:\dot{\mathbf{V}}-\rho\frac{\partial\phi}{\partial(\nabla T)}\cdot\overset{\cdot}{(\nabla T)}-\frac{1}{T}\boldsymbol{q}\cdot\nabla T-\left(\frac{\partial\phi}{\partial v}\mathbf{U}+\mathbf{P}\right):\mathbf{V}\geq\mathbf{0}, \tag{1.103}$$

where use has been made of the mass conservation law

$$\rho\dot{v} = \nabla\cdot\boldsymbol{v} = \mathbf{V}:\mathbf{U}. \tag{1.104}$$

It is worth noticing that inequality (1.103) is linear in $\dot{T}$, $\dot{\mathbf{V}}$, and $\overset{\cdot}{(\nabla T)}$. Now it is assumed (Coleman 1964) that there always exist body forces and energy supplies that ensure that the balance equations of momentum and internal energy are identically satisfied. Therefore the balance laws do not impose constraints on the set $\dot{T}$, $\dot{\mathbf{V}}$, $\overset{\cdot}{(\nabla T)}$, and we assign these time derivatives arbitrary and independent values. It then appears that unless the coefficients of these terms vanish, (1.103) could be violated. This gives the following results:

$$\frac{\partial \phi}{\partial T} + s = 0 \quad \text{(a)}, \quad \frac{\partial \phi}{\partial \mathbf{V}} = 0 \quad \text{(b)}, \quad \frac{\partial \phi}{\partial (\nabla T)} = 0 \quad \text{(c)}. \tag{1.105}$$

Equation (1.105a) is classical while (1.105b and c) express the idea that ϕ is independent of $\mathbf{V}$ and ∇T. As a consequence, the constitutive equations for ϕ and s simply read

$$\phi = \phi(v, T), \tag{1.106a}$$

$$s = s(v, T). \tag{1.106b}$$

The above derivation rests on the controversial argument (Woods 1981) that the body forces $\boldsymbol{F}$ and the radiation sources r can be assigned arbitrarily in order that the balance laws are identically satisfied. Although this procedure is at variance with the usual way of thinking, where $\boldsymbol{F}$ and r are regarded as assigned a priori, it may also be asked what happens when $\boldsymbol{F}$ and (or) r are zero. To circumvent these difficulties, an alternative method was proposed by Liu (1972), who considers the balance laws as constraints for the Clausius–Duhem inequality and accounts for them by means of the well-known Lagrange multipliers. The delicate points in Liu's method are the derivation and the physical interpretation of the Lagrange multipliers, but the results (1.105) remain unchanged.

Defining the equilibrium pressure by

$$p = -\frac{\partial \phi}{\partial v} \tag{1.107}$$

and decomposing $\mathbf{P}$ according to (1.18), (1.103) reduces to

$$-\frac{1}{T}\boldsymbol{q} \cdot \nabla T - \mathbf{P}^{v} : \mathbf{V} \geq 0. \tag{1.108}$$

This expression is nothing but the rate of energy dissipation ($= T\sigma^{s}$) calculated earlier in the framework of CIT (see (1.62), with diffusive, chemical, and electrical effects being ignored in this case).

Using the representation theorems of tensors, one obtains within the linear approximation the following constitutive equations for $\boldsymbol{q}$ and $\mathbf{P}^{v}$:

$$\boldsymbol{q} = -\lambda(v, T)\nabla T, \tag{1.109a}$$

$$\mathbf{P}^{v} = -\eta_1(v, T)(\nabla \cdot \boldsymbol{v})\mathbf{U} - 2\eta(v, T)\mathbf{V}. \tag{1.109b}$$

The coefficients λ, η_1, and η may depend on v, T, and the first invariant of $\mathbf{V}$. After splitting $\mathbf{V}$ into its bulk and its deviatoric part, one obtains

$$\mathbf{P}^{v} = -\zeta(\nabla \cdot \boldsymbol{v})\mathbf{U} - 2\eta\overset{0}{\mathbf{V}}, \tag{1.110}$$

where ζ stands for $\left(\eta_1 + \frac{2}{3}\eta\right)$. We recognize (1.109a) as the classical constitutive Fourier's equation and (1.109b) as the classical constitutive Newton–Stokes' equation, with λ the heat conductivity, ζ the bulk viscosity, and η the shear viscosity. Substitution of (1.109a) and (1.110) into (1.108) gives

$$\frac{\lambda}{T}(\nabla T) \cdot (\nabla T) + \zeta(\nabla \cdot \boldsymbol{v})^2 + 2\eta\overset{0}{\mathbf{V}} : \overset{0}{\mathbf{V}} \geq 0, \tag{1.111}$$

from which it follows that $\lambda > 0$, $\zeta > 0$, $\eta > 0$.

Likewise, it is an easy matter to recover the Gibbs equation. From (1.106a), one has

$$\mathrm{d}\phi = \frac{\partial \phi}{\partial T}\mathrm{d}T + \frac{\partial \phi}{\partial v}\mathrm{d}v, \tag{1.112}$$

and, in view of (1.105a) and (1.107),

$$\mathrm{d}\phi = -s\mathrm{d}T - p\mathrm{d}v. \tag{1.113}$$

Unlike CIT, where the Gibbs equation is postulated at the outset, it can be said that in rational thermodynamics the Gibbs relation is derived.

The steps leading to the establishment of the constitutive relations and the constraints on the signs of the transport coefficients are elegant and employ a minimum of hypotheses. At no time does one call upon symmetry relations of the Onsager type. Besides, the theory is not limited to linear constitutive equations. Attempts to develop the bases of rational thermodynamics further have been made Coleman and Owen (1974) and Silhavy (1997).

1.4.3 Critical Remarks

Rational thermodynamics has not been free of criticisms, such as:

1. Temperature and entropy remain undefined objects. For example, it is not possible to check whether or not the temperature measured by a thermocouple corresponds to the temperature T used in rational thermodynamics. Concerning the entropy, no prescription is given for determining its actual functional dependence, either by experiment or by calculation from a physical model. Furthermore, it has been demonstrated by Day (1977), who examined the problem of the temperature distribution in a rigid heat conductor with memory, that the value of the entropy is not unique.
2. The fundamental inequality (1.88) used in rational thermodynamics is not, strictly speaking, the Clausius inequality. Indeed, the latter is given by (1.85) and connects two equilibrium states. In rational thermodynamics, Clausius' expression is generalised to arbitrary non-equilibrium states. When dealing with the

Clausius–Duhem inequality in rational thermodynamics, it must be understood that the existence of a specific entropy that satisfies the fundamental inequality (1.88) has been postulated. The latter also implies that the entropy flux is given by the heat flux divided by the temperature, a result only valid in the vicinity of equilibrium, as shown in the kinetic theory of gases.

3. Likewise, rational thermodynamics predicts unphysical properties in some classes of rheological materials. If it is admitted that the Rivlin–Ericksen model (see Chap. 15) provides a good description of rheological bodies, then the signs of some material coefficients, as given by the rational approach, are found to be in contradiction with experimental data.
4. Although the principle of material frame-indifference has revealed itself as a useful tool in establishing constitutive equations in continuum mechanics, it has recently been stressed that the two requirements of the principle, namely form invariance and frame independence, are not satisfied in several disciplines, such as classical mechanics, kinetic theory of gases, turbulence, rheology, and molecular hydrodynamics. In kinetic theory, it has been shown that the Burnett constitutive relations are frame-dependent (Müller 1972; Edelen and McLennan 1973); the origin of the frame-dependence lies in the Coriolis force of the rotating frame. It was also noticed that when the objective time derivatives (1.98–1.100) are used in stress–rate constitutive equations, one obtains results that are contradicted by Grad's kinetic model (Lebon and Boukary 1988). A similar problem arises in turbulence theory (Lumley 1983); there is an ample experimental confirmation that turbulence, in a non-inertial frame, is quite different from turbulence in an inertial frame, owing to the dependence of the turbulent viscosity on the angular velocity of the reference frame. The validity of frame-indifference in viscoelastic materials has been discussed by Bird and de Gennes (1983). It was concluded that inertial forces can contribute to the material functions of viscoelastic media and that frame indifference is useful only whenever inertial effects are negligible. Another example of violation of the principle of material frame-indifference is provided by the phenomenological coefficients $L_{\alpha\beta}$ of CIT. When measured in a rotating frame, the $L_{\alpha\beta}$ are known to depend on the angular velocity, as pointed out earlier. Hoover et al. (1981) performed a molecular dynamics simulation for a fluid modelled by two-dimensional rotating disks: they found an angular component for the heat flux, in contradiction with the material frame-indifference. All these observations have cast serious doubts about the general validity of the principle of material frame-indifference (Murdoch 1983; Ryskin 1988).

In RT, the presence of the source terms $\boldsymbol{F}$ and $\boldsymbol{r}$ is required to guarantee that the state variables and their time derivatives can be varied independently. The quantities $\boldsymbol{F}$ and $\boldsymbol{r}$ are selected in order that the momentum and energy equations are identically satisfied. In normal circumstances, the situation is reversed: $\boldsymbol{F}$ and $\boldsymbol{r}$ are known from the start and take well-defined values. This limits seriously the domain of applicability of the theory but this difficulty can be circumvented by using a technique proposed by I.S. Liu (1972) and based on the introduction of Lagrange multipliers.

5. From a practical point of view, the constitutive equations, when they are written in their general form involving functionals dependent on the whole history of the variables, are not easily tractable and generally require the knowledge of too vast an amount of information.

1.5 A Hamiltonian Formulation: the GENERIC Formalism

In Classical and Rational Thermodynamics, the limitations on the possible forms of the state and constitutive equations are obtained as a consequence of the application of the second law. However, no restriction is placed on the reversible parts of these relations as they do not contribute to the entropy production. We will see one of the merits of a Hamiltonian structure is that it provides restrictions on the reversible dynamics.

Hamiltonian formulations have been identified at various levels of description: the microscopic one (classical mechanics), the kinetic theory (based on a distribution function rather than on precise values for the mechanical variables of particles), and some macroscopic approaches (as, for instance, hydrostatics or equilibrium thermodynamics). Therefore, it is natural to ask whether such a structure is preserved in more sophisticated descriptions and more particularly in non-equilibrium thermodynamics. There are several reasons that militate in favour of a Hamiltonian description: it is attractive because of its conciseness and its physical content. Indeed, the whole set of balance equations is now expressed in terms of one or several generating functionals which may be generally identified with a well-defined physical quantity such as the energy, the entropy, or the Gibbs free energy. Moreover, there exist many elegant results and powerful methods of numerical solution typically developed for Hamiltonian systems.

Early Hamiltonian versions of non-equilibrium thermodynamics were proposed by Grmela (1984) and were based on one single generator; the time evolution of the basic variables was expressed in terms of a non-dissipative Poisson bracket plus a dissipative bracket (Beris 1994). Several papers have been devoted to this early formulation but it has been recently superseded in some aspects by the so-called GENERIC (General Equation for the Non-Equilibrium Reversible–Irreversible Coupling) theory as proposed by Grmela and Öttinger (1997) and developed recently in Öttinger's book (2005). In the foregoing, we briefly present this approach.

In GENERIC it is assumed that the time evolution equations can be given the form

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \mathbf{L} \cdot \frac{\delta E}{\delta \boldsymbol{x}} + \frac{\delta \Psi}{\delta(\delta S/\delta \boldsymbol{x})}, \tag{1.114}$$

where x represents a set of independent state variables required for the complete description of the non-equilibrium system (for instance, hydrodynamic fields and additional structural variables), E is the total energy, Ψ the dissipation potential and S the total entropy, $\mathbf{L}$ and $\mathbf{M}$ are linear functional operators, expressing reversible and irreversible kinematics, respectively. The dissipation potential Ψ is a real-valued function of the derivatives $\delta S/\delta \mathbf{x}$ with the following properties: $\Psi(0) = 0$ and convex in the vicinity of 0. The quantity $\delta/\delta \boldsymbol{x}$ stands for the Volterra functional derivative, which reduces to the usual partial derivative $\partial/\partial \boldsymbol{x}$ in the absence of non-local effects, otherwise it is of the form $\delta/\delta \boldsymbol{x} = \partial/\partial \boldsymbol{x} - \nabla \cdot [\partial/\partial(\nabla \mathbf{x})] +$. The first term in the right-hand side of (1.114) is purely Hamiltonian and represents the reversible contribution to the time evolution equations of $\boldsymbol{x}$, whereas the second term corresponds to the irreversible contributions. In the particular case that Ψ is a quadratic function of $\delta S/\delta \boldsymbol{x}$, say $\Psi = \frac{1}{2}[(\delta S/\delta \boldsymbol{x}) \cdot \mathbf{M} \cdot (\delta S/\delta \boldsymbol{x})]$, expression (1.114) takes the more familiar form

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \mathbf{L} \cdot \frac{\delta E}{\delta \boldsymbol{x}} + \mathbf{M} \cdot \frac{\delta S}{\delta \boldsymbol{x}}. \tag{1.115}$$

Equation (1.115) is supplemented by the following degeneracy requirements

$$\mathbf{L} \cdot \frac{\delta S}{\delta \boldsymbol{x}} = 0, \tag{1.116a}$$

$$\mathbf{M} \cdot \frac{\delta E}{\delta \boldsymbol{x}} = 0. \tag{1.116b}$$

The first condition expresses that $\delta S/\delta \boldsymbol{x}$ is in the null space of $\mathbf{L}$ and that the functional form of the entropy cannot contribute to the reversible part of the dynamics. The second one expresses that the total energy is not affected by the irreversible contribution to the dynamics. Note that these degeneracy requirements express fundamental and general physical aspects.

Furthermore, one associates to the matrices $\mathbf{L}$ and $\mathbf{M}$ the following brackets:

$$\{A, B\} = \left\langle \frac{\delta A}{\delta \boldsymbol{x}} \cdot \mathbf{L} \cdot \frac{\delta B}{\delta \boldsymbol{x}} \right\rangle, \tag{1.117a}$$

$$[A, B] = \left\langle \frac{\delta A}{\delta \boldsymbol{x}} \cdot \mathbf{M} \cdot \frac{\delta B}{\delta \boldsymbol{x}} \right\rangle, \tag{1.117b}$$

where $\langle\ ,\ \rangle$ denotes a scalar product. Braces $\{\ ,\ \}$ stand for the Poisson bracket of classical mechanics, whereas the brackets $[\ ,\ ]$ are intended to describe the dissipative behaviour (Grmela 1984; Beris 1994).

In terms of these brackets and the chain rule, (1.115) yields the following form for the evolution equation of an arbitrary function $A(\boldsymbol{x})$:

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \{A, E\} + [A, S]\,. \tag{1.118}$$

Further conditions about $\mathbf{L}$ and $\mathbf{M}$ are obtained from the following properties of the brackets:

$$\{A, B\} = -\{B, A\} \text{ (skew symmetry)} \tag{1.119a}$$

$$\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0 \text{ (Jacobi identity)} \tag{1.119b}$$

which are the well-known properties of Poisson brackets in classical mechanics. Note that the Jacobi identity guarantees that the bracket $\{A, B\}$ is preserved in the reversible time evolution. In some problems, it may be a difficult task to prove the Jacobi identity, which in certain circumstances may require to be numerically checked.

From condition (1.119a) it follows that $\mathbf{L}$ is skew symmetric:

$$\mathbf{L}(\boldsymbol{x}) = -\mathbf{L}^T(\boldsymbol{x}). \tag{1.120}$$

The properties of $\mathbf{M}$ are derived from the symmetry condition

$$[A, B] = [B, A] \tag{1.121}$$

and the non-negative condition

$$[A, A] \geq 0. \tag{1.122}$$

This implies that $\mathbf{M}$ is symmetric (provided that all the variables $\boldsymbol{x}$ have the same time-reversal parity) and semi-positive definite:

$$\mathbf{M}(\boldsymbol{x}) = \mathbf{M}^T(\boldsymbol{x}), \tag{1.123}$$

$$\boldsymbol{y} \cdot \mathbf{M}(\boldsymbol{x}) \cdot \boldsymbol{y} \geq 0 \text{ for } \forall \boldsymbol{y}. \tag{1.124}$$

This non-negativeness, together with the degeneracy requirement (1.116a and b), guarantees that $\mathrm{d}S/\mathrm{d}t \geq 0$, while the symmetry property (1.123) is directly related to Onsager's reciprocal relations (1.81). The symmetry of $\mathbf{M}$ is only valid for variables with the same parity. Otherwise, $\mathbf{M}$ should contain a non-symmetrical part in agreement with Onsager–Casimir theory (1.82).

GENERIC may be viewed as an extension of Ginzburg–Landau equation (e.g. Öttinger 2005) describing evolution towards equilibrium and given by

$$\frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t} = -\mathbf{M} \cdot \frac{\delta \phi}{\delta \boldsymbol{x}}, \tag{1.125}$$

where $\mathbf{M}$ is a positive-definite linear operator and ϕ a given potential. The interest of GENERIC lies in its compact, abstract and general framework. Details of the evolution equation (1.115) depend of course on the specific choice made for the two generators E and S and the two matrices $\mathbf{L}$ and $\mathbf{M}$. Restrictions on $\mathbf{L}$ and $\mathbf{M}$ are imposed by (1.116a and b), (1.120), (1.121) and (1.122).

The main innovation of GENERIC with respect to earlier bracket formalisms is the use of two different generators, E and S, instead of a single one: this gives more flexibility to the theory and emphasizes the central role played by the thermodynamic potentials E and S. The matrix $\mathbf{L}$ is determined by the behaviour of the variables $\boldsymbol{x}$ under space transformations, whereas the dynamical material information enters in the friction matrix $\mathbf{M}$, which is related to transport coefficients.

From the properties $\{A, B\} = 0$ and $[A, A] \geq 0$ and the degeneracy conditions (1.116a and b), one sees that

$$\frac{\mathrm{d}E}{\mathrm{d}t} = 0, \qquad \frac{\mathrm{d}S}{\mathrm{d}t} \geq 0, \tag{1.126}$$

indicating that the system is isolated from its environment.

GENERIC has been the subject of several applications in statistical mechanics, quantum mechanics, relativity, cosmology but mainly in rheology (Öttinger 2005). Its structure is universal and is applicable whatever the level of description, microscopic, mesoscopic or macroscopic. GENERIC leaves the state variables undetermined and provides no hint to determine them. The formalism requires the knowledge of the following quantities: the Poisson bracket, the total energy E, the dissipation function Ψ, and the total entropy S, as Ψ is a function of $\delta S/\delta \boldsymbol{x}$. To be sure that the bracket is a true Poisson bracket, it is necessary to check for each individual problem that Jacobi's identity (1.119b) is satisfied, this represents a complicated and tedious task. In recent publications of GENERIC, there is a tendency in favour of the use of the following blocks: E, S and the two operators **L** (skew-symmetric) and **M** (symmetric).

The main difficulty concerning GENERIC is the construction of the appropriate Poisson bracket, or equivalently, the block operators **L** and **M**. Technical problems arise also when the system is not isolated as in fluids submitted to external forces, like Bénard's convection under external temperature gradients. In presence of coupled heat and mass transports, the procedure is rather intricate and introduces non-physical variables as peculiar combinations of entropy and mass fluxes (Grmela et al. 2003). Like Rational Thermodynamics, GENERIC remains silent about the definitions of non-equilibrium temperature and entropy.

1.6 Problems

Solutions of the problems proposed in this book may be found, as Solutions Manual for Extended Irreversible Thermodynamics, on the site http://telemaco.uab.es.

1.1. *Onsager's reciprocity relations in a triangular chemical reaction scheme.* The cycle of chemical reactions A $\rightleftarrows$ B $\rightleftarrows$ C $\rightleftarrows$ A was analysed by Onsager as an illustration of the reciprocity relations. Let k_i $(i = 1, 2, 3)$ be the kinetic constants, J_i the respective fluxes of the reactions, which, according to the mass action law, are given by $J_1 = k_1 c_\mathrm{A} - k_{-1} c_\mathrm{B}$, $J_2 = k_2 c_\mathrm{B} - k_{-2} c_\mathrm{C}$, $J_3 = k_3 c_\mathrm{C} - k_{-3} c_\mathrm{A}$, and $\mathcal{A}_i$ the respective affinities, i.e. $\mathcal{A}_1 = \mu_\mathrm{A} - \mu_\mathrm{B}$, $\mathcal{A}_2 = \mu_\mathrm{B} - \mu_\mathrm{C}$, $\mathcal{A}_3 = \mu_\mathrm{C} - \mu_\mathrm{A}$ Since the process is cyclic, only two reactions are independent and $\mathcal{A}_1 + \mathcal{A}_2 + \mathcal{A}_3 = 0$. Show that when the relations between fluxes and forces are expressed in the form

$$J_1 - J_3 = L_{11}\mathcal{A}_1 + L_{12}\mathcal{A}_2,$$
$$J_2 - J_3 = L_{21}\mathcal{A}_1 + L_{22}\mathcal{A}_2,$$

the Onsager reciprocal relation $L_{12} = L_{21}$ is automatically satisfied near equilibrium if the principle of detailed balance is valid, i.e. if $J_1 = J_2 = J_3 = 0$ is verified. Note that this assumption does not follow from the constitutive equations, since non-zero values $J_1 = J_2 = J_3 \neq 0$ are compatible with $\mathcal{A}_1 + \mathcal{A}_2 + \mathcal{A}_3 = 0$.

1.2. *The mass action law.* Consider the chemical reaction

$$\nu_X \mathrm{X} + \nu_Y \mathrm{Y} \rightleftarrows \nu_Z \mathrm{Z} + \nu_W \mathrm{W},$$

with ν_i the stoichiometric coefficients. According to the mass action law, the reaction rate will be given by

$$J = \frac{1}{\nu_Z}\frac{\mathrm{dZ}}{\mathrm{d}t} = k_+ \, [\mathrm{X}]^{\nu_X} \, [\mathrm{Y}]^{\nu_Y} - k_- \, [\mathrm{Z}]^{\nu_Z} \, [\mathrm{W}]^{\nu_W} \, ,$$

where k_+ and k_- are respectively the forward and backward kinetic constants. (a) Show that for ideal gases, whose chemical potential has the form $\mu_i = RT \ln[i] + \zeta_i(T, p)$, where $[i]$ is the molar concentration and $\zeta_i(T, p)$ is an arbitrary function of T and p, the constitutive relation between J and the affinity $\mathcal{A}$ is

$$J = k_- \, [\mathrm{Z}]^{\nu_Z} \, [\mathrm{W}]^{\nu_W} \, [\exp(\mathcal{A}/RT) - 1] \, .$$

(b) Show that when $\mathcal{A}/RT \ll 1$, this relation reduces to $J = L(\mathcal{A}/T)$ with $L = (k_-/R) \times \; [\mathrm{Z}]_{\mathrm{eq}}^{\nu_Z} \, [\mathrm{W}]_{\mathrm{eq}}^{\nu_W} = (k_+/R) \, [\mathrm{X}]_{\mathrm{eq}}^{\nu_X} \, [\mathrm{Y}]_{\mathrm{eq}}^{\nu_Y}$, where subscript eq refers to equilibrium concentrations.

1.3. *The Einstein relation.* A dilute suspension of small particles in a viscous fluid at homogeneous temperature T is under the action of the gravitational field. The friction coefficient of the particles with respect to the fluid is α ($\alpha = 6\pi\eta r$ for spherical particles of radius r in a solvent with viscosity η). Owing to gravity, the particles have a sedimentation velocity $v_{\mathrm{sed}} = m'g \, / \, \alpha$, with m' the mass of one particle minus the mass of the fluid displaced by one particle (Archimedes' principle); the corresponding sedimentation flux is $J_{\mathrm{sed}} = n v_{\mathrm{sed}}$, with n being the number of particles per unit volume. Against the sedimentation flux a diffusion flux $J_{\mathrm{dif}} = -D\nabla n$ acts, D being the diffusion coefficient. (a) Find the vertical distribution of the concentration $n(z)$ of particles in equilibrium when the upward diffusion flux cancels exactly the downward sedimentation flux. (b) Compare this expression with Boltzmann's general expression

$$n(z) = n(0) \exp\left(-\frac{m'gz}{k_B T}\right),$$

where k_{B} is the Boltzmann constant, and demonstrate Einstein's relation $D = k_{\mathrm{B}}T \,/\, \alpha$.

1.4. (a) Determine the entropy production per unit volume in a two-component diffusing mixture at rest; the system is chemically inert and the viscous effects are assumed to be negligible. (b) Show that the relevant phenomenological equations are

$$\begin{aligned} \boldsymbol{q}_1 &= -\lambda \nabla T - \frac{\mu_{11}}{c_2} D_{\mathrm{F}} \nabla c_1 \ \text{(Dufour law)} \\ \boldsymbol{J}_1 &= -D_{\mathrm{S}} \nabla T - D \nabla c_1 \ \text{(Soret law)} \end{aligned}$$

where $D_{\mathrm{F}} = D_{\mathrm{S}}$; $\boldsymbol{q}_1$ is the reduced heat flux vector, $\boldsymbol{q}_1 = \boldsymbol{q} - \sum_k h_k \boldsymbol{J}_k$, $\boldsymbol{J}_1$ is the flux of matter of component 1, subscripts 1, 2 refer to components 1, 2 respectively, μ_{11} stands for $\partial \mu_1 \,/\, \partial c_1$, and D, D_{F} and D_{S} are respectively given by $D = L_{11}\mu_{11}/c_2$, $D_{\mathrm{F}} = L_{q1}$, $D_{\mathrm{S}} = L_{1q}$.

1.5. *Micropolar fluids*. In some fluids (composed of elongated particles or rough spheres) the pressure tensor is non-symmetric. Its antisymmetric part is related to the rate of variation of an intrinsic angular momentum, and thus, it contributes to the balance equation of angular momentum (see, for instance, Snider and Lewchuk (1967) or Rubí and Casas-Vázquez (1980)). The antisymmetric part of the tensor is usually related to an axial vector $\boldsymbol{P}^{va}$, whose components are defined as $\boldsymbol{P}_1^{va} = \boldsymbol{P}_{23}^{va}$, $\boldsymbol{P}_2^{va} = \boldsymbol{P}_{31}^{va}$, $\boldsymbol{P}_3^{va} = \boldsymbol{P}_{12}^{va}$. The equation of balance for the internal angular momentum is

$$\rho j \dot{\boldsymbol{\omega}} + \nabla \cdot \mathbf{Q} = -2\boldsymbol{P}^{va},$$

with j the microinertia per unit mass of the fluid, $\boldsymbol{\omega}$ the angular velocity, and $\mathbf{Q}$ the flux of the intrinsic angular momentum, which is usually neglected. (a) Show that the entropy production is given by

$$\sigma^s = -T^{-1} p^v \nabla \cdot \boldsymbol{v} - T^{-1} \overset{0}{\mathbf{P}}{}^{vs} : (\overset{0}{\nabla} \boldsymbol{v})^s - T^{-1} \mathbf{P}^{va} \cdot (\nabla \times \boldsymbol{v} - 2\boldsymbol{\omega}) + \boldsymbol{q} \cdot \nabla T^{-1},$$

where $\mathbf{P}^{vs}$ is the symmetric part of $\mathbf{P}^{v}$. (*Hint*: Note that $\partial s / \partial \boldsymbol{\omega} = -\rho j T^{-1} \boldsymbol{\omega}$). (b) Show that the corresponding constitutive equation for $\boldsymbol{P}^{va}$ is

$$\boldsymbol{P}^{va} = -\eta_r (\nabla \times \boldsymbol{v} - 2\boldsymbol{\omega}),$$

where η_r is the so-called rotational viscosity; explain why there is no coupling between $\boldsymbol{P}^{va}$ and $\boldsymbol{q}$.

1.6. Prove that the symmetric part $\mathbf{V}$ of the velocity gradient tensor is objective; prove that the following quantities are not objective: $\nabla \mathbf{v}$ (the velocity gradient tensor), $\mathbf{W}$ (the skew-symmetric velocity gradient tensor), $\dot{\boldsymbol{q}}$ (the material time derivative of the heat flux).

1.7. Consider an incompressible fluid characterized by a specific entropy s, a specific Helmholtz free energy ϕ, a heat flux $\boldsymbol{q}$, and a pressure tensor $\mathbf{P}$

depending on the temperature T, the temperature gradient ∇T, the symmetric velocity gradient tensor $\mathbf{V}$, and their first-order material time derivatives. Determine the corresponding constitutive equations in the framework of rational thermodynamics.

1.8. *The efficiency of energy conversion.* Consider two coupled chemical reactions, with rates J_1 and J_2 and affinities $\mathcal{A}_1$ and $\mathcal{A}_2$ respectively. The entropy production is given by $T\sigma^s = J_1\mathcal{A}_1 + J_2\mathcal{A}_2 > 0$. Assume $J_1\mathcal{A}_1 < 0$ and $J_2\mathcal{A}_2 > 0$, which means that reaction 2 liberates an amount of free energy, which is used in reaction 1. This situation is common in biology: the free energy liberated by ATP is used to pump ions against their chemical potential gradient, or the free-energy liberated by oxidation–reduction reactions in the respiratory process is utilized to produce ATP by phosphorylation of ADP (Kaplan and Essig 1983; Jou and Llebot 1990). Assume linear constitutive laws of the form

$$\begin{aligned} J_1 &= L_{11}\mathcal{A}_1 + L_{12}\mathcal{A}_2, \\ J_2 &= L_{21}\mathcal{A}_1 + L_{22}\mathcal{A}_2. \end{aligned}$$

The degree of coupling of the process is defined as $q = L_{12}\left(L_{11}L_{22}\right)^{-1/2}$ and the efficiency of the energy conversion is given by

$$\eta = -(J_1\mathcal{A}_1)/\left(J_2\mathcal{A}_2\right)$$

(a) Show that $-1 \le q \le 1$. (b) Show that the maximum possible value of the efficiency of the energy conversion is

$$\eta_{\max} = \frac{q^2}{\left[1 + (1 - q^2)^{1/2}\right]^2}.$$

1.9. It is known that by writing a linear relation of the form $J_\alpha = \sum_\beta L_{\alpha\beta} X_\beta$ between n independent fluxes J_α ($\alpha = 1, \dots, n$) and n independent thermodynamic forces X_β, the matrix $L_{\alpha\beta}$ of phenomenological coefficients is symmetric, according to Onsager. (a) Show that the matrix $L_{\alpha\beta}$ is still symmetric when not all the fluxes are independent but one of them is a linear combination of the other ones, i.e. $J_n = \sum_\alpha a_\alpha J_\alpha$ ($\alpha = 1, \dots, n-1$). (b) Does this conclusion remain true when instead of a linear relation between the fluxes there exists a linear relation between the forces $X_n = \sum_\beta b_\beta X_\beta$? Check this result on the cyclic reaction of Problem 1.1.

1.10. *Non-linear constitutive relations.* Some authors have postulated an extension of the Onsager relations to non-linear situations in the form

$$\left(\partial J_i/\partial X_j\right) = \left(\partial J_j/\partial X_i\right)$$

with J_i and X_j being the thermodynamic fluxes and forces. (a) Show that for linear flux–force relations, this result is equivalent to Onsager's reciprocal relations. (b) Consider now the following second-order expansion:

$$J_1 = L_{11}X_1 + L_{12}X_2 + L_{111}X_1^2 + L_{112}X_1X_2 + L_{122}X_2^2,$$
$$J_1 = L_{21}X_1 + L_{22}X_2 + L_{211}X_1^2 + L_{212}X_1X_2 + L_{222}X_2^2.$$

What are the relations between the phenomenological coefficients L if the equality of cross derivatives is applied to these expressions? (c) Consider the sequence of reactions $\mathrm{A} \rightleftarrows \mathrm{B} \rightleftarrows \mathrm{C}$. Using the mass action law, express J_1 and J_2 in terms of $\mathcal{A}_1 = \mu_\mathrm{A} - \mu_\mathrm{B}$ and $\mathcal{A}_2 = \mu_\mathrm{B} - \mu_\mathrm{C}$. Expand these relations up to second order and show that the reciprocal relations obtained in (b) are not satisfied. This result is important, since it shows that in general there are not reciprocal properties for non-linear expansions.

1.11. *Minimum entropy production.* A system is described by the two linear phenomenological laws $J_1 = L_{11}X_1 + L_{12}X_2$ and $J_2 = L_{21}X_1 + L_{22}X_2$. Assume that the thermodynamic force X_2 is kept fixed at a non-vanishing value. (a) Show that when the L_{ij} are constant and satisfy Onsager's reciprocal relations the entropy production $\sigma^s = \sum_{\alpha\beta} L_{\alpha\beta} X_\alpha X_\beta$ is minimum in the steady state, i.e. for a value of X_1 such that $J_1 = 0$. (b) The entropy production in a rigid heat conductor is found to be given by $\sigma^s = L(\nabla T^{-1})\cdot(\nabla T^{-1})$ with $L = \lambda T^2$. Keeping the temperature T fixed at the boundaries of the sample, show that, for constant L, the total entropy production, i.e. $P = \int \sigma^s \mathrm{d}V$, is a minimum in the steady state $\nabla \cdot \boldsymbol{q} = 0$.

1.12. *Cycles with finite time.* In a Carnot engine, the working fluid is kept in contact with heat reservoirs at respective temperatures T_1 and T_2 during the isothermal parts of the cycle. Assume that the temperatures of the reservoirs are different from the temperature of the fluid, i.e. $T_1 > T_1'$ and $T_2' > T_2$, and that the heat exchanged per unit time during these processes is given by $\text{đ}Q_1/\mathrm{d}t = \alpha\left(T_1 - T_1'\right)$, $\text{đ}Q_2/\mathrm{d}t = \alpha\left(T_2' - T_2\right)$, with α being a constant. (a) Determine the power developed by this Carnot engine, assuming that the total duration of each cycle is proportional to the sum of the duration of the isothermal branches. (b) For given values of T_1 and T_2, find the values of T_1' and T_2' which maximise the power. (c) Show that the efficiency at maximum power is

$$\eta_{\text{maximun power}} = 1 - (T_2/T_1)^{1/2}.$$

Compare this expression with the efficiency of a reversible Carnot cycle $\eta = 1 - (T_2/T_1)$. (Note that for a reversible Carnot engine the power is zero, because a cycle lasts an infinite time.) (See Curzon and Ahlborn 1975.)

1.13. Consider the following Poisson bracket

$$\{A, B\} = \int \left[u_i \left(\left(\partial_j A_{u_i}\right) B_{u_j} - \left(\partial_j B_{u_i}\right) A_{u_j}\right)\right]\mathrm{d}V,$$

where $A = \int a\mathrm{d}V$ and $B = \int b\mathrm{d}V$ are functionals of the momentum vector $u_i\ (= \rho v_i)$, $\partial_j\ \left(= \partial/\partial r_j\right)$, and $A_{u_i} = \delta A/\delta u_i$. Show that the above Poisson bracket satisfies the properties (1.119a and b).

1.14. Determine the **L** and **M** operators for classical hydrodynamics, namely, for

$$\begin{aligned}
\frac{\partial \rho}{\partial t} &= -\partial_\gamma(\rho v_\gamma),\\
\frac{\partial u_\alpha}{\partial t} &= -\partial_\gamma\left(\rho v_\alpha v_\gamma\right) - \partial_\alpha p + \eta\partial_\gamma\partial_\gamma v\alpha\\
\frac{\partial \varepsilon}{\partial t} &= -\partial_\gamma\left(\varepsilon v_\gamma\right) - p\partial_\gamma v_\gamma + \lambda\partial_\gamma\partial_\gamma T + \eta\left(\partial_\gamma v_\alpha \partial_\gamma v_\alpha\right)
\end{aligned}$$

Check that the consistency conditions (1.116 a and b) are satisfied (Grmela and Öttinger 1997).

Chapter 2
Extended Irreversible Thermodynamics: Evolution Equations

Our general purpose is to propose a theory which goes beyond the classical formulation of irreversible thermodynamics (CIT). This is achieved by enlarging the space of basic independent variables through the introduction of non-equilibrium variables, such as the dissipative fluxes appearing in the balance equations of mass, momentum and energy. The next step is to find evolution equations for these extra variables. Whereas the evolution equations for the classical variables are given by the usual balance laws, no general criteria exist concerning the evolution equations of the fluxes, with the exception of the restrictions imposed on them by the second law of thermodynamics.

The independent character of the fluxes is made evident in high-frequency phenomena. In general, they are *fast* variables that decay to their local-equilibrium values after a short relaxation time. Whereas many authors have studied the elimination of such *fast* variables in order to obtain a description of the system in terms of slow variables, our objective is the opposite one. We want to describe phenomena at frequencies comparable to the inverse of the relaxation times of the fluxes. Therefore, at such time scales, it is natural to include the fast variables among the set of basic independent variables.

A simple way to obtain the evolution equations for the fluxes from a macroscopic basis is to generalise the classical theories presented in the previous chapter. In that spirit, we assume the existence of a generalised entropy which depends on the dissipative fluxes and on the classical variables as well. A physical interpretation of the different contributions to the generalised entropy is proposed. Once this expression is known, it is an easy matter to derive generalised equations of state, which are of interest in the description of non-equilibrium steady states.

For pedagogical reasons, we shall first study the simple problem of heat transport in a rigid isotropic body when only the heat flux is introduced as an extra variable. Afterwards, we shall consider the more general case of a one-component isotropic fluid, where the heat flux, the bulk viscous pressure, and the viscous pressure tensor are taken as supplementary independent variables, on the same footing as the classical ones. After having obtained the evolution equations for the flux variables by methods which generalise those of CIT, we will show how to obtain them in the framework of rational extended thermodynamics. The respective merits of both approaches are also discussed.

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_2,

2.1 Heat Conduction in Rigid Solids

Let us first outline the motivations for introducing fluxes as independent variables for the simple problem of heat conduction in rigid bodies. Afterwards, we will take advantage of this simple situation to introduce the main tenets of the theory.

2.1.1 Motivations

The best known model for heat conduction in rigid solids is Fourier's law, which relates linearly the temperature gradient ∇T to the heat flux $\boldsymbol{q}$ according to

$$\boldsymbol{q} = -\lambda \nabla T, \tag{2.1}$$

where λ is the heat conductivity, depending generally on the temperature. By substituting (2.1) in the energy balance equation (written in absence of source terms and in a system at rest)

$$\rho \frac{\partial u}{\partial t} = -\nabla \cdot \boldsymbol{q}, \tag{2.2}$$

where the specific internal energy u is related to the temperature by $\mathrm{d}u = c_v \mathrm{d}T$, with c_v being the heat capacity per unit mass at constant volume, one obtains a parabolic differential equation for the temperature given by

$$\rho c_v \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T). \tag{2.3}$$

This equation shows excellent agreement with experiments for most practical problems, but it suffers from some main deficiencies over short times or at high frequencies. In particular, Onsager (1931) noted that Fourier's model contradicts the principle of microscopic reversibility, but this contradiction '... *is removed when we recognize that [Fourier's law] is only an approximate description of the process of conduction, neglecting the time needed for acceleration of the heat flow'*. In other words, Fourier's law has the unphysical property that it lacks inertial effects: if a sudden temperature perturbation is applied at one point in the solid, it will be felt instantaneously and everywhere at distant points. Moreover, Fourier's model is not adequate for describing heat transport at very high frequencies and short wavelengths. Such situations are met when the phenomena are very fast or very steep (as ultrasound propagation, light scattering in gases, neutron scattering in liquids, heat propagation at low temperatures, shock waves, etc.) or when the relaxation times of the fluxes are very long (as in polymer solutions, suspensions, superfluids or superconductors). Historically, Maxwell (1867) was the first to introduce inertia in transport equations.

To eliminate these anomalies, Cattaneo (1948) proposed a damped version of Fourier's law by introducing a heat–flux relaxation term, namely

$$\tau \frac{\partial \boldsymbol{q}}{\partial t} = -\left(\boldsymbol{q} + \lambda \nabla T\right). \tag{2.4}$$

The relaxation time τ is the response time for the onset of heat flow after a temperature gradient is suddenly imposed. When τ is negligible or when the time variation of the heat flux is slow, Eq. (2.4) reduces to Fourier's law.

Introduction of (2.4) into (2.2) results in a hyperbolic equation of the telegrapher type,

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} - \chi \nabla^2 T = 0. \tag{2.5}$$

By establishing (2.5) it is assumed that τ and λ are constant and positive, while the quantity $\chi = \lambda/\rho c_v$ designates the heat diffusivity. For $t \ll \tau$, the first term of (2.5) is dominant and the above relation reduces to

$$\tau \frac{\partial^2 T}{\partial t^2} = \chi \nabla^2 T, \tag{2.6}$$

which is a wave equation with the same wave speed as (2.5), namely $u = (\chi/\tau)^{1/2}$; it describes a reversible process, as it is invariant with respect to time reversal $t \to -t$. In contrast, for time scales longer than $\tau(t \gg \tau)$, the first term in (2.5) is negligible and one is led to the classical heat diffusion equation

$$\frac{\partial T}{\partial t} = \chi \nabla^2 T, \tag{2.7}$$

which describes an irreversible process, as it is not invariant under time inversion. Thus, at short times, expression (2.5) is reversible and heat propagates at finite speed, microscopically this may be interpreted as the motion of ballistic heat carriers moving freely without experiencing collisions; at longer times, the process becomes irreversible and heat is diffused everywhere throughout the whole system. Therefore, the time τ can be interpreted as the characteristic time for the crossover between ballistic motion and the onset of diffusion. In the context of chaotic deterministic systems, τ may be viewed as the Lyapunov time beyond which predictivity is lost (Nicolis and Prigogine 1989).

The dynamical properties of Eq. (2.4) have been thoroughly analysed. However, the thermodynamic consequences are less known and are therefore worth examining. Indeed, from the expression for the classical entropy production, namely, $\sigma^s = \boldsymbol{q} \cdot \nabla T^{-1}$ one obtains

$$\sigma^s = \frac{\lambda}{T^2}(\nabla T^2) + \frac{\tau}{T^2}\frac{\partial \boldsymbol{q}}{\partial t} \cdot \nabla T, \tag{2.8}$$

which is no longer definite positive, because of the second term. To illustrate the problems raised by the local-equilibrium entropy, let us examine the time evolution of entropy in an isolated rigid body with an initial sinusoidal temperature profile by using (2.5); one obtains non-monotonic behaviour, as exhibited by the dashed curve

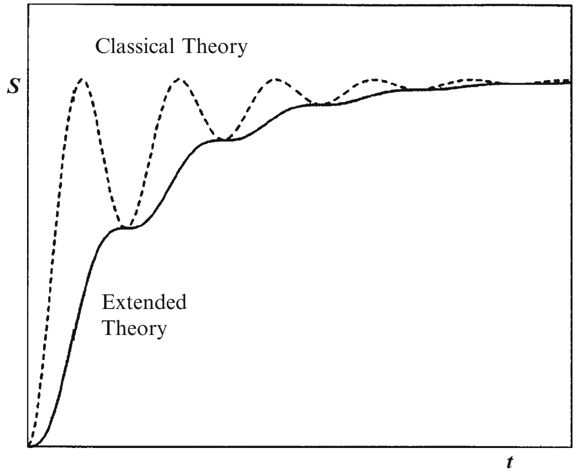


Fig. 2.1 The evolution of the classical entropy S_{CIT} during the equilibration of an isolated system described by the Cattaneo equation (2.1.9) is given by the dashed curve. The evolution of the extended entropy S_{EIT}, obtained from (2.1.17), is represented by the solid curve, which, in contrast with that of S_{CIT}, increases monotonically

shown in Fig. 2.1. The details are found in Box 2.1 wherein an analysis of a discrete system composed of two rigid solids in contact at different temperatures is carried out.

Box 2.1 Entropy evolution in an isolated system: an illustrative example

In this section we compare the behaviour of classical entropy and extended entropy shown in Fig. 2.1 during thermal equilibration, for a discrete system. Consider heat transfer between two rigid bodies at different temperatures and isolated from the outside world. Initially, the bodies are separated by an adiabatic wall. If the adiabatic constraint is removed, heat will flow from one body to the other without either work being performed or mass carried. Let us start with the classical local-equilibrium formulation. Each of the two subsystems, at temperatures T_1 and T_2 $(< T_1)$ respectively, is in internal equilibrium, i.e. the internal temperature changes are negligible compared to the temperature difference $T_1 - T_2$. In virtue of the extensivity property, the total entropy of the whole system S is the sum of the entropies of each subsystem, S_1 and S_2, which are functions of the internal energies U_1 and U_2 of subsystems 1 and 2 respectively, even during the heat transfer process, namely $S(U_1, U_2) = S_1(U_1) + S_2(U_2)$. When the adiabatic wall separating the two subsystems is replaced by a diathermal one, the time-rate variation of total entropy is

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\mathrm{d}S_1}{\mathrm{d}t} + \frac{\mathrm{d}S_1}{\mathrm{d}t} = T_1^{-1}\frac{\mathrm{d}U_1}{\mathrm{d}t} + T_2^{-1}\frac{\mathrm{d}U_2}{\mathrm{d}t}. \tag{2.1.1}$$

Since the global system is isolated, $\mathrm{d}U_1 + \mathrm{d}U_2 = 0$, and using the first law of thermodynamics we can write

$$\frac{\mathrm{d}U_1}{\mathrm{d}t} = -\frac{\mathrm{d}U_2}{\mathrm{d}t} = -\dot{Q}, \tag{2.1.2}$$

where $\dot{Q}$ is the amount of heat exchanged between subsystems 1 and 2 per unit time, i.e. the heat flux integrated over the surface separating the two bodies. Recall that, by convention, energy input is positive and energy release negative.

For an isolated system, (2.1.1) represents the rate of entropy produced inside the system; in virtue of (2.1.2), it can be written as

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -(T_1^{-1} - T_2^{-1})\dot{Q}. \tag{2.1.3}$$

According to the second law of thermodynamics, this quantity must be non-negative. This implies that heat only flows from the region of highest temperature to the region of lowest temperature, which is the original Clausius formulation of the second law.

To ensure the positiveness of (2.1.3) is to assume that the heat flux $\dot{Q}$ is proportional to the driving force $(T_1^{-1} - T_2^{-1})$, so that

$$\dot{Q} = -K(T_1^{-1} - T_2^{-1}), \tag{2.1.4}$$

with K being a positive coefficient. If the temperature difference is small, one may linearize this relation and write it in the usual form

$$\dot{Q} = K'(T_1 - T_2), \tag{2.1.5}$$

with $K' = KT^{-2}$ assumed to be a constant and T an intermediate temperature between T_1 and T_2.

In the course of time, the evolution equation for the temperature of each subsystem is easily found by recalling that $\mathrm{d}U_1 = C_1\mathrm{d}T_1$ and $\mathrm{d}U_2 = C_2\mathrm{d}T_2$, with C_1 and C_2 being the heat capacities of the respective subsystems. Combining this result with (2.1.2), it is found that the temperature difference $\varepsilon = T_1 - T_2$ varies as

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = -\dot{Q}C_{\mathrm{eff}}^{-1}, \tag{2.1.6}$$

with $C_{\mathrm{eff}}^{-1} = C_1^{-1} + C_2^{-1}$. When (2.1.5) is introduced into (2.1.6) one finds that

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = -K''\varepsilon, \tag{2.1.7}$$

with $K'' = K'C_{\mathrm{eff}}^{-1}$. Thus ε decays exponentially as $\varepsilon = \varepsilon_0 \exp(-K''t)$, and after an infinite lapse of time the temperature inside the system becomes uniform. In view of (2.1.3) and (2.1.6) the rate of evolution of entropy may be written in terms of ε as

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -T^{-2}\frac{K'}{K''}\varepsilon\frac{\mathrm{d}\varepsilon}{\mathrm{d}t}. \tag{2.1.8}$$

It is thus seen that the entropy is a monotonically increasing function of time.

Consider now the more general situation in which heat transfer is described by a Cattaneo-type relation

$$\tau\frac{\mathrm{d}\dot{Q}}{\mathrm{d}t} + \dot{Q} = -K(T_1^{-1} - T_2^{-1}), \tag{2.1.9}$$

where τ is the relaxation time of the heat flux $\dot{Q}$. This expression is analogous to the Cattaneo equation (2.4). After combining (2.1.6) and (2.1.9), one finds for the evolution of ε that

$$\tau\frac{\mathrm{d}^2\varepsilon}{\mathrm{d}t^2} + \frac{\mathrm{d}\varepsilon}{\mathrm{d}t} + K''\varepsilon = 0. \tag{2.1.10}$$

This equation is similar to the equation of motion of a damped pendulum. The decay of ε will not in general be exponential but may exhibit an oscillatory behaviour when $4\tau K'' > 1$. In continuous systems, the exponential decay observed in the discrete model would correspond to a diffusive perturbation, whereas an oscillation in ε would correspond to the propagation of a heat wave. According to (2.1.8), in the case of oscillatory decay of ε, the classical entropy S behaves as a non-monotonic function of time, as indicated by the dashed curve of Fig. 2.1.

In extended irreversible thermodynamics (EIT), the heat flux $\dot{Q}$ is viewed as an independent variable of the entropy. The proposed form of the generalised entropy in EIT is therefore $S_{\mathrm{EIT}}(U_1, U_2, \dot{Q})$. The rate of variation of S_{EIT} is, up to the second order in $\dot{Q}$,

$$\frac{\mathrm{d}S_{\mathrm{EIT}}}{\mathrm{d}t} = T_1^{-1}\frac{\mathrm{d}U_1}{\mathrm{d}t} + T_2^{-1}\frac{\mathrm{d}U_2}{\mathrm{d}t} - a\dot{Q}\frac{\mathrm{d}\dot{Q}}{\mathrm{d}t}. \tag{2.1.11}$$

Using the conservation of energy (2.1.2), one may write (2.1.11) as

$$\frac{\mathrm{d}S_{\mathrm{EIT}}}{\mathrm{d}t} = -(T_1^{-1} - T_2^{-1})\dot{Q} - a\dot{Q}\frac{\mathrm{d}\dot{Q}}{\mathrm{d}t}. \tag{2.1.12}$$

For small temperature differences, $\mathrm{d}S_{\mathrm{EIT}}/\mathrm{d}t$ simplifies to

$$\frac{\mathrm{d}S_{\mathrm{EIT}}}{\mathrm{d}t} = \left(T^{-2}\varepsilon - a\frac{\mathrm{d}\dot{Q}}{\mathrm{d}t}\right)\dot{Q}. \tag{2.1.13}$$

The simplest way to guarantee the positiveness of the entropy production $\mathrm{d}S_{\mathrm{EIT}}/\mathrm{d}t$ is to assume the linear relation

$$\dot{Q} = K\left(T^{-2}\varepsilon - a\frac{\mathrm{d}\dot{Q}}{\mathrm{d}t}\right), \tag{2.1.14}$$

where K is a positive constant and, in analogy with the Cattaneo equation (2.9), aK may be interpreted as a relaxation time, namely $aK = \tau$. In view of this identification, the entropy variation can be written as

$$\frac{\mathrm{d}S_{\mathrm{EIT}}}{\mathrm{d}t} = -(T_1^{-1} - T_2^{-1})\dot{Q} - \frac{\tau}{K}\dot{Q}\frac{\mathrm{d}\dot{Q}}{\mathrm{d}t}, \tag{2.1.15}$$

or, in an integrated form,

$$S_{\mathrm{EIT}}(U_1, U_2, \dot{Q}) = S_1(U_1) + S_2(U_2) - \frac{\tau}{2K}\dot{Q}^2. \tag{2.1.16}$$

Observe that in the limiting case $\tau = 0$, the above expression reduces to the local-equilibrium entropy. The last term on the right-hand side of (2.1.16) may be viewed as expressing the interaction between subsystems 1 and 2.

According to (2.1.13) and (2.1.14), the time variation of S_{EIT} may simply be written as

$$\frac{\mathrm{d}S_{\mathrm{EIT}}}{\mathrm{d}t} = K^{-1}\dot{Q}^2 = K^{-1}C_{\mathrm{eff}}^2\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}t}\right)^2. \tag{2.1.17}$$

This expression is either positive or zero, but never negative, since it was found that $K > 0$, and therefore $S_{\mathrm{EIT}}[U_1(t), U_2(t), \dot{Q}(t)]$,,whose evolution is represented by the continuous curve of Fig. 2.1, increases monotonically in the course of time and is thus compatible with evolution equations of the Cattaneo type. The corresponding analysis for a continuous system has been treated by Criado-Sancho et al. (1993).

It is seen in Fig. 2.1 that instead of being monotonically increasing, the classical entropy behaves in an oscillatory way. Strictly speaking this result is not incompatible with the Clausius formulation of the second law, which states that the entropy of the final equilibrium state must be higher than the entropy of the initial equilibrium state. However, the non-monotonic behaviour of the entropy is in contradiction with the local-equilibrium formulation of the second law, which requires that the entropy production must be positive everywhere at any time in the evolution.

It is thus found that the Cattaneo law (2.4), which has been shown to be very applicable in the description of the results of many experiments on heat waves, is not compatible with the local-equilibrium hypothesis, which ought therefore to be reconsidered. This is precisely the aim of the Sect. 2.1.2.

2.1.2 The Generalised Gibbs Equation

As in CIT, the entropy and the Gibbs equation play a central role in extended irreversible thermodynamics (EIT). Here, it is assumed that the entropy will not only depend on the classical variable, namely the specific internal energy u, but in addition on the heat flux $\boldsymbol{q}$, whose initial value must be specified in order to solve Eq. (2.4):

$$s = s(u, \boldsymbol{q}). \tag{2.9}$$

The generalised entropy $s = s(u, \boldsymbol{q})$ will be assigned the following properties:

- It is an additive quantity.
- It is a concave function of the whole set of variables, which means that it is a function which lies everywhere below its family of tangent lines.
- Its rate of production is locally positive.

The hypothesis of a generalised macroscopic entropy depending on the fluxes was advanced by Machlup and Onsager (1953) in an indirect way. During the 1960s a more direct formulation applied to fluids was developed by Nettleton (1959) and Müller (1967). In the 1970s, new reformulations were proposed independently by several authors and have inspired much research (e.g. Gyarmati 1970; Jou et al. 1979; Lebon et al. 1980; Garcia-Colin et al. 1984; Eu 1992) which has been reviewed by Jou and Zakari (1995, 1999) and Sieniutycz and Salamon (1992).

The differential form of the generalised entropy is written as follows:

$$ds = \left(\frac{\partial s}{\partial u}\right) \mathrm{d}u + \left(\frac{\partial s}{\partial \boldsymbol{q}}\right) \cdot \mathrm{d}\boldsymbol{q}. \tag{2.10}$$

In analogy with the classical theory, we define the non-equilibrium temperature θ by

$$\theta^{-1}(u, \boldsymbol{q}) = \left(\frac{\partial s}{\partial u}\right)_{\boldsymbol{q}}, \tag{2.11}$$

not to be confused with the local-equilibrium temperature

$$T^{-1} = \left(\frac{\partial s}{\partial u}\right)_{\boldsymbol{q}=0}. \tag{2.12}$$

The quantity θ^{-1} can be expanded around the inverse of the local-equilibrium temperature T and written as

$$\theta^{-1}(u, \boldsymbol{q}) = T^{-1}(u) + a(u)q^2, \tag{2.13}$$

when terms of order higher than q^2 are neglected; the coefficient $a(u)$ depends generally on u, and q^2 stands for $\boldsymbol{q} \cdot \boldsymbol{q}$ The remaining partial derivative in (2.10) will be denoted as

$$\left(\frac{\partial s}{\partial \boldsymbol{q}}\right) = -v\boldsymbol{\alpha}_1(u, \boldsymbol{q}), \tag{2.14}$$

wherein the minus sign and the factor v are introduced for convenience. Without loss of generality, we may write $\boldsymbol{\alpha}_1$ as

$$\boldsymbol{\alpha}_1 = \alpha_{10}(u, q^2)\boldsymbol{q}. \tag{2.15}$$

Substituting (2.11–2.15) into (2.10) results in the final expression of the generalised Gibbs equation when third-order terms in the heat flux are omitted:

$$\mathrm{d}s = \theta^{-1}\mathrm{d}u - v\alpha_{10}\boldsymbol{q} \cdot \mathrm{d}\boldsymbol{q}. \tag{2.16}$$

From this expression and the internal energy balance law (2.2), one obtains for the time derivative $\dot{s}$ of the entropy,

$$\rho\dot{s} = -\theta^{-1}\nabla \cdot \boldsymbol{q} - \alpha_{10}\boldsymbol{q} \cdot \dot{\boldsymbol{q}} \tag{2.17}$$

or, equivalently,

$$\rho\dot{s} = -\nabla \cdot (\theta^{-1}\boldsymbol{q}) + \boldsymbol{q} \cdot (\nabla\theta^{-1} - \alpha_{10}\dot{\boldsymbol{q}}). \tag{2.18}$$

This equation can be cast in the general form of a balance equation,

$$\rho\dot{s} = -\nabla \cdot \boldsymbol{J}^s + \sigma^s, \tag{2.19}$$

in order to identify the expressions for the entropy flux $\boldsymbol{J}^s$ and the (positive) entropy production σ^s. By comparison of (2.18) and (2.19), it is inferred that

$$\boldsymbol{J}^s = \theta^{-1}\boldsymbol{q} \tag{2.20}$$

and

$$\sigma^s = \boldsymbol{q} \cdot (\nabla\theta^{-1} - \alpha_{10}\dot{\boldsymbol{q}}). \tag{2.21}$$

Relation (2.21) has the structure of a bilinear form in a flux $\boldsymbol{q}$ and a force $\boldsymbol{X}$

$$\sigma^s = \boldsymbol{q} \cdot \boldsymbol{X}, \tag{2.22}$$

the force $\boldsymbol{X}$ may be identified with the quantity within parentheses in (2.21). To obtain an evolution equation for $\boldsymbol{q}$ compatible with the positiveness of σ^s, let us assume that the force $\boldsymbol{X}$ is related to u and $\boldsymbol{q}$ by

$$\boldsymbol{X} = \mu_1(u, q^2)\boldsymbol{q}, \tag{2.23}$$

wherein μ_1 may depend on u and q^2. Replacing $\boldsymbol{X}$ by its value drawn from (2.21), relation (2.23) can be rewritten as

$$\nabla\theta^{-1} - \alpha_{10}\dot{\boldsymbol{q}} = \mu_1\boldsymbol{q}, \tag{2.24}$$

Introducing (2.23) into (2.22) results in the following expression for the entropy production

$$\sigma^s = \mu_1\boldsymbol{q}\cdot\boldsymbol{q} \geq 0. \tag{2.25}$$

and the requirement that σ^s is positive leads to the restriction $\mu_1 \geq 0$.

When dealing with non-linear flux–force relations as in (2.23), some particular attention must be paid on the sign of the phenomenological coefficients. To be more explicit, let us consider for example the non-linear law

$$\boldsymbol{X}_1 = \frac{\boldsymbol{q}}{\mu_1\sqrt{1+aq^2}}; \tag{2.26}$$

the corresponding entropy production is given by

$$\sigma^s = \boldsymbol{q}\cdot\boldsymbol{X}_1 = \frac{q^2}{\mu_1\sqrt{1+aq^2}}. \tag{2.27}$$

The quantity σ^s is clearly positive for any value of $\boldsymbol{q}$ provided that μ_1 and a are positive. However, if one expands the square root in series of q^2, one has

$$\sigma^s = \boldsymbol{q}\cdot\boldsymbol{X}_1 = \frac{q^2}{\mu_1}\left(1 - \frac{1}{2}aq^2 + \frac{1}{4}a^2q^4 + \ldots\right), \tag{2.28}$$

from which it is seen that by truncating the expansion after a finite number of terms it may happen that σ^s could become negative. Therefore, if one deals with a series expansion, the condition $\sigma^s \geq 0$ only imposes restrictions on the sign of the quadratic term, but not on the fourth and higher-order terms in $\boldsymbol{X}_1$.

In expression (2.24) there appear two non-defined coefficients α_{10} and μ_1 which must be identified on physical grounds. Assume first a situation characterized by a stationary flux so that (2.24) simplifies to

$$\boldsymbol{q} = -\frac{1}{\mu_1\theta^2}\nabla\theta. \tag{2.29}$$

A comparison with Fourier's law $\boldsymbol{q} = -\lambda\nabla\theta$ yields

$$\mu_1 = \frac{1}{\lambda\theta^2}. \tag{2.30}$$

In the next step, let us compare (2.24) with Cattaneo's equation (2.4). Writing (2.24) in the form

$$\lambda\theta^2\alpha_{10}\dot{\boldsymbol{q}} + \boldsymbol{q} = -\lambda\nabla\theta, \tag{2.31}$$

suggests the identification

$$\alpha_{10} = \frac{\tau}{\lambda\theta^2}. \tag{2.32}$$

In virtue of this result, the generalised Gibbs equation (2.16) will be written as

$$\mathrm{d}s = \theta^{-1}\mathrm{d}u - \frac{\tau}{\rho\lambda\theta^2}\boldsymbol{q}\cdot\mathrm{d}\boldsymbol{q}, \tag{2.33}$$

wherein the coefficient of the new term in $\mathrm{d}\boldsymbol{q}$ has been completely identified in terms of physical quantities. When the contribution of the quadratic terms in $\boldsymbol{q}$ is negligible in the expression of θ^{-1}, the latter reduces to T^{-1} and Gibbs's equation (2.33) is given by

$$\mathrm{d}s = T^{-1}\mathrm{d}u - \frac{\tau}{\rho\lambda T^2}\boldsymbol{q}\cdot\mathrm{d}\boldsymbol{q}. \tag{2.34}$$

In this case, the integrability condition, i.e. the equality of the second-order cross derivatives of s, namely $\partial^2 s/(\partial u\partial\boldsymbol{q})$ and $\partial^2 s/(\partial\boldsymbol{q}\partial u)$, infers that $\tau/(\rho\lambda T^2)$ is a constant. Expression (2.34) was widely used in the first developments of EIT. In the local-equilibrium approximation, (2.33) reads simply as $\mathrm{d}s = T^{-1}\mathrm{d}u$ as it should, and at this level of approximation θ is identical to T. The integrability condition of (2.33) yields in general

$$\frac{\partial\theta^{-1}}{\partial\boldsymbol{q}} = -\frac{\partial}{\partial u}\left(\frac{\tau}{\rho\lambda\theta^2}\right)\boldsymbol{q}, \tag{2.35}$$

and, after integration,

$$\theta^{-1}(u,q^2) = T^{-1}(u) - \frac{1}{2}\int\frac{\partial}{\partial u}\left[\tau/(\rho\lambda\theta^2)\right]\mathrm{d}q^2. \tag{2.36}$$

When $\tau/(\rho\lambda\theta^2)$ is independent on q^2, expression (2.36) reduces to

$$\theta^{-1}(u,q^2) = T^{-1}(u) - \frac{1}{2}\frac{\partial}{\partial u}\left(\frac{\tau}{\rho\lambda T^2}\right)q^2. \tag{2.37}$$

After substitution of this result in (2.33) and integration, one obtains an explicit expression for entropy outside (local) equilibrium up to second-order terms in $\boldsymbol{q}$

$$s(u,\boldsymbol{q}) = s_{\mathrm{eq}}(u) - \frac{1}{2}\frac{\tau}{\rho\lambda T^2}\boldsymbol{q}\cdot\boldsymbol{q}. \tag{2.38}$$

In virtue of (2.25) and (2.30), the entropy production is

$$\sigma^s = \frac{1}{\lambda\theta^2}\boldsymbol{q}\cdot\boldsymbol{q}, \tag{2.39}$$

and its positiveness implies that $\lambda > 0$. This expression of σ^s is to be compared with σ^s obtained from CIT when Cattaneo's law is used instead of Fourier's, namely

$$\sigma^s_{\mathrm{CIT}} = \frac{1}{\lambda T^2}(\boldsymbol{q} \cdot \boldsymbol{q} - \tau \boldsymbol{q} \cdot \dot{\boldsymbol{q}}). \tag{2.40}$$

Clearly, the positiveness of the entropy production is no longer guaranteed due to the presence of the second term on the right-hand side of (2.40).

Going back to Fig. 2.1 it is seen that the extended entropy (2.38) has a monotonic increase, in contrast with the classical local-equilibrium entropy s_{eq}. It can thus be concluded that the Cattaneo law (2.4) is not compatible with the local-equilibrium version of the second law, but is consistent with EIT.

In this section, we have selected u and $\boldsymbol{q}$ as variables. This choice is not unique, for instance instead of u we can as well choice its Legendre transformation, i.e. the temperature θ as variable; similarly, instead of $\boldsymbol{q}$, it is equivalent to adopt its Legendre transformation as independent variable as shown in Box 2.2.

Box 2.2 Entropy evolution in an isolated system: an illustrative example
The selection of the heat flux as independent variable has been the subject of criticism as it constitutes a response to interaction with the environment rather than expressing intrinsic non-equilibrium properties of the system. It is argued that a non-equilibrium variable should be written in terms of typical non-equilibrium quantities like the heat conductivity and the relaxation time. To meet these objections, we shall replace the variable $\boldsymbol{q}$ by a normalized expression, say $\boldsymbol{q}^*$ taking into account the constitutive properties of the heat conductor. A possible choice is to select $\boldsymbol{q}^*$ as the variable conjugated to $\boldsymbol{q}$ in Gibbs' equation (2.34), namely

$$\boldsymbol{q}^* = -\frac{\tau}{\rho \lambda T^2}\boldsymbol{q}. \tag{2.2.1}$$

By writing Gibbs' equation in the form (2.34), it is implicitly admitted that temperature is not dependent on the heat flux. A more complete analysis including non-linear contributions in q^2 can be found in Lebon et al. (2008a).

Defining the Legendre transform of $s(u, \boldsymbol{q})$ by

$$s[u, \boldsymbol{q}^*] = s - \boldsymbol{q} \cdot \boldsymbol{q}^*, \tag{2.2.2}$$

it follows from (2.2.2) and (2.34) that the corresponding Gibbs' relation is

$$\mathrm{d}s[u, \boldsymbol{q}^*] = T^{-1}\mathrm{d}u - \boldsymbol{q} \cdot \mathrm{d}\boldsymbol{q}^*. \tag{2.2.3}$$

It remains to establish the evolution equation of the new variable $\boldsymbol{q}^*$. Starting from (2.18) and following the procedure of the previous section, it is checked that

$$\rho \dot{s} = -\nabla \left(-\frac{\boldsymbol{q}^*}{\gamma T}\right) - \frac{1}{\gamma}\boldsymbol{q}^* \cdot (\nabla \cdot T^{-1} + \rho \dot{\boldsymbol{q}}^*) + \frac{\rho}{\gamma^2}\frac{\partial \gamma}{\partial u}\dot{u}(\boldsymbol{q}^* \cdot \boldsymbol{q}^*), \tag{2.2.4}$$

where γ stands for the "weighting" coefficient $\gamma = \tau/(\rho\lambda T^2)$; the last term vanished because in the approximation that the temperature is flux independent, one has $\partial\gamma/\partial u = -\partial T^{-1}/\partial q^2 = 0$ Expression 2.2.4 suggests that the entropy flux is given by

$$\boldsymbol{J}^s = -\frac{\boldsymbol{q}^*}{\gamma T} = \frac{\boldsymbol{q}}{T}, \tag{2.2.5}$$

while the entropy production will take the form

$$\sigma^s = -\frac{1}{\gamma}\boldsymbol{q}^* \cdot (\nabla T^{-1} + \rho\dot{\boldsymbol{q}}^*) \geq 0, \tag{2.2.6}$$

the term in $\partial\gamma/\partial u$ has disappeared because, as mentioned before, in our approximation $\partial\gamma/\partial u = 0$. Positiveness of σ^s is satisfied if

$$\nabla T^{-1} + \rho\dot{\boldsymbol{q}}^* = -\frac{\mu}{\gamma}\boldsymbol{q}^*, \tag{2.2.7}$$

with $\mu/\gamma > 0$, setting $\mu = (\lambda T)^{-1}$ one obtains

$$\rho\dot{\boldsymbol{q}}^* = -\nabla T^{-1} - \frac{\rho}{\tau}\boldsymbol{q}^*, \tag{2.2.8}$$

which is an equation of the Cattaneo type, reducing to Fourier's law in the steady state case. It is worth to stress that, in comparison with original Cattaneo's relation (2.4), expression (2.2.8) contains one single phenomenological coefficient, the relaxation time τ. A supplementary advantage of using the state variable $\boldsymbol{q}^*$ is that it contains a small parameter τ allowing the control the accurateness of higher-order expansions in the fluxes. An illustration of the use of this "weighting" variable may be found in Sect. 6.7.

2.3 One-Component Viscous Fluid

We now proceed to the more general case of a compressible one-component fluid. According to EIT, the space of the thermodynamic state variables is the union of the classical one (internal energy u, specific volume v) and the space of flux variables $\boldsymbol{q}$, p^v, and $\overset{0}{\mathbf{P}}{}^v$.

The generalised Gibbs equation takes the form

$$\begin{aligned} \mathrm{d}s = {} & (\partial s/\partial u)_{v,\boldsymbol{q},p^v,\overset{0}{\mathbf{P}}{}^v}\,\mathrm{d}u + (\partial s/\partial v)_{u,\boldsymbol{q},p^v,\overset{0}{\mathbf{P}}{}^v}\,\mathrm{d}v + (\partial s/\partial \boldsymbol{q})_{u,v,p^v,\overset{0}{\mathbf{P}}{}^v} \cdot \mathrm{d}\boldsymbol{q} \\ & + (\partial s/\partial p^v)_{u,v,\boldsymbol{q},\overset{0}{\mathbf{P}}{}^v}\,\mathrm{d}p^v + (\partial s/\partial \overset{0}{\mathbf{P}}{}^v)_{u,\boldsymbol{q},v,p^v} : \mathrm{d}\overset{0}{\mathbf{P}}{}^v. \end{aligned} \tag{2.41}$$

In analogy with the classical theory of irreversible processes, we define a non-equilibrium absolute temperature θ and a non-equilibrium thermodynamic pressure π by respectively

$$\theta^{-1}(u, v, \boldsymbol{q}, p^v, \overset{0}{\mathbf{P}}{}^v) = (\partial s/\partial u)_{v,\boldsymbol{q},p^v,\overset{0}{\mathbf{P}}{}^v}, \tag{2.42a}$$

$$\theta^{-1}\pi(u, v, \boldsymbol{q}, p^v, \overset{0}{\mathbf{P}}{}^v) = (\partial s/\partial v)_{u,\boldsymbol{q},p^v,\overset{0}{\mathbf{P}}{}^v}. \tag{2.42b}$$

Without loss of generality, the remaining partial derivatives in (2.41) can be cast in the form

$$(\partial s/\partial \boldsymbol{q})_{u,v,p^v,\overset{0}{\mathbf{P}}{}^v} = -v\alpha_{10}(u, v, \boldsymbol{q}, p^v, \overset{0}{\mathbf{P}}{}^v)\boldsymbol{q}, \tag{2.43a}$$

$$(\partial s/\partial p^v)_{u,v,\boldsymbol{q},\overset{0}{\mathbf{P}}{}^v} = -v\alpha_{00}(u, v, \boldsymbol{q}, p^v, \overset{0}{\mathbf{P}}{}^v)p^v, \tag{2.43b}$$

$$(\partial s/\partial \overset{0}{\mathbf{P}}{}^v)_{u,v,\boldsymbol{q},p^v} = -v\alpha_{21}(u, v, \boldsymbol{q}, p^v, \overset{0}{\mathbf{P}}{}^v)\,\overset{0}{\mathbf{P}}{}^v, \tag{2.43c}$$

wherein the coefficients α_{10}, α_{00} and α_{21} are unknown scalar functions of their arguments. Introducing (2.42–2.43) into (2.41) yields the generalised Gibbs equation

$$\mathrm{d}s = \theta^{-1}\mathrm{d}u + \theta^{-1}\pi\mathrm{d}v - v\alpha_{00}p^v\mathrm{d}p^v - v\alpha_{10}\boldsymbol{q}\cdot\mathrm{d}\boldsymbol{q} - v\alpha_{21}\,\overset{0}{\mathbf{P}}{}^v : \mathrm{d}\,\overset{0}{\mathbf{P}}{}^v. \tag{2.44}$$

The evolution of entropy is governed by the balance law (2.19), and our objective is to determine the corresponding expressions for the entropy flux $\boldsymbol{J}^s$ and entropy production σ^s. To this end, let us substitute into (2.44) the expressions of $\dot{u}$ and $\dot{v}$ as derived from the balance laws of energy and mass (1.10–1.11). After direct calculations it is found that

$$\rho\dot{s} = -\theta^{-1}\nabla\cdot\boldsymbol{q} - \theta^{-1}p^v\nabla\cdot\boldsymbol{v} - \theta^{-1}\,\overset{0}{\mathbf{P}}{}^v : \overset{0}{\mathbf{V}} - \alpha_{00}p^v\dot{p}^v - \alpha_{10}\boldsymbol{q}\cdot\dot{\boldsymbol{q}} - \alpha_{21}\,\overset{0}{\mathbf{P}}{}^v : (\overset{0}{\mathbf{P}}{}^v)^{\cdot}. \tag{2.45}$$

To derive this result it was assumed that the total pressure tensor $\mathbf{P}$ was decomposed as follows

$$\mathbf{P} = \pi\mathrm{U} + p^v\mathrm{U} + \overset{0}{\mathbf{P}}{}^v, \tag{2.46}$$

where π in the first term on the right-hand side has replaced p as found usually in classical hydrodynamics and in Chap. 1. It should be realized that at equilibrium π reduces to the classical hydrostatic equilibrium pressure p and that when second-order contributions in the fluxes are negligible, π is still identical to p. The motivation for substituting p with π in (2.46) will be discussed in detail in Chap. 3; for the moment, we may accept it is the analogue of changing T into θ in the generalised Gibbs equation (2.44).

2.4 The Generalised Entropy Flux and Entropy Production

Before we determine the expression for entropy production, defined by

$$\sigma^s = \rho\dot{s} + \nabla\cdot\boldsymbol{J}^s \geq 0, \tag{2.47}$$

we need a relation for the entropy flux $\boldsymbol{J}^s$. For isotropic systems, the most general vector depending on the variables u, v, $\boldsymbol{q}$, $\overset{0}{\mathbf{P}}{}^v$, and p^v is, up to second-order terms in the fluxes,

$$\boldsymbol{J}^s = \beta\boldsymbol{q} + \beta' p^v\boldsymbol{q} + \beta''\overset{0}{\mathbf{P}}{}^v\cdot\boldsymbol{q}, \tag{2.48}$$

where the coefficients β' and β'' are generally functions of u and v; to recover the results of the heat conduction problem, the coefficient β must be made θ^{-1}. Accordingly

$$\boldsymbol{J}^s = \theta^{-1}\boldsymbol{q} + \beta' p^v\boldsymbol{q} + \beta''\overset{0}{\mathbf{P}}{}^v\cdot\boldsymbol{q}. \tag{2.49}$$

The entropy production is easily derived from (2.47) by replacing $\rho\dot{s}$ and $\boldsymbol{J}^s$ respectively by their expressions in (2.45) and (2.48). The final result is

$$\begin{aligned}\sigma^s = \boldsymbol{q}\cdot[\nabla\theta^{-1} + \nabla\cdot(\beta''\overset{0}{\mathbf{P}}{}^v) + \nabla(\beta' p^v) - \alpha_{10}\dot{\boldsymbol{q}}] + p^v[-\theta^{-1}\nabla\cdot\boldsymbol{v}\\ -\alpha_{00}\dot{p}^v + \beta'\nabla\cdot\boldsymbol{q}] + \overset{0}{\mathbf{P}}{}^v : [-\theta^{-1}\overset{0}{\mathbf{V}} - \alpha_{21}(\overset{0}{\mathbf{P}}{}^v)^{\cdot} + \beta''\nabla(\overset{0}{\boldsymbol{q}})^s].\end{aligned} \tag{2.50}$$

One observes that (2.50) has the structure of a bilinear form,

$$\sigma^s = \boldsymbol{q}\cdot\boldsymbol{X}_1 + p^v X_0 + \overset{0}{\mathbf{P}}{}^v : \overset{0}{\mathbf{X}}_2 \tag{2.51}$$

consisting of a sum of products of the fluxes $\boldsymbol{q}$, p^v, and $\overset{0}{\mathbf{P}}{}^v$ and their conjugate generalised forces $\boldsymbol{X}_1$, X_0, and $\overset{0}{\mathbf{X}}_2$. The latter follows from direct comparison of (2.51) with (2.50). They are similar to the expressions obtained in CIT, except for the substitution of T by θ and the fact that they contain additional terms depending on the time and space derivatives of the fluxes.

Upon defining the proper expressions of the forces $\boldsymbol{X}_1$, $\overset{0}{\mathbf{X}}_2$, and X_0, it can be noted that there exists a class of transformations of the time derivatives of $\boldsymbol{q}$ and $\overset{0}{\mathbf{P}}{}^v$ which leave the entropy production invariant. An example of such a transformation is provided by

$$\mathrm{D}_a\boldsymbol{q} = \dot{\boldsymbol{q}} + a\mathbf{W}\cdot\boldsymbol{q}, \tag{2.52a}$$

$$\mathrm{D}_b\overset{0}{\mathbf{P}}{}^v = (\overset{0}{\mathbf{P}}{}^v)^{\cdot} + b(\mathbf{W}\cdot\overset{0}{\mathbf{P}}{}^v - \overset{0}{\mathbf{P}}{}^v\cdot\mathbf{W}), \tag{2.52b}$$

where a and b are constants and $\mathbf{W}$ is an antisymmetric tensor, for instance, the antisymmetric part of the velocity gradient. Indeed, it is easy to verify that

$$\boldsymbol{q} \cdot \mathrm{D}_a \boldsymbol{q} = \boldsymbol{q} \cdot \dot{\boldsymbol{q}}, \tag{2.53a}$$

$$\overset{0}{\mathbf{P}}{}^v : \mathrm{D}_b \overset{0}{\mathbf{P}}{}^v = \overset{0}{\mathbf{P}}{}^v : \overset{\cdot}{(\overset{0}{\mathbf{P}}{}^v)}. \tag{2.53b}$$

This means that the expression of the entropy production remains unchanged when general derivatives of the form (2.52) are used instead of the material time derivatives of the fluxes.

Obviously, thermodynamics cannot give any information about the coefficients a and b in (2.52), since they do not appear explicitly either in the entropy production or in the Gibbs equation. However, they can be determined by other means: (a) from general invariance requirements, such as the frame-indifference principle, which leads to $a = b = 1$, and in this case the derivatives defined by (2.52) coincide with the corotational time derivative; (b) from a microscopic description, e.g. the kinetic theory of gases; a comparison with kinetic theory yields $a = b = -1$ (for a detailed discussion on the compatibility between kinetic theory and frame indifference, see Lebon and Boukary 1988); (c) from experiments on rotating systems (e.g. Müller 1972), however, such experiments turn out to be very difficult in view of the smallness of the terms involved.

The simplest way to guarantee that $\sigma^s \geq 0$ is to assume that the forces $\boldsymbol{X}_1$, X_0, $\overset{0}{\mathbf{X}}_2$ identified in (2.50) are linear in the fluxes, namely

$$\boldsymbol{X}_1 = \mu_1 \boldsymbol{q}, \quad X_0 = \mu_0 p^v, \quad \overset{0}{\mathbf{X}}_2 = \mu_2 \overset{0}{\mathbf{P}}{}^v, \tag{2.54}$$

wherein the phenomenological coefficients μ_1, μ_0, μ_2 are allowed to depend on u and v. These are the simplest flux–force relations ensuring the positiveness of σ^s. Indeed when these expressions are introduced into (2.51), we are led to

$$\sigma^s = \mu_1 \boldsymbol{q} \cdot \boldsymbol{q} + \mu_0 p^v p^v + \mu_2 \overset{0}{\mathbf{P}}{}^v : \overset{0}{\mathbf{P}}{}^v, \tag{2.55}$$

while the requirement that σ^s must be positive leads to the restrictions

$$\mu_1 \geq 0, \quad \mu_0 \geq 0, \quad \mu_2 \geq 0. \tag{2.56}$$

As in the problem of heat conduction, non-linear flux–force relations raise some important conceptual questions concerning the interpretation of the second law. Consider, for instance, a force given by the form $X_0 = \mu_0 p^v + \mu_{00}(p^v)^2 + \cdots$, such that the entropy production becomes $\sigma^s = \mu_0 (p^v)^2 + \mu_{00}(p^v)^3 + \cdots$ It is clear that the positiveness of σ^s implies that the coefficient of $(p^v)^2$ must be positive, i.e. $\mu_0 > 0$. However, the restrictions on the coefficients of $(p^v)^3$ and higher-order terms depend on the interpretation given to the status of the constitutive equations. If one considers a given material which satisfies *exactly* $X_0 = \mu_0 p^v + \mu_{00}(p^v)^2$, then $\sigma^s > 0$ for every value of p^v would require that $\mu_{00} = 0$. By assuming that $X_0 = \mu_0 p^v + \mu_{00}(p^v)^2 + \cdots$ is only a second-order *approximation* with respect to an unknown exact constitutive relation, then one cannot conclude anything about the sign of μ_{00}. Nevertheless, the requirement that σ^s must be positive provides a useful limitation on the domain of validity of the constitutive equations and on their possible forms.

2.5 Linearized Evolution Equations of the Fluxes

Identifying the forces as the conjugate terms of the fluxes in (2.50) and substituting these expressions into (2.54), one obtains in the linear approximation (quadratic terms in the fluxes and products of fluxes times gradients of the "local" variables u and v are omitted), the following set of evolution equations:

$$\nabla T^{-1} - \alpha_{10}\dot{\boldsymbol{q}} = \mu_1 \boldsymbol{q} - \beta''\nabla \cdot \overset{0}{\mathbf{P}}{}^{v} - \beta'\nabla p^v, \tag{2.57}$$

$$-T^{-1}\nabla \cdot \boldsymbol{v} - \alpha_{00}\dot{p}^v = \mu_0 p^v - \beta'\nabla \cdot \boldsymbol{q}, \tag{2.58}$$

$$-T^{-1}\overset{0}{\mathbf{V}} - \alpha_{21}(\overset{0}{\mathbf{P}}{}^{v})^{\boldsymbol{\cdot}} = \mu_2 \overset{0}{\mathbf{P}}{}^{v} - \beta''(\nabla \boldsymbol{q})^s. \tag{2.59}$$

As a consequence of linearity, θ has been identified with T everywhere while the coefficients α are only function of u and v. The main features issued from the above thermodynamic formalism are:

- The positiveness of the coefficients μ_1, μ_0, and μ_2.
- The equality of the cross terms relating $\boldsymbol{q}$ with $\nabla \cdot \overset{0}{\mathbf{P}}{}^{v}$ and $\overset{0}{\mathbf{P}}{}^{v}$ with $(\overset{0}{\nabla \boldsymbol{q}})^s$ on the one side, and $\boldsymbol{q}$ with ∇p^v and p^v with $\nabla \cdot \boldsymbol{q}$ on the other. The equality of these coefficients, confirmed by the kinetic theory, are Onsager-type reciprocal relations. However, in contrast with the usual Onsager relations, they have been obtained here from purely thermodynamic arguments.
- The coefficients β' and β'' appearing in the second-order terms of the entropy flux are the same as the coefficients of the cross terms in the evolution equations (2.57–2.59) and establish the connection between thermodynamics (the entropy flux) and dynamics (the evolution equations).This result finds a confirmation in the kinetic theory (see Chap. 4).
- The terms involving the gradients of the fluxes are responsible of spatial non-local effects as shown in the forthcoming chapters.

As in the heat conduction problem, relations (2.57)–(2.59) contain several coefficients, which must be assigned a physical identification. Consider first a stationary and homogeneous situation, which means that the time and space derivatives of the fluxes are zero. Equations (2.57–2.59) then reduce to

$$\nabla T^{-1} = \mu_1 \boldsymbol{q}, \quad -T^{-1}\nabla \cdot \boldsymbol{v} = \mu_0 p^v, \quad -T^{-1}\overset{0}{\mathbf{V}} = \mu_2 \overset{0}{\mathbf{P}}{}^{v}. \tag{2.60}$$

Comparison with the Fourier and Newton–Stokes laws,

$$\boldsymbol{q} = -\lambda \nabla T, \quad p^v = -\zeta \nabla \cdot \boldsymbol{v}, \quad \overset{0}{\mathbf{P}}{}^v = -2\eta \overset{0}{\mathbf{V}}, \tag{2.61}$$

leads to the identifications

$$\mu_1 = (\lambda T^2)^{-1}, \quad \mu_0 = (\zeta T)^{-1}, \quad \mu_2 = (2\eta T)^{-1}, \tag{2.62}$$

with λ, ζ, and η being the thermal conductivity, bulk viscosity, and shear viscosity, respectively.

Consider now a non-stationary (but homogeneous) flow, so that (2.57)–(2.59) reduce to

$$\nabla T^{-1} - \alpha_{10}\dot{\boldsymbol{q}} = (\lambda T^2)^{-1}\boldsymbol{q}, \tag{2.63}$$

$$-T^{-1}\nabla \cdot \boldsymbol{v} - \alpha_{00}\dot{p}^v = (\zeta T)^{-1} p^v, \tag{2.64}$$

$$-T^{-1} \overset{0}{\mathbf{V}} - \alpha_{21} \overset{\cdot}{(\overset{0}{\mathbf{P}}{}^v)} = (2\eta T)^{-1} \overset{0}{\mathbf{P}}{}^v. \tag{2.65}$$

These equations can be identified with the so-called Maxwell–Cattaneo laws

$$\tau_1 \dot{\boldsymbol{q}} + \boldsymbol{q} = -\lambda \nabla T, \tag{2.66}$$

$$\tau_0 \dot{p}^v + p^v = -\zeta \nabla \cdot \boldsymbol{v}, \tag{2.67}$$

$$\tau_2 \overset{\cdot}{(\overset{0}{\mathbf{P}}{}^v)} + \overset{0}{\mathbf{P}}{}^v = -2\eta \overset{0}{\mathbf{V}}, \tag{2.68}$$

where τ_1, τ_0, and τ_2 are the relaxation times of the respective fluxes. We are then led to the identifications

$$\alpha_{10} = \tau_1 (\lambda T^2)^{-1}, \tag{2.69a}$$

$$\alpha_{00} = \tau_0 (\zeta T)^{-1}, \tag{2.69b}$$

$$\alpha_{21} = \tau_2 (2\eta T)^{-1}. \tag{2.69c}$$

In terms of λ, ζ, η, and the relaxation times τ_1, τ_0, and τ_2, the linearized evolution equations (2.57–2.59) take the following form:

$$\tau_1 \dot{\boldsymbol{q}} = -(\boldsymbol{q} + \lambda \nabla T) + \beta'' \lambda T^2 \nabla \cdot \overset{0}{\mathbf{P}}{}^v + \beta' \lambda T^2 \nabla p^v, \tag{2.70}$$

$$\tau_0 \dot{p}^v = -(p^v + \zeta \nabla \cdot \boldsymbol{v}) + \beta' \zeta T \nabla \cdot \boldsymbol{q}, \tag{2.71}$$

$$\tau_2 \overset{\cdot}{(\overset{0}{\mathbf{P}}{}^v)} = -(\overset{0}{\mathbf{P}}{}^v + 2\eta \overset{0}{\mathbf{V}}) + 2\beta'' \eta T (\overset{0}{\nabla \boldsymbol{q}})^s. \tag{2.72}$$

In Table 2.1 the values of some of the coefficients appearing in (2.70)–(2.72) are reported.

Table 2.1 Values of τ_1, τ_2, λ, and η for some liquids at 20°C and 1atm, according to Nettleton (1960) (first three columns) and international tables

Liquid	$10^{13}\tau_1$(s)	10λ(J/ms°C)	$10^{12}\tau_2$(s)	$10^4\eta$(Ns/m^2)
Carbon tetrachloride	2.15	1.03	2.46	9.69
Chloroform	1.54	1.16	2.08	5.80
Carbon disulphide	1.43	1.61	1.38	3.63
Benzene	1.22	1.48	1.67	6.52
Toluene	1.63	1.35	1.60	5.90
Acetone	1.36	1.61	2.19	3.20

When relaxation times tend to infinity but their ratio to the respective transport coefficients (λ ζ η, etc.) remains finite (or in the high-frequency regime $\tau\omega \gg 1$), the Maxwell–Cattaneo equations become reversible (or time-reversal invariant), for example, Cattaneo's law simplifies as $\dot{\boldsymbol{q}} = -(\lambda/\tau)\nabla T$. In these particular circumstances, there is no dissipation associated with the fluxes (e.g. electric current in superconductors). Nevertheless, for the sake of simplicity, we will keep "dissipative" flux as a generic term throughout this book.

2.6 Rational Extended Thermodynamics

EIT can be seen not only as an extension of CIT, but it may also be formulated along the line of thought of rational thermodynamics (RT); in this case, it is convenient to speak about rational extended thermodynamics (RET). As seen in Chap. 1, Rational Thermodynamics, whose main objective is to provide a method for deriving constitutive equations, offers an approach whose rationale is drastically different from that of CIT. It is interesting to consider EIT from both "rational" and "classical" perspectives because it provides a common ground for comparison in spite of the divergences of their original formulations.

Although we borrow in this section some methods and concepts from RT, we depart from it in many other aspects. Essentially, the choice of the independent variables is different: in RT the variables are the histories of the classical state variables $u, v, \ldots$, while in RET the space of independent variables is enlarged in such a way that the history is no longer needed; accordingly, the response of the material system is described by evolution differential equations for the additional independent variables rather than in terms of the constitutive functionals as used in RT. Here, RT is used as a working method rather than as a definite theory.

2.6.1 Heat Conduction

To illustrate RET, let us go back to the problem of heat conduction in a rigid isotropic body at rest. The relevant variables are selected as the non-equilibrium temperature θ and the heat flux $\boldsymbol{q}$. The time evolution of θ is governed by the balance law of energy (2.1) while the evolution equation of $\boldsymbol{q}$ will be cast in the general form

$$\dot{\boldsymbol{q}} = -\nabla \cdot \mathbf{Q} + \sigma^q. \tag{2.73}$$

The first term on the right-hand side of (2.73) expresses the exchange with the outside environment, with $\mathbf{Q}$ denoting the flux of the heat flux, while σ^q is a source term. The quantity $\mathbf{Q}$ is a tensor of second rank and σ^q is a vector. At this stage of the analysis, these quantities are unknowns and must be formulated by means of constitutive equations:

$$\mathbf{Q} = \mathbf{Q}(\theta, \boldsymbol{q}), \tag{2.74}$$

$$\sigma^q = \sigma^q(\theta, \boldsymbol{q}). \tag{2.75}$$

After substitution of (2.74–2.75) into (2.73), we are faced with a set of four scalar equations for the four unknowns θ (scalar) and $\boldsymbol{q}$ (vector).

The constitutive equations (2.74–2.75) cannot take an arbitrary form. They have to comply with the laws of thermodynamics, and in particular the second law. To satisfy the latter condition, it is assumed that there exists a regular and continuous function of the whole set of variables, called the non-equilibrium entropy s, which obeys a balance equation given by

$$\rho \dot{s} + \nabla \cdot \boldsymbol{J}^s = \sigma^s \geq 0, \tag{2.76}$$

where $\boldsymbol{J}^s$ is the entropy flux; the positive entropy production σ^s can be calculated by performing the operations indicated on the left-hand side of (2.76). As in RT, the positiveness of σ^s is used to place restrictions on the field equations.

At this point, let us emphasize some of the main differences between RET and RT. First, whereas in the latter theory the quantity $\boldsymbol{q}$ is given by a constitutive relation, in RET it is counted among the set of independent variables. Second, the balance law of energy is not regarded as a mere definition of the energy supply; in RET this quantity is given a priori. Third, the second law is not in the form of the Clausius–Duhem inequality as it is not imposed that the entropy flux is a priori to be given by the ratio of the heat flux and the temperature, but may contain extra terms. Fourth, the entropy is assumed to depend on the heat flux.

Since the temperature has been selected as independent variable rather than the internal energy, it is convenient to formulate the second law (2.76) in terms of the free energy $\phi = u - \theta s$ for which temperature is an independent variable; this leads to

$$\theta \sigma^s = \rho \dot{u} - \rho s \dot{\theta} - \rho \dot{\phi} + \theta \nabla \cdot \boldsymbol{J}^s \geq 0. \tag{2.77}$$

To take into account the restrictions placed by the second law (2.77) on the constitutive equations, we follow the method of Lagrange multipliers proposed by Liu and widely used by Muller and Ruggeri (1998) in their formulation of RET. It must be observed that the inequality (2.77) does not hold for all the set of variables θ and $\boldsymbol{q}$ but only for the solutions of the energy balance (2.1) and the evolution equation

(2.73) for $\boldsymbol{q}$. This means that we can consider the evolution equations as constraints for the entropy inequality to hold. To take these constraints into account is a difficult task and will lead to rather intricate calculations. An elegant way to circumvent this difficulty was proposed by Liu (1972); he was able to show that the entropy inequality becomes completely arbitrary when inequality (2.77) is complemented with a linear combination of the balance laws. The factors multiplying the balance equations are called Lagrange multipliers by analogy with the extremization problem to constraints in mathematics, although the present situation is not strictly a problem of extremals.

We shall bypass the constraint expressed by the energy law by replacing in (2.77) the quantity $\rho\dot{u}$ by $-\nabla \cdot \boldsymbol{q}$. The only constraint left is the evolution equation (2.73) of $\boldsymbol{q}$ so that the entropy inequality (2.77) will be reformulated as follows

$$\theta\sigma^s = -\nabla \cdot \boldsymbol{q} - \rho s\dot{\theta} - \rho\dot{\phi} + \theta\nabla \cdot \boldsymbol{J}^s + \Lambda \cdot (\dot{\boldsymbol{q}} + \nabla \cdot \mathbf{Q} - \sigma^q) \geq 0, \tag{2.78}$$

wherein $\Lambda(\theta, \boldsymbol{q})$ is the corresponding Lagrange multiplier. This inequality is satisfied for arbitrary values of the independent variables θ and $\boldsymbol{q}$, it contains three unknown quantities $\boldsymbol{J}^s$, $\mathbf{Q}$ and σ^q assumed to be given by the following constitutive relations

$$\boldsymbol{J}^s = \varepsilon(\theta, q^2)\boldsymbol{q}, \tag{2.79}$$

$$\mathbf{Q} = a(\theta, q^2)\mathbf{U}, \tag{2.80}$$

$$\sigma^q = -b(\theta, q^2)\boldsymbol{q}, \tag{2.81}$$

wherein ε, a and b are unknown scalar functions of θ and q^2. More general expressions of $\boldsymbol{J}^s$ and $\mathbf{Q}$ are found in Lebon et al. (2003) and Lebon et al. (2008b). Introducing (2.79)–(2.81) in (2.78) and invoking the differentiation rule for $\phi(\theta, q^2)$, one obtains

$$\begin{aligned}\theta\sigma^s = &-\rho\left(s + \frac{\partial\phi}{\partial\theta}\right)\dot{\theta} - \left(2\rho\frac{\partial\phi}{\partial q^2}\boldsymbol{q} - \Lambda\right) \cdot \dot{\boldsymbol{q}} + \left(\theta\frac{\partial\phi}{\partial\theta}\boldsymbol{q} + \Lambda\frac{\partial a}{\partial\theta}\right) \cdot \nabla\theta \\ &+ \left[2\theta\frac{\partial\varepsilon}{\partial q^2}\boldsymbol{q}\boldsymbol{q} + 2\frac{\partial a}{\partial \boldsymbol{q}^2}\Lambda\boldsymbol{q} + (\theta\varepsilon - 1)\mathbf{U}\right] : \nabla\boldsymbol{q} + b\Lambda \cdot \boldsymbol{q} \geq 0.\end{aligned} \tag{2.82}$$

which is linear in $\dot{\theta}$, $\dot{\boldsymbol{q}}$, $\nabla\theta$ and $\nabla\boldsymbol{q}$. Positiveness of (2.82) would be destroyed unless the coefficients of these derivatives are zero, which results in

$$\frac{\partial\phi}{\partial\theta} = -s, \tag{2.83}$$

$$\Lambda = 2\rho\frac{\partial\phi}{\partial q^2}\boldsymbol{q}, \tag{2.84}$$

$$\theta\frac{\partial\varepsilon}{\partial\theta} + 2\rho\frac{\partial a}{\partial\theta}\frac{\partial\phi}{\partial q^2} = 0, \tag{2.85}$$

$$\theta\frac{\partial\varepsilon}{\partial q^2}+2\rho\frac{\partial a}{\partial q^2}\frac{\partial\phi}{\partial q^2}=0, \tag{2.86}$$

$$\varepsilon=\frac{1}{\theta}, \tag{2.87}$$

with the dissipation inequality (2.82) given by

$$\theta\sigma^s=b\Lambda\cdot\boldsymbol{q}=2\rho b\frac{\partial\phi}{\partial q^2}q^2\geq 0, \tag{2.88}$$

in virtue of (2.84). The following generalized Gibbs equation is obtained from (2.83) and (2.84):

$$\mathrm{d}\phi(\theta,\boldsymbol{q})=\frac{\partial\phi}{\partial\theta}\mathrm{d}\theta+\frac{\partial\phi}{\partial\boldsymbol{q}}\cdot\mathrm{d}\boldsymbol{q}=-s\mathrm{d}\theta+\frac{1}{\rho}\Lambda\cdot\mathrm{d}\boldsymbol{q}, \tag{2.89}$$

the first term at the right-hand-side is classical while the second one reflects the property that the Lagrange multiplier Λ is the variable conjugated to $\boldsymbol{q}$.

The result (2.87) is important as it confirms that the expression of the entropy flux is similar to the classical result $\boldsymbol{J}^s=\boldsymbol{q}/\theta$ but with the equilibrium temperature T replaced by the non-equilibrium temperature θ. From (2.86) and (2.87) it follows that $\partial a/\partial q^2=0$ which means that the factor a is independent of q^2; moreover, in virtue of (2.85), it is found that

$$\frac{\partial\phi}{\partial q^2}=\frac{1}{2\rho\theta}\frac{1}{(\partial a/\partial\theta)}, \tag{2.90}$$

with the property to be also q^2-independent. Recalling that stability of equilibrium requires that ϕ is a convex function, it is inferred that

$$\partial a/\partial\theta>0. \tag{2.91}$$

To gain more information about the undetermined coefficients a and b, substitute (2.80) and (2.81) in the evolution equation (2.73) which takes the form

$$\dot{\boldsymbol{q}}=-\frac{\partial a}{\partial\theta}\nabla\theta-b\boldsymbol{q}, \tag{2.92}$$

this relation is identical to Cattaneo's generalized law at the condition to operate the identifications

$$b=\frac{1}{\tau},\quad \frac{1}{b}\frac{da}{d\theta}=\lambda, \tag{2.93}$$

with τ the relaxation time and λ the heat conductivity; in virtue of (2.88) and (2.91), both quantities b and a are proven to be positive. Making use of the above identification, expression (2.90) will take the more familiar form

$$\frac{\partial\phi}{\partial q^2}=\frac{\tau}{2\rho\lambda\theta}. \tag{2.94}$$

To summarize, the final expressions of the generalized Gibbs equation, entropy flux and evolution equation for $\boldsymbol{q}$ can be written as

$$\mathrm{d}\phi = -s\mathrm{d}\theta + \frac{\tau}{\rho\lambda\theta}\boldsymbol{q}\cdot\mathrm{d}\boldsymbol{q}, \tag{2.95}$$

$$\boldsymbol{J}^{s} = \frac{1}{\theta}\boldsymbol{q}, \tag{2.96}$$

$$\tau\dot{\boldsymbol{q}} = -\lambda\nabla\theta - \boldsymbol{q}. \tag{2.97}$$

These results comply fully with those derived by following the procedure of Sect. 2.1. Clearly, by using more general expressions for $\mathbf{Q}$ and σ^{q} (e.g. Lebon et al. 1998), one would have obtained more complicated expressions for the Gibbs equation, the entropy flow and the Cattaneo equation.

2.6.2 *Viscous Fluids*

The above procedure is easily generalised to other systems, such as viscous heat-conducting fluids in motion. The space of the variables, denoted $\mathcal{V}$, is formed by the union of the space of the classical variables $\mathcal{C}$ (the density ρ, the specific internal energy u, the velocity $\boldsymbol{v}$) and the space of the fluxes $\mathcal{F}$ (here the heat flux $\boldsymbol{q}$, and the viscous pressure $\mathbf{P}^{v}$). In total, the space $\mathcal{V}$ contains 14 independent variables (ρ, u, and p^{v}, plus three components of $\boldsymbol{v}$ and three components of $\boldsymbol{q}$ and five components of the symmetric traceless tensor $\overset{0}{\mathbf{P}}{}^{v}$). The evolution of the classical variables is governed by the balance equations of mass, momentum and energy, while the evolution of the flux variables obeys equations of the form

$$\dot{\boldsymbol{q}} = -\nabla\cdot\mathbf{J}^{q} + \sigma^{q}, \tag{2.98}$$

$$\dot{p}^{v} = -\nabla\cdot\boldsymbol{j}^{v} + \sigma^{v}, \tag{2.99}$$

$$(\overset{0}{\mathbf{P}}{}^{v})^{\dot{}} = -\nabla\cdot\overset{0}{\mathbf{J}}{}^{v} + \overset{0}{\sigma}{}^{v}. \tag{2.100}$$

$\mathbf{J}^{q}$ is a tensor of rank two representing the flux of the heat flux, and σ^{q} is a vector corresponding to the supply of heat flux; $\boldsymbol{j}^{v}$ is a vector denoting the flux of the scalar viscous pressure, and σ^{v} is the corresponding scalar source term; $\overset{0}{\mathrm{J}}{}^{v}$ is a third-rank tensor designating the flux of the traceless viscous pressure tensor, and $\overset{0}{\mathbf{J}}{}^{v}$ is its source term. Of course, at this stage of the analysis these quantities are not determined and must be specified by means of constitutive relations, which in view of the principle of equipresence will be written as

$$\begin{aligned}
&\mathbf{J}^{q} = \mathbf{J}^{q}(\mathcal{V}), \quad \boldsymbol{j}^{v} = j^{v}(\mathcal{V}), \quad \overset{0}{\mathbf{J}}{}^{v} = \overset{0}{\mathbf{J}}{}^{v}(\mathcal{V}),\\
&\sigma^{q} = \sigma^{q}(\mathcal{V}), \quad \sigma^{v} = \sigma^{v}(\mathcal{V}), \quad \overset{0}{\sigma}{}^{v} = \overset{0}{\sigma}{}^{v}(\mathcal{V}).
\end{aligned} \tag{2.101}$$

The evolution equations (2.98)–(2.100) and the constitutive relations (2.101) are not arbitrary. They have to comply with the following three constraints:

- Euclidean invariance (criterion of objectivity)
- Positiveness of the rate of entropy production
- Concavity of entropy

As a consequence of objectivity, the material time rates must be replaced by objective ones. Therefore, in Eqs. (2.98) and (2.100), the material time derivatives should be replaced by $\mathrm{D}\boldsymbol{q}$ and $\mathrm{D}\overset{0}{\mathbf{P}}{}^{v}$, respectively, where D denotes an objective time derivative, say Jaumann's derivative.

As above, we will introduce Lagrange multipliers so that entropy inequality will take the form

$$\begin{aligned}\rho\dot{s} + \nabla\cdot\boldsymbol{J}^{s} + \Lambda_0(\rho\dot{v} + \nabla\cdot\boldsymbol{v}) + \Lambda_1(\rho\dot{u} + \nabla\cdot\boldsymbol{q} + \mathbf{P}^{T} : \nabla\boldsymbol{v})\\ +\Lambda_2\cdot(\rho\dot{\boldsymbol{v}} + \nabla\cdot\mathbf{P} + \rho\boldsymbol{F}) + \Lambda_3\cdot(\dot{\boldsymbol{q}} + \nabla\cdot\boldsymbol{J}^{q} + \sigma^{q})\\ +\Lambda_4(\dot{p}^{v} + \nabla\cdot\boldsymbol{j}^{v} + \sigma^{v}) + \Lambda_5 : [(\overset{0}{\mathbf{P}}{}^{v})^{\cdot} + \nabla\cdot\overset{0}{\mathbf{J}}{}^{v} + \overset{0}{\sigma}{}^{v}] \geq 0 \quad (2.102)\end{aligned}$$

wherein the Lagrange multipliers Λ_i $(i = 0, 1, \ldots, 5)$ are unknown functions of the set of variables $\mathcal{V}$. The procedure is the same as in Sect. 2.6.1 but will not be pursued further because the calculations are long and cumbersome outside the linear approximation.

It is interesting to summarize the main differences between the standard and rational presentations of EIT in Sects. 2.3 and 2.5:

(a) In RET, the restrictions on the balance equations are explicitly taken into account in the formulation of the second law by means of Lagrange multipliers.
(b) The Gibbs equation is not postulated a priori, as in the previous formulation, but is derived from the restrictions placed by the second law.

However, in the linear approximation, the results of the two approaches are identical both for the evolution equations of the fluxes and for the Gibbs equation. In the nonlinear range, the complete equivalence is not yet established. The existence of both formalisms is useful and stimulating, as each point of view has its own advantages. For instance, the use of Lagrange multipliers in RET is elegant and appealing, but the standard description of EIT provides for them a physical identification in a more direct way and gives a more straightforward description of fluctuations, as will be shown in Chap. 5.

2.7 Some Comments and Perspectives

To shed further light on the scope and perspectives of EIT, let us add some general comments.

1. In EIT, the state variables are the classical hydrodynamic fields supplemented by the fluxes appearing on the governing equations of classical hydrodynamics, i.e. the extra stress (or pressure) tensor (the total stress tensor minus its hydrostatic part) and the extra energy flux (the total energy flux minus the fluxes due to advection of energy and to mechanical work). EIT can be viewed as an extension of classical thermo-hydrodynamics wherein inertial effects are included. In classical mechanics, inertia is introduced by considering the right-hand side of the evolution equation $\dot{\boldsymbol{r}} = \boldsymbol{v}$ ($\boldsymbol{r}$ is the position vector of a particle and $\boldsymbol{v}$ its velocity) as an independent state variable, whose behaviour is governed by an additional equation (Newton's equation of motion).
2. It could be asked why it is not preferable to select internal variables rather than dissipative fluxes as additional variables. Indeed, thermodynamics with internal variables has been successfully applied to a wide variety of problems (e.g. Maugin 1999; Lebon et al. 2008a). Conceptually, however, there are several differences between both approaches. First, internal variables are measurable but not controllable, whereas the fluxes are controllable and measurable. Quoting Kestin (1992), by non-controllable variables it is meant 'that they are coupled to no external force variable which might provide the means of control. And, not being coupled to a force variable, they cannot part in the mechanical work.' Second, internal variables are related to the microstructure of the system. Third, they are usually related to local relaxation, whereas the fluxes are more closely connected to non-local effects. Actually, the two points of view are not so opposite as it might appear at first sight. Indeed, in polymer solutions, for instance, the viscous pressure tensor is directly related to the macromolecular conformation tensor used in thermodynamics with internal variables. According to the specific problem to be investigated, one of the two theories may be preferable. For instance, for systems in steady states, the controllable character of the viscous pressure or the heat flux presents an advantage, as it allows the system to be maintained in the required state; this is no longer true when one is working with the conformation tensor. Finally, the use of the viscous pressure tensor as an independent variable allows us to present under a unified formalism the viscoelastic properties of ideal and real gases and of polymer solutions (see Chaps. 12 and 15). This would not be possible in the framework of thermodynamics with internal variables, because monatomic ideal gases without internal degrees of freedom are not characterized by particular internal variables.
3. There are also several reasons for choosing the fluxes rather than the gradients of the classical variables as independent quantities. (a) The fluxes are associated with well-defined microscopic operators, and as such allow for a more direct comparison with non-equilibrium statistical mechanics. (b) The use of the fluxes is more convenient than use of the gradients for fast processes, whereas for slow or steady-state phenomena the use of both sets of variables is equivalent because under these conditions the former ones are directly related to the latter. (c) By expressing the entropy in terms of the fluxes, the classical theory of fluctuations can be easily generalised to evaluate the coefficients of the non-classical part of the entropy. This would not be possible by taking the gradients as variables.

(d) Finally, the selection of the gradients as extra variables leads to divergence problems in the expansion of constitutive equations, as well known from the kinetic theory.

4. Every dissipative flux has been considered here to be a quantity characterized by a single evolution equation. It is easily conceivable that fluxes may be split into several independent contributions, each with its own evolution equation. Typical examples are treated in Chap. 4 for non-ideal gases and in Chap. 15 for polymers. EIT is shown there to be able to cope in a quite natural way with these situations.
5. The space of the extra variables is not generally restricted to the ordinary dissipative fluxes, such as the heat flux, the viscous pressure, or the flux of matter. To cope with the complexity of some fast phenomena, it is necessary to introduce more variables. It is shown in Chap. 5 how EIT is able to account for such more general descriptions, when higher-order fluxes are considered as supplementary variables.
6. An important issue is the measurability of the dissipative fluxes. The heat flux may be simply evaluated by measuring the amount of energy transported per unit area and time through the boundaries of the system. The viscous pressure can be measured from the tangential shear force exerted per unit area. In practice, it may be difficult to evaluate these quantities at each instant of time and at every point in space. Nevertheless, for several problems of practical interest, such as wave propagation, the fluxes are eliminated from the final equations, although the corresponding dispersion relations contain explicitly the whole set of parameters appearing in the evolution equations of the fluxes. Thus the predictions of EIT concerning these parameters may be checked without direct measurement of the fluxes.
7. EIT provides a connection between thermodynamics and dynamics. In EIT, the fluxes are no longer considered as mere control parameters but as independent variables. The fact that EIT makes a connection between dynamics and thermodynamics should be underlined. Moreover, EIT does not only provide a natural framework for a wide class of dynamical models, it also generates original results, as shown in Chaps. 10 and 13. Most of the dynamical models dealt with in this book did not receive thermodynamic foundations before EIT was proposed; one reason is that non-equilibrium thermodynamics was simply ignored and investigations were exclusively performed on dynamical aspects.
8. EIT enlarges the range of applicability of non-equilibrium thermodynamics to a vast domain of phenomena where memory, non-local, and non-linear effects are relevant. A non-exhaustive list of applications in various fields of physics is given in Table 2.2. Many of them have been the object of technological applications, which in turn, enlarges the experimental possibilities for the observation of non-classical effects in a wider range of non-equilibrium situations.
9. It should be emphasised that EIT has fostered the use of generalised causal transport equations in several domains where, up to now, only non-causal transport equations were used. In connection with this, it is interesting to recall that, historically, one of the motivations for formulating EIT was to circumvent the problem met in classical theories: the prediction that the application of a perturbation

Table 2.2 Some examples of application of EIT

High-frequency phenomena	*Short-wavelength phenomena*
Ultrasounds in gases	Light scattering in gases
Light scattering in gases	Neutron scattering in liquids
Neutron scattering in liquids	Ballistic phonon propagation
Second sound in solids	Phonon hydrodynamics
Heating of solids by laser pulses	Microfluidics
Nuclear collisions	Nano devices
	Shock waves
	Fast moving interfaces
Long relaxation times	*Long correlation lengths*
Polyatomic molecules	Rarefied gases
Suspensions, polymer solutions	Transport in harmonic chains
Diffusion in polymers	Cosmological decoupling eras
Propagation of fast crystallization fronts	Transport near critical points
Superfluids, superconductors	

should be felt instantaneously everywhere inside the whole system. Thus, the number of motivations is much increased, many of them arising from experimental observations and practical applications rather than from purely theoretical arguments.

2.8 Problems

2.1. Assume that the entropy S is a function of a variable α and its time derivative $\eta = \mathrm{d}\alpha/\mathrm{d}t$, and that α satisfies the differential equation

$$M\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2} + \frac{\mathrm{d}\alpha}{\mathrm{d}t} = L\frac{\partial S}{\partial \alpha}.$$

(a) Show that the positiveness of the entropy production demands that $L > 0$ but does not imply any restriction on the sign of M. (Hint: Write $\mathrm{d}\alpha/\mathrm{d}t$ and $\mathrm{d}\eta/\mathrm{d}t$ in terms of $\partial S/\partial\alpha$ and $\partial S/\partial\eta$.) (b) Assume that $\partial S/\partial\eta = a\eta$, with a being a constant. Show that the stability condition $\delta^2 S < 0$ implies that $M > 0$ and $a = -M/L$.

2.2. The positiveness of the entropy production requires the positiveness of the second-order terms in the expression of the entropy production, but does not imply any criterion about the sign of the fourth- and higher-order terms in the entropy production. (a) As an illustration, study the sign of the entropy production and its second- and fourth-order terms in ∇T for a hypothetical system where $\sigma^s = \boldsymbol{q}\cdot\nabla T^{-1}$ and

$$\boldsymbol{q} = -\lambda \exp\left[-a(\nabla T)^2\right]\nabla T,$$

with a being a constant parameter. (b) The fact that no criterion may be obtained about the sign of the higher-order terms in the entropy production does not imply that the positiveness of the entropy production must be abandoned. As an illustration, study the sign of the entropy production and its second-order terms in ∇T for a constitutive law of the form

$$\boldsymbol{q} = -\lambda \sin\left[a(\nabla T)^2\right] \nabla T,$$

with a being a (positive) constant. Despite the fact that the second-order terms are positive, is a constitutive equation of this form admissible?

2.3. Show that

$$\boldsymbol{q}(t) = \int_{-\infty}^{t} G(t-t')\nabla T(t')\mathrm{d}t'$$

with $G(t-t')$ being a memory function given by $G(t-t') = -(\lambda/\tau)\exp[-(t-t')/\tau]$, is a solution of the Maxwell–Cattaneo equation.

2.4. Show that by combining the generalised Fourier law

$$\boldsymbol{q} = -\lambda \nabla T + \lambda_1 \frac{\partial}{\partial t}(\nabla T)$$

with the energy balance law of a rigid heat conductor one obtains a parabolic evolution equation for the temperature. Compare with the Maxwell–Cattaneo equation.

2.5. In order to reconcile the results obtained from the material frame-indifference principle (see Sect. 1.4) and from the kinetic theory, Lebon and Boukary (1988) proposed replacing the Jaumann derivative D_J by the following time derivative

$$\mathcal{D}\boldsymbol{q} = \mathrm{D}_J \boldsymbol{q} - 2(\boldsymbol{\Omega} + \mathbf{W}) \cdot \boldsymbol{q},$$

where $\boldsymbol{\Omega}$ is the angular velocity tensor and $\mathbf{W}$ is the antisymmetric part of the velocity gradient $\nabla \boldsymbol{v}$. The two quantities are related to the angular velocity vector $\boldsymbol{\omega}$ and the vorticity $\nabla \times \boldsymbol{v}$ by $\omega_i = \frac{1}{2}\varepsilon_{ijk}\Omega_{jk}$, $(\nabla \times \boldsymbol{v})_i = \varepsilon_{ijk} W_{jk}$, respectively. In both expressions ε_{ijk} is the permutation tensor. Prove that the time derivative $\mathcal{D}$ is objective.

2.6. (a) Show that in the presence of several fluxes J_i the generalised Gibbs equation is

$$\mathrm{d}s = \mathrm{d}s_{\mathrm{eq}} - v \sum_{ikl} J_i (L^{-1})_{ik} \tau_{kl} \mathrm{d}J_l,$$

when the quantities J_i obey generalised constitutive laws

$$\sum_j \tau_{ij} \frac{\mathrm{d}J_j}{\mathrm{d}t} + J_i = \sum_j L_{ij} X_j,$$

where X_j are the usual thermodynamic forces of the classical theory, L_{ij} the elements of the matrix of phenomenological coefficients $\mathbf{L}$, and τ_{ij} the elements of the matrix of relaxation times $\boldsymbol{\tau}$. (b) Assume linear transformations of the fluxes $J_i^* = \sum_j A_{ij} J_j$ and of the forces $X_i^* = \sum_j [(A^T)^{-1}]_{ij} X_j$. Find the new tensors $\mathbf{L}^*$ and $\boldsymbol{\tau}^*$.

2.7. Internal-variable theories include additional variables which allow for a more detailed description than the local-equilibrium approach. Suppose a vectorial internal variable $\boldsymbol{g}$, related to the heat flux, and an entropy s depending on the internal energy u and $\boldsymbol{g}$. The corresponding Gibbs equation is

$$\mathrm{d}s = \theta^{-1}\mathrm{d}u - v\alpha' \boldsymbol{g} \cdot \mathrm{d}\boldsymbol{g}.$$

Show that if the heat flux is required to obey a relaxational equation of the Maxwell–Cattaneo type, then $\boldsymbol{g}$ can be identified with $\boldsymbol{q}$ and the Gibbs equation coincides with (2.33) (Jou et al. (1999)).

2.8. Assume that heat propagation in a rigid isotropic solid is governed by

$$\dot{\boldsymbol{q}} = -\nabla \cdot \mathbf{Q} + \boldsymbol{\sigma}^q,$$

with

$$\mathbf{Q} = a(\theta, q^2)\mathrm{U} + d(\theta)\boldsymbol{qq}, \; \boldsymbol{\sigma}^q = -b(\theta, q^2)\boldsymbol{q},$$

$\boldsymbol{q}$ is the heat flux vector, $\mathbf{Q}$ is the flux of $\boldsymbol{q}$, a, b and d are phenomenological coefficients. Making use of Liu's technique, determine the expressions of Gibbs' equation and the entropy flux, formulate the time evolution equation of $\boldsymbol{q}$. Under which restrictions does one recover a Cattaneo type equation (Jou et al. 2004)?

2.9. The initial temperature profile in a rigid wire of length L is given by

$$t = 0: \quad T(x,0) = T^0 + \delta T^0 \cos \frac{2n\pi x}{L} \quad (n = 0, 1, 2, \ldots),$$

wherein T^0 is a uniform reference temperature. Assuming a perturbation of the form (Criado-Sancho et al. 1993)

$$\delta T = \delta T^0 \cos(kx) f(t),$$

where $(k = 2n\pi/L)$ and $f(t)$ is a undetermined function of time t, find the law of decay of temperature towards equilibrium. Show that the law of evolution of total entropy is

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \int_0^L \frac{1}{\lambda T^2} q^2 \mathrm{d}x \geq 0.$$

2.10. A possible thermodynamic framework for the Maxwell–Cattaneo equation is to assume that the heat flux is given by $\boldsymbol{q} = -\lambda \nabla \beta$, with λ the heat conductivity and β a dynamical temperature related to a local-equilibrium temperature ϑ by Cimmelli and Frischmuth (2005)

$$\dot{\beta} = -\frac{1}{\tau}(\beta - \vartheta).$$

(a) Show that combining the equations for $\boldsymbol{q}$ and $\dot{\beta}$, the Maxwell–Cattaneo equation is obtained in the linear approximation. (b) Compare the evolution equation for heat waves attained from the energy conservation equation $c_v\dot{\vartheta} = -\nabla \cdot \boldsymbol{q}$ and the Maxwell–Cattaneo equation with heat flux deduced from the formalism presented in this problem for the non-linear case in which $\lambda(\vartheta)$, $\tau(\vartheta)$, and $c_v(\vartheta)$ depend on temperature.

Chapter 3
Extended Irreversible Thermodynamics: Non-equilibrium Equations of State

In Chap. 2, we postulated the existence of a generalised entropy which is compatible with some classes of evolution equations for the fluxes. Otherwise stated, our formalism aims to describe the class of processes which are compatible with the existence of a non-equilibrium entropy whose rate of production is non-negative. Once the expression of the entropy is known, there is no difficulty in deriving the corresponding equations of state, which are directly obtained as the first derivatives of the entropy with respect to the basic variables. A natural question concerns the physical meaning of these equations of state, which, of course, depend on the fluxes and therefore differ from their analogous local-equilibrium expressions. In classical thermodynamics, it is known that the derivative of the entropy with respect to the internal energy (by keeping fixed the volume and the composition of the system) is the reciprocal of the absolute temperature; the derivatives with respect to the volume and to the number of moles yield the equilibrium pressure and (with a minus sign) the chemical potentials respectively (divided by the absolute temperature). It may then be asked whether the derivatives of the generalised entropy introduced in extended irreversible thermodynamics (EIT) still allow an absolute temperature to be defined, as well as a non-equilibrium pressure and a non-equilibrium chemical potential. Another important problem is to determine whether the non-equilibrium temperature and pressure are measurable by a thermometer and a manometer. These are subtle and unsolved problems which have however received partial answers during the last years stimulated by recent developments in glasses, granular matter, flowing suspensions, nuclear collisions, nano-systems, molecular dynamics and computer simulations, or in the analysis of fluctuations. The objective of the present chapter is to better apprehend the physical meaning of the generalised entropy and to pay detailed attention to the nature of the corresponding equations of state.

3.1 Physical Interpretation of the Non-equilibrium Entropy

Consider a volume V of a fluid which is sufficiently small so that within it the spatial variations of pressure and temperature are negligible; if the fluid element is subject to a heat flux $\boldsymbol{q}$ and a viscous pressure $\overset{0}{\mathbf{P}}{}^{v}$ (viscous bulk effects are ignored

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_3, © Springer Science+Business Media LLC 2010

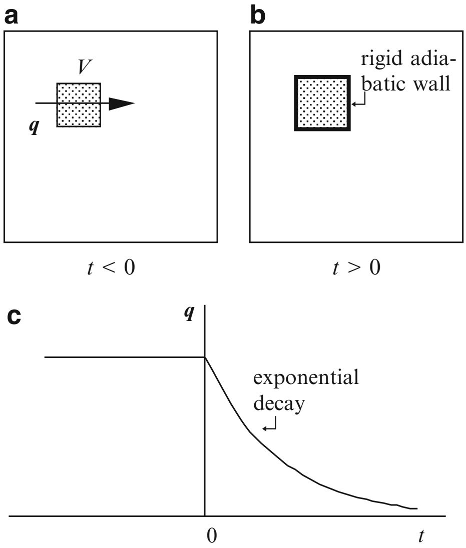


Fig. 3.1 (**a**) System under a heat flux; (**b**) at time $t = 0$ the system is completely isolated; (**c**) time evolution of heat flux

here for the sake of simplicity), it can then be asked which entropy may be ascribed to it. To answer this question, the volume element, at $t = 0$, is suddenly isolated, i.e. bounded by adiabatic and rigid walls, and allowed to decay to equilibrium. The decay of $\boldsymbol{q}$ and $\overset{0}{\mathbf{P}}{}^{v}$ to their final vanishing equilibrium values is accompanied by a production of entropy, so that the final equilibrium entropy value is given by

$$S_{\mathrm{eq},f} = S_{\mathrm{neq},i} + V \int_0^\infty \sigma^s \mathrm{d}t. \tag{3.1}$$

Indices i and f refer to the initial non-equilibrium state and the final equilibrium state respectively, S is the entropy of the small system of volume V and σ^s is the rate of entropy production per unit volume. A sketch of the situation when only heat flux is present is given in Fig. 3.1.

In Fig. 3.1, the non-equilibrium state (a) and the local-equilibrium state (b) corresponding to the same values of U and V are represented, respectively, before and after insulation. The second term in (3.1) corresponds to the non-compensated heat introduced by Clausius and will be commented on below.

The explicit form of the non-equilibrium contribution in the case of the Maxwell–Cattaneo equations may be obtained in a rather straightforward way. According to (2.55) and the identifications $\mu_1 = (\lambda T^2)^{-1}$ and $\mu_2 = (2\eta T)^{-1}$, σ^s is given by

$$\sigma^s = (\lambda T^2)^{-1} \boldsymbol{q} \cdot \boldsymbol{q} + (2\eta T)^{-1} \overset{0}{\mathbf{P}}{}^{v} : \overset{0}{P}{}^{v} \tag{3.2}$$

If the decay of $\boldsymbol{q}$ and $\overset{0}{\mathbf{P}}{}^{v}$ is governed by the Maxwell–Cattaneo equations (2.66–2.68), we have

$$\boldsymbol{q}(t) = \boldsymbol{q}(0)\exp(-t/\tau_1), \quad \overset{0}{\mathbf{P}}{}^{v}(t) = \overset{0}{\mathbf{P}}{}^{v}(0)\exp(-t/\tau_2). \tag{3.3}$$

By inserting these expressions into (3.1) and integrating with respect to the time, one obtains for the non-equilibrium entropy S

$$S = S_{\mathrm{eq}} - \tau_1 V/(2\lambda T^2)\boldsymbol{q}\cdot\boldsymbol{q} - \tau_2 V/(4\eta T)\,\overset{0}{\mathbf{P}}{}^{v} : \overset{0}{\mathbf{P}}{}^{v}, \tag{3.4}$$

which is the integrated form of the entropy (2.44) in the absence of bulk viscous pressure. Note that S and S_{eq} correspond to entropies of the fluid element of volume V and that s and s_{eq} in (2.44) are given per unit mass, and consequently the ratio S/s and V/v, with v being the specific volume, is the mass of the fluid element. The above derivation is suggestive as it assigns a meaning to the non-classical terms in the equation for the entropy, by relating them to a physical operational definition.

However, it must be realized that the above procedure exhibits three limitations: it is based on the hypotheses that $\boldsymbol{q}$ and $\overset{0}{P}{}^{v}$ are the relevant additional variables, it is assumed that $\boldsymbol{q}$ and $\overset{0}{\mathbf{P}}{}^{v}$ decay exponentially, and it is restricted to a given non-equilibrium process (namely, relaxation of the fluxes after sudden isolation of the elementary volume). It would be of interest to get rid of these restrictions.

In this respect, the idea of the uncompensated heat may be helpful to clarify in more general terms the nature of the non-equilibrium contributions (Eu 1991). In 1865, Clausius wrote his famous inequality for a cyclic process:

$$\oint \frac{đQ}{\theta} \leq 0, \tag{3.5}$$

where θ is the absolute temperature of the heat reservoir which is in thermal contact with the system during the infinitesimal process of exchange of an amount of heat $đQ$ (we write θ rather than T to stress that it is not necessary that the heat reservoir is itself in equilibrium). Inequality (3.5) may still be expressed as

$$-N \equiv \oint \frac{đQ}{\theta} \leq 0, \tag{3.6}$$

where N is the (positive) uncompensated heat. By expressing N in the form of a contour integral over an irreversible cycle $N = \oint đN$, Clausius inequality may be rewritten as

$$\oint \left(\frac{đQ}{\theta} + đN\right) = 0. \tag{3.7}$$

The assumption of a cyclic integral implies the assumption of a good choice of variables, i.e. a complete set of relevant macroscopic variables. The vanishing of integral (3.7) for arbitrary cycles implies the existence of the exact differential of a given quantity which is called the generalised entropy in our formalism (or the calortropy in Eu's work (1991, 1998), such that

$$\mathrm{d}S = \frac{đQ}{\theta} + đN. \tag{3.8}$$

Note that neither $đQ/\theta$ nor $đN$ are exact differentials, only their sum is. Furthermore, $đN$ is always positive, and it vanishes for reversible processes. In the latter case, $đN = 0, đQ = đQ_{\mathrm{rev}}$, $\theta = T$ and $S = S_{\mathrm{eq}}$, and one recovers Clausius definition of entropy

$$\mathrm{d}S_{\mathrm{eq}} = \frac{đQ_{\mathrm{rev}}}{T}. \tag{3.9}$$

The quantity S defined in (3.8) generalises Clausius definition of entropy, and it is important to note that $\mathrm{d}S \neq \mathrm{d}S_{\mathrm{eq}}$.

The above argument is more general than the one given before, as it does not require a priori specification of either the nature of the non-equilibrium variables, or the dynamics of the variables, or the nature of the process being involved. It can be objected that a theory based on the choice of fluxes $\boldsymbol{q}$ and $\overset{0}{\mathbf{P}}{}^{v}$ as variables is too restrictive. Indeed, a more refined formalism would demand inclusion of more non-equilibrium higher-order fluxes. The choice of $\boldsymbol{q}$ and $\overset{0}{\mathbf{P}}{}^{v}$ is useful when the evolution equations for $\boldsymbol{q}$ and $\overset{0}{\mathbf{P}}{}^{v}$ are those given by (2.66) and (2.68). The choice of the relevant variables must always be motivated either by experimental considerations or by microscopic theories when these are available. Note that the family of states whose adiabatic projection (i.e. the set of states which when isolated decay to a given equilibrium state) is a given equilibrium state may be considered as a fibre in the general thermodynamic space, which by this procedure is given the structure of a fibred space (Grmela 1993; Chen 1999).

3.2 Non-equilibrium Equations of State: Temperature

Having identified in Sect. 2.5 the parameters α_{10}, α_{00}, and α_{21} in physical terms, we are now in a position to evaluate explicitly the contributions of the fluxes to the equations of state. Up to the second order terms in the fluxes, the Gibbs equation (2.44) may be written as

$$\mathrm{d}s = \theta^{-1}\mathrm{d}u + \theta^{-1}\pi\mathrm{d}v - \frac{v\tau_1}{\lambda T^2}\boldsymbol{q}\cdot\mathrm{d}\boldsymbol{q} - \frac{v\tau_0}{\zeta T}p^v\mathrm{d}p^v - \frac{v\tau_2}{2\eta T}\overset{0}{\mathbf{P}}{}^{v} : \mathrm{d}\overset{0}{\mathbf{P}}{}^{v}. \tag{3.10}$$

From the integrability condition of (3.10), i.e. equality of the second crossed derivatives as for instance $\partial^2 s/\partial u\partial\boldsymbol{q} = \partial^2 s/\partial\boldsymbol{q}\partial u$, it follows that

$$\frac{\partial\theta^{-1}}{\partial \boldsymbol{q}} = -\left(\frac{\partial[v\tau_1/(\lambda T^2)]}{\partial u}\right)\boldsymbol{q}, \quad \frac{\partial\theta^{-1}}{\partial \overset{0}{\mathbf{P}}{}^v} = -\left(\frac{\partial[v\tau_2/(2\eta T)]}{\partial u}\right)\overset{0}{\mathbf{P}}{}^v, \tag{3.11}$$
$$\frac{\partial\theta^{-1}}{\partial p^v} = -\left(\frac{\partial[v\tau_0/(\zeta T)]}{\partial u}\right)p^v,$$

$$\frac{\partial(\theta^{-1}\pi)}{\partial \boldsymbol{q}} = -\left(\frac{\partial[v\tau_1/(\lambda T^2)]}{\partial v}\right)\boldsymbol{q}, \quad \frac{\partial(\theta^{-1}\pi)}{\partial \overset{0}{\mathbf{P}}{}^v} = -\left(\frac{\partial[v\tau_2/(2\eta T)]}{\partial v}\right)\overset{0}{\mathbf{P}}{}^v, \tag{3.12}$$
$$\frac{\partial(\theta^{-1}\pi)}{\partial p^v} = -\left(\frac{\partial[v\tau_0/(\zeta T)]}{\partial v}\right)p^v.$$

As a consequence of (3.11, 3.12), and keeping in mind that for vanishing values of the fluxes one must recover the local-equilibrium values of T and p, one obtains

$$\begin{aligned}\theta^{-1} &= T^{-1} - \frac{1}{2}\left[\frac{\partial[v\tau_1/(\lambda T^2)]}{\partial u}\boldsymbol{q}\cdot\boldsymbol{q} + \frac{\partial[v\tau_0/(\zeta T)]}{\partial u}(p^v)^2\right.\\ &\qquad\left. + \frac{\partial[v\tau_2/(2\eta T)]}{\partial u}\overset{0}{\mathbf{P}}{}^v : \overset{0}{\mathbf{P}}{}^v\right]\\ \theta^{-1}\pi &= T^{-1}p - \frac{1}{2}\left[\frac{\partial[v\tau_1/(\lambda T^2)]}{\partial v}\boldsymbol{q}\cdot\boldsymbol{q} + \frac{\partial[v\tau_0/(\zeta T)]}{\partial v}(p^v)^2\right.\\ &\qquad\left. + \frac{\partial[v\tau_2/(2\eta T)]}{\partial v}\overset{0}{\mathbf{P}}{}^v : \overset{0}{\mathbf{P}}{}^v\right].\end{aligned} \tag{3.13}$$

These expressions can be viewed as non-equilibrium equations of state for the temperature and pressure. In this section, we focus our analysis on temperature, which allows us a rather extensive discussion of the conceptual problems found in this context. In the Sect. 3.3, we will deal with the non-equilibrium pressure.

3.2.1 Zeroth Law, Second Law, and Temperature

Temperature may be defined from several perspectives: starting from general laws of thermodynamics, in particular the zeroth and second laws; from fundamental thermodynamic equations based on entropy and entropy flux; from thermodynamic equations of state or phenomenological transport equations; and from microscopic approaches: kinetic theories and theory of fluctuations. In equilibrium states, all these definitions are mutually consistent and lead to the same value for the temperature. Out of equilibrium, however, the several definitions lead in general to different values of temperature (Casas-Vázquez and Jou 2003; Crisanti and Ritort 2003). Thus, a basic topic of thermodynamics and statistical mechanics out of equilibrium should be how to relate the different effective temperatures with each other. In this perspective, for instance, it would be of interest to relate the thermodynamic absolute temperature, defined from the entropy differential, with the kinetic temperature, with the temperature describing fluctuations, and so on.

Here, we focus our discussion on the zeroth and second laws. As it is well known, the concept of absolute temperature is closely connected to these two principles of thermodynamics. The zeroth principle expresses the transitivity of thermal equilibrium: it states that if a system C is in thermal equilibrium with two systems A and B, then A and B will be in mutual thermal equilibrium if they are put in direct thermal contact. This principle allows an infinite number of empirical temperatures to be defined, which characterize the different classes of equivalence established in the space of states by the condition of mutual thermal equilibrium. To define an absolute temperature scale independent of the thermometric working substance, the second law is needed (for instance, in the form of Carnot's theorem, which states that the efficiency of Carnot's reversible heat engines is independent of the working substance). This result was used by William Thomson (Lord Kelvin) in 1848 to introduce for the first time the absolute temperature. Here we will clarify the concept of non-equilibrium temperature in the light of these two laws of thermodynamics.

The problem concerning these laws out of equilibrium is that different microscopic degrees of freedom may be characterized by different temperatures; for instance, when stating the zeroth law it will be necessary to specify the kind of interaction between the systems. If systems A and B exchange energy involving other degrees of freedom, the equality of effective temperatures of A and B – based on a set of degrees of freedom – will not imply the equality of temperatures between B and C, based on a different set of degrees of freedom. Therefore, to state the zeroth law out of equilibrium, the kind of interaction between the subsystems must be explicitly taken into account.

A second problem is the lack of a unique non-equilibrium entropy, from which temperature may be derived. Indeed, entropy may be different in a system under an imposed heat flux or the same system under an imposed viscous pressure. Here, we will restrict, as an illustration of the difficulties raised by this topic, to systems described by relaxational transport laws, i.e. by the entropy of extended irreversible thermodynamics.

First of all, recall the definition of the temperature θ which, according to (3.10), is

$$\theta^{-1} = \left(\frac{\partial s}{\partial u}\right)_{v,\boldsymbol{q},p^v,\overset{0}{\mathbf{P}}{}^v} . \tag{3.14}$$

If the entropy is known in terms of the various variables, (3.14) gives directly the equation of state of θ. Conversely, when all the equations of state are known, they may be integrated to obtain the expression of the entropy. From a geometrical point of view, the difference between θ and T may be easily understood as exhibited in Fig. 3.2.

The actual non-equilibrium state is A, the equilibrium state reached by an adiabatic projection is B. The slope of the non-equilibrium entropy at A (corresponding to $1/\theta$) is different from the slope of the equilibrium entropy at B (corresponding to $1/T$). Thus, when one refers to the local-equilibrium temperature T, one

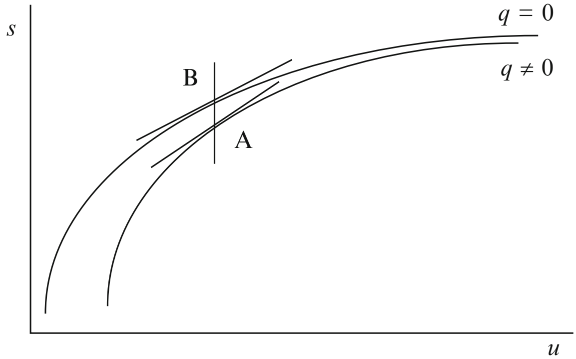


Fig. 3.2 The local-equilibrium entropy $s_{\mathrm{eq}}(u)$ (*upper curve*) and the generalised non-equilibrium entropy $s(u, \boldsymbol{q})$ (*lower curve*) are shown. The two temperatures θ and T mentioned in the text are given by the inverse of the slopes of the curves at points A and B respectively

is taking as reference state the accompanying local-equilibrium state B rather than the actual non-equilibrium state A. Note that $\theta^{-1} > T^{-1}$. This is a rather general feature because $s(u, \boldsymbol{q}) \leq s_{\mathrm{eq}}(u)$; it is also worth noticing that $s(u, \boldsymbol{q}) \to s_{\mathrm{eq}}(u)$ when $u \to \infty$ at constant $\boldsymbol{q}$ (this results from the fact that the value of $\tau v q^2/(\lambda T^2)$ decreases with increasing u at constant $\boldsymbol{q}$). Therefore, the curve $s(u, \boldsymbol{q})$ will be steeper than $s_{\mathrm{eq}}(u)$ yielding generally $\theta \leq T$. Since a non-equilibrium steady state is characterized by less entropy than the corresponding equilibrium state, it is therefore more ordered than the equilibrium state (recall that entropy may be related to molecular disorder). One could qualitatively split the internal energy per unit volume as $\rho u = \rho u_{\mathrm{ord}} + \rho u_{\mathrm{dis}}$ where u_{ord} and u_{dis} can be interpreted as the 'ordered' and 'disordered' parts of the internal energy per unit mass, respectively. These energies can be expressed as $\rho u_{\mathrm{dis}} = \frac{3}{2} n k_{\mathrm{B}} \theta$ and $\rho u_{\mathrm{ord}} = \frac{3}{2} n k_{\mathrm{B}} (T - \theta)$, with n the number density and k_B the Boltzmann constant, so that in total one finds the classical expression for the internal energy of monatomic gases per unit volume, given by $\rho u = \frac{3}{2} n k_{\mathrm{B}} T$ (see Sect. 3.3 for additional comments on this interpretation). In equilibrium, for which $T = \theta$, one has $u_{\mathrm{ord}} = 0$ and $u_{\mathrm{dis}} = u$.

To discuss the connection of temperature with the zeroth law, consider the experimental setup depicted in Fig. 3.3 (Casas-Vázquez and Jou 2003). A reference system Σ_r and the system under consideration Σ_s are thermally connected through a highly conducting rod of length L. We denote by q_s and q_{rs} the heat fluxes flowing through Σ_s and the rod respectively. Then we introduce the following statement: Σ_r and Σ_s are in mutual thermal equilibrium when $q_{rs} = 0$. This does not necessarily mean that $q_s = 0$.

Each of the two systems may be internally out of equilibrium notwithstanding the condition $q_{rs} = 0$. Naturally, in complete equilibrium $q_s = q_{rs} = 0$. Note that heat is the only quantity allowed to be exchanged between both systems along the rod. Otherwise, the coupling between several thermodynamic forces (for instance,

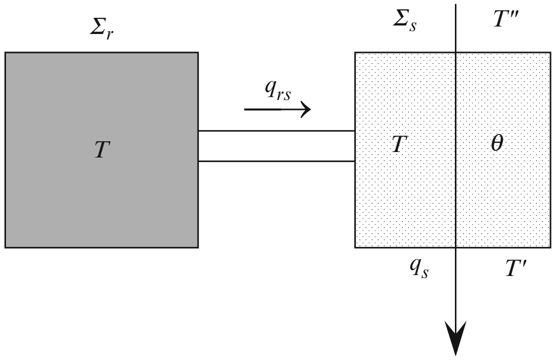


Fig. 3.3 Gedanken experiment to illustrate the difference between the local-equilibrium temperature and the non-equilibrium temperature

temperature and con-centration gradients) could give a vanishing net heat flow between systems at different temperatures.

Of course, these considerations do not directly help the decision of whether θ or T is truly the (non-equilibrium) temperature. To answer this question it is necessary to know whether the relation between heat flux and temperature gradient is $\boldsymbol{q} = -\lambda\nabla\theta$ rather than $\boldsymbol{q} = -\lambda\nabla T$. The answer is provided by the second law; indeed, as shown in Sect. 2.1, the first alternative is the only one following from the positive definite character of the entropy production. This means that the heat exchange between Σ_r and Σ_s is directly governed by the non-equilibrium temperature θ. If Σ_r and Σ_s are both at equilibrium, θ coincides with the local-equilibrium temperature T. However, if Σ_r and Σ_s are out of equilibrium, with $q_{rs} = 0$, then one will observe that $\theta_r = \theta_s$ rather than $T_r = T_s$.

To be more specific, assume that the system Σ_r on the left in Fig. 3.3 is at equilibrium at temperature T. The system on the right is in a non-equilibrium steady state under a heat flux q_s generated by a temperature difference. Assume that both ends of the conducting rod are at the same local-equilibrium absolute temperature T. According to the classical theory, no heat flow will be observed from one system to another. In contrast, EIT predicts a flow q_{rs} proportional to the gradient of the non-equilibrium temperature θ, namely $(\theta_r - \theta_s)/L$. Since the system Σ_r is in equilibrium, one has $\theta_r = T_r$, but $\theta_s = T_s(1 - \gamma q_s^2)$, with $\gamma = \frac{2}{5}m/(n^2 k_{\mathrm{B}}^3 T^3)$ for ideal monatomic gases, so that $\theta_s < T_s$. Consequently, a heat flux q_{rs} will flow from the left to the right. This example corroborates the statement that a thermometer will measure the generalised temperature θ rather than the local-equilibrium T: heat transfer between the two systems will take place until they have reached the same generalised temperature, rather than the same local-equilibrium temperature. A confirmation is found in the kinetic theory; indeed, it may be shown (Casas-Vázquez and Jou 2003) that when both systems Σ_s and Σ_r of Fig. 3.3 are composed of an ideal gas with the same mean kinetic energy at the position of the thermal contact, energy flows from the equilibrium gas to the gas submitted to the vertical heat flux. Another confirmation is provided by computer simulations, as discussed in Sect. 8.4.

3.2.2 Evaluation of θ in Some Special Situations

To be specific, we focus on situations where the heat flux $\boldsymbol{q}$ is the only non-equilibrium flux, and we try to give a numerical estimation of the differences between θ and T. The first of the expressions (3.11) reduces to

$$\theta^{-1}(u, \boldsymbol{q}) = T^{-1}(u) - \frac{1}{2}\frac{\partial[\tau_1 v/(\lambda T^2)]}{\partial u}\boldsymbol{q} \cdot \boldsymbol{q}, \tag{3.15}$$

wherein $T(u)$ only depends on the internal energy, not on the heat flux.

For monatomic ideal gases obeying the Boltzmann equation, a well-known result of kinetic theory is that $\tau_1/(\lambda T^2) = \frac{2}{5}m/(k_B^2 T^3 n)$, with m being the mass of a molecule, k_B the Boltzmann constant, and n the number density, so that the inverse of the temperature is given by

$$\theta^{-1}(u, \boldsymbol{q}) = T^{-1}(u) + \frac{2}{5}\frac{\rho}{p^3 T}\boldsymbol{q} \cdot \boldsymbol{q}. \tag{3.16}$$

This expression provides an explicit estimation of the difference between T and θ.

For metallic rigid conductors, (3.15) is given by Casas-Vázquez and Jou (2003)

$$\theta^{-1}(u, \boldsymbol{q}) = T^{-1}(u) + \frac{9}{\pi^4}\frac{m^2 \varepsilon_F}{n k_B^4 T^5}\boldsymbol{q} \cdot \boldsymbol{q}, \tag{3.17}$$

with m being the electron mass, n the electron number density, and ε_F the Fermi energy of the metal. Since the coefficients of the term in $\boldsymbol{q} \cdot \boldsymbol{q}$ are very small, it turns out that in many practical situations the corrective term may be neglected. Indeed, for CO_2 at 300 K and 0.1 atm, and for a heat flux of 10^9 W/m^2, the difference $T - \theta$ is 9.6×10^{-2} K. However, in other circumstances the difference is not minute: in nuclear collisions (as studied in Sect. 17.4) $T - \theta$ is of the order of 7% of T, and in radiation near the surface of stars, the difference is close to 3% (Fort et al. 1998, 1999).

3.2.3 Alternative Definitions of Generalised Temperature

The problems of the definition and measurement of a non-equilibrium temperature have raised some questions (Hoover et al. 1992; Nettleton 1994; Eu and Garcia-Colín 1996). A first one is related to the nature of the variables to be kept constant during the differentiation of the entropy in (3.14). With v and $\boldsymbol{q}$ fixed, one recovers (3.11). If instead one keeps constant v and the quantity $[\tau_1/(\rho\lambda T^2)]^{1/2}\boldsymbol{q}$ (Banach and Pierarski 1993), the derivatives of the generalised entropy and of the local-equilibrium entropy coincide. Indeed, since

$$s(u,v,\boldsymbol{q}) = s_{\mathrm{eq}}(u,v) - \tau v(2\lambda T^2)^{-1}\boldsymbol{q}\cdot\boldsymbol{q}, \tag{3.18}$$

then it follows

$$\left(\frac{\partial s}{\partial u}\right)_{v,\sqrt{\tau/(\lambda T^2)}\boldsymbol{q}} = \left(\frac{\partial s_{\mathrm{eq}}}{\partial u}\right)_v . \tag{3.19}$$

Still another possibility (Brey and Santos 1992) is to maintain the temperature gradient fixed and, since (3.18) implies that for steady situations

$$s = s_{\mathrm{eq}} - \frac{\tau v\lambda}{2T^2}\nabla T\cdot\nabla T, \tag{3.20}$$

one is led to

$$\left(\frac{\partial s}{\partial u}\right)_{v,\nabla T} = \frac{1}{T} + (1+2b)\frac{\tau\lambda}{2\rho c_v T^3}\nabla T\cdot\nabla T, \tag{3.21}$$

where b is the exponent which characterizes the dependence of τ with T according to $\tau \approx T^{-b}$ (i.e. $b = 0$ for Maxwell molecules and $b = 1/2$ for hard spheres). It can be argued that not all these definitions may be valid: recall, indeed, that in equilibrium thermodynamics $(\partial s/\partial u)_v = T^{-1}$, but if one keeps pressure constant instead of volume during the differentiation, $(\partial s/\partial u)_p \neq T^{-1}$; clearly $(\partial s/\partial u)_p = T^{-1}[1-(pv\alpha/c_p)]^{-1}$ with α being the coefficient of thermal expansion and c_p the specific heat at constant pressure. At the present time, it is not evident which among the above restrictions is the most suitable to define the non-equilibrium temperature.

The presence of a generalised temperature is not exclusive to EIT. In his entropy-free formulation of non-equilibrium thermodynamics, Meixner (1973a, b) postulated the existence of a dynamical temperature depending on the interactions of the system with the outside. Much more recently other authors have introduced dynamical temperatures which decay exponentially towards the local-equilibrium temperature (Cimmelli and Kosinsky 1991). Müller (1971) used a 'coldness' function assumed to depend on the empirical temperature and its time derivative: in a steady state, the 'coldness' reduces to the local-equilibrium temperature, in contrast with the generalised temperature appearing in EIT. Some years later, Muschik (1977) introduced the notion of contact temperatures and explored the conceptual difficulties of their measurement; this contact temperature is not identical to the local-equilibrium temperature. Finally, Keizer (1987) proposed a non-equilibrium temperature defined as the derivative with respect to the internal energy of a generalised entropy based on statistical considerations of molecular fluctuations; this temperature depends not only on the classical variables but also on the second moments of fluctuations. It is worth stressing that the EIT generalised temperature may also be expressed in terms of the second moments of the energy fluctuations, in analogy with Keizer's approach (see Chap. 5).

3.2.4 Experimental Hints for the Non-equilibrium Temperature

There is some experimental confirmation of the difference between the non-equilibrium temperature and the local-equilibrium temperature. There are strong indications from experiments on modulation optical spectrometry in laser-induced plasma in semiconductors submitted to an external electric field, that the temperature appearing in the non-equilibrium distribution function depends not only on the local-equilibrium variables but also on the fluxes (Luzzi 1997). In these experiments, one measures the intensity of radiative recombination $I(\omega)$, as a function of the frequency ω. It is found that

$$I(\omega) = g(\omega) \exp\left(-\frac{\hbar\omega - E_G}{k_B\theta}\right), \tag{3.22}$$

wherein E_G is the energy gap of the semiconductor and $g(\omega)$ the absorption coefficient, which depends only weakly on ω. Thus, a plot of $\ln I(\omega)$ as a function of ω allows θ to be determined. When the system is perturbed around an equilibrium state, it is seen that θ coincides with T. However, when the system is perturbed around a non-equilibrium steady state in the presence of an electric field E, it turns out that θ is indeed different from T and depends on the electric flux. For more details, the reader is referred to Luzzi (1997).

Examples of systems for which the difference between local-equilibrium and non-equilibrium entropy have been studied in detail are: (a) a set of forced oscillators in thermal baths, where the kinetic energy and configurational energy – average potential elastic energy – are different from each other (Hatano and Jou 2003); (b) flowing ideal gases in a Couette flow, for which kinetic temperature, thermodynamic temperature, and fluctuation–dissipation temperature have been evaluated for different shear rates (Criado-Sancho et al. 2006); (c) flowing interacting gases in the presence of an operational "thermometer" as analysed from molecular dynamics (Baranyai 2000); (d) relaxating glasses, where the fluctuations and the dissipation coefficient are related through a fluctuation–dissipation theorem involving a temperature different from the local-equilibrium temperature (Crisanti and Ritort 2003); (e) shaked granular media, where temperature is defined by means of an Einstein relation between the diffusion coefficient and the friction coefficient (D'Anna et al. 2003). In summary, the influence of fluxes on the several non-equilibrium effective temperatures is an active topic which needs further clarification beyond the local-equilibrium hypothesis.

3.3 Non-equilibrium Equations of State: Thermodynamic Pressure

In (2.46) we wrote for the pressure tensor the expression $\mathbf{P} = \pi\mathbf{U} + p^v\mathbf{U} + \overset{0}{\mathbf{P}}{}^v$, where π on the right-hand side is replacing the equilibrium pressure p, which is usually found in the expressions for $\mathbf{P}$ in classical irreversible thermodynamics (CIT) (see, for instance, Lambermont and Lebon 1974). In Sect. 2.4 we have provisionally accepted (2.46) as a consistent analogy with the replacement of temperature T by temperature θ and of pressure p by π in the generalised Gibbs equation (2.44). Here, we analyse this hypothesis in more depth.

The definition of a non-equilibrium pressure requires subtler considerations than that of the non-equilibrium temperature. It must be recalled from equilibrium thermodynamics that the entropy is a characteristic function (i.e. all conceivable thermodynamic information about the system is ascertainable from it) on condition that it is expressed in terms of extensive variables. Therefore, rather than the fluxes themselves, one should use $v\boldsymbol{q}$, vp^v and $v\overset{0}{\mathbf{P}}{}^v$ as independent variables. Indeed, these variables are extensive in the following sense: if we have two systems of volumes V_1 and V_2 crossed by the same heat flux $\boldsymbol{q}$, the variable $V\boldsymbol{q}$ is additive, i.e. $V_{\text{tot}}\boldsymbol{q} = V_1\boldsymbol{q} + V_2\boldsymbol{q}$, although $\boldsymbol{q}$ itself is not additive. The consequence of this choice will be reflected in the definition of the non-equilibrium pressure, which is obtained as the derivative of the entropy with respect to the volume at constant $v\boldsymbol{q}$ rather than at constant $\boldsymbol{q}$. Since the temperature is related to the differential of the entropy at constant v, the fact that $v\boldsymbol{q}$ or $\boldsymbol{q}$ are kept constant does not modify the results, because v is a constant.

In view of the above considerations, the most suitable definition for the non-equilibrium pressure is

$$\pi\theta^{-1} = \left(\frac{\partial s}{\partial v}\right)_{u,v\boldsymbol{q}}. \tag{3.23}$$

However, now a conceptual problem arises, because in an ideal gas the equilibrium pressure is defined as one third of the trace of the pressure tensor. Since for an ideal gas $p = \frac{2}{3}\rho u$ is independent of the fluxes, it seems that we are faced with a contradiction. It is however easy to convince oneself that there is no problem. Consider, for instance, an ideal gas submitted to a heat flux and that its contribution to $\mathbf{P}^v$ has the form $\mathbf{P}^v = \alpha\boldsymbol{q}\boldsymbol{q}$, where α is a phenomenological coefficient function of u and v. Expression (2.46) then takes the form

$$\mathbf{P} = \pi\mathbf{U} + \alpha\boldsymbol{q}\boldsymbol{q}. \tag{3.24}$$

Since the pressure tensor must satisfy $\mathrm{Tr}\mathbf{P} = 3p$, it is required that the coefficient α in (3.24) to be given by the condition $\mathrm{Tr}\mathbf{P} = 3\pi + \alpha\boldsymbol{q}\cdot\boldsymbol{q} = 3p$. This result makes clear that although the derivative of the entropy with respect to the volume depends on $\boldsymbol{q}$, it is not in contradiction with the property that the trace of the tensor is not dependent on the flux. We add that the expression (3.24) is supported by other approaches, such as microscopic analyses of electromagnetic radiation (Domínguez and Jou 1995; Nettleton 1996; Domínguez-Cascante and Faraudo 1996), the Hamiltonian methods introduced in Chap. 1 and the information methods presented in Chap. 6.

It is helpful to write **P** explicitly in a simple situation, namely, when the heat flux is in the y direction, so

$$\mathbf{P} = \begin{pmatrix} \pi & 0 & 0 \\ 0 & \pi & 0 \\ 0 & 0 & \pi \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & \alpha q_y^2 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{3.25}$$

This expression implies that the work of compression or expansion will depend on the relative direction between the axis of compression and the heat flux. This has been found in some computer simulations (see Sect. 8.4), where the thermodynamic pressure is seen to be equal to the minimum eigenvalue of the pressure tensor. This is indeed the situation found in (3.25), because $\pi < p$ and therefore $\alpha q_y^2 > 0$. A Gedanken experiment analogous to that in Fig. 3.3 could be devised for the non-equilibrium pressure, by replacing the rigid conducting rod connecting the systems in Fig. 3.3 by a mobile piston.

Note that for an ideal gas under a heat flux, the definition (3.23) taken with $v\boldsymbol{q}$ as a constant yields $\pi/\theta = p/T$. Indeed,

$$\frac{\pi}{\theta} = \left(\frac{\partial s_{\text{eq}}}{\partial v}\right)_{u,v\boldsymbol{q}} = \left(\frac{\partial s_{\text{eq}}}{\partial v}\right)_u - \frac{1}{2}\frac{\partial}{\partial v}\left(\frac{\tau_1}{\lambda T^2}\right) v\boldsymbol{q} \cdot v\boldsymbol{q}. \tag{3.26}$$

But, according to kinetic theory (see (4.44)) $\lambda = \frac{5}{2}(nk_{\text{B}}T^2/m)\tau_1$, and therefore $\tau_1/v\lambda$ is independent of v, as $vn = 1/m$. Therefore, the second term on the right-hand side in (3.26) vanishes and it is found that

$$\frac{\pi}{\theta} = \left(\frac{\partial s_{\text{eq}}}{\partial v}\right)_u = \frac{p}{T} = nk_{\text{B}}. \tag{3.27}$$

Note that the result would have been different if the derivative was performed at constant $\boldsymbol{q}$. In this case one would have

$$\left(\frac{\partial s_{\text{eq}}}{\partial v}\right)_{u,\boldsymbol{q}} = \left(\frac{\partial s_{\text{eq}}}{\partial v}\right)_u - \frac{1}{2}\frac{\partial}{\partial v}\left(\frac{\tau_1 v}{\lambda T^2}\right)\boldsymbol{q} \cdot \boldsymbol{q} = \frac{p}{T} - \frac{\tau_1}{\lambda T^2}\boldsymbol{q} \cdot \boldsymbol{q}. \tag{3.28}$$

Let us go back to expression (3.25) for the pressure tensor when $\boldsymbol{q}$ is directed along the y axis; it is easy to see that $P_{xx} = P_{zz} = \pi < p$, and $P_{yy} = 3p - 2\pi > p$. Since for an ideal gas the components of the pressure tensor are related to the second moments of the velocity, we have

$$\left\langle \tfrac{1}{2} m v_x v_x \right\rangle = \left\langle \tfrac{1}{2} m v_z v_z \right\rangle = \tfrac{1}{2} k_{\text{B}} \theta < \tfrac{1}{2} k_{\text{B}} T, \tag{3.29a}$$

$$\left\langle \tfrac{1}{2} m v_y v_y \right\rangle = \tfrac{1}{2} k_{\text{B}} (3T - 2\theta) > \tfrac{1}{2} k_{\text{B}} T. \tag{3.29b}$$

Three points are worth noticing: (a) the average molecular kinetic energy $\langle \frac{1}{2}mv^2 \rangle$ is given by $\frac{3}{2}k_B T$, in agreement with the definition of T in kinetic theory; (b) out of equilibrium, the equipartition theorem, implying that the average kinetic energy along the three axes is the same, is no longer valid: the average energy is lower in the direction orthogonal to the heat flux. This consequence could in principle be checked, for instance, by analysing the Doppler broadening of emission lines in excited rarefied gases along the direction of the heat flux and perpendicularly to it (Camacho and Jou 1995); and (c) a fraction $\frac{3}{2}k_B\theta$ is equally distributed in the three degrees of freedom along the three axes, whereas the remaining fraction $\frac{3}{2}k_B(T-\theta)$ is ordered along the axis corresponding to the heat flux. This observation supports the remark in Sect. 3.2.1 about the splitting of the internal energy in an 'ordered' and a 'disordered' part.

These considerations remind us that thermometry is not a trivial subject. Since the mean kinetic molecular energy along the direction x is not the same along the direction y, a thermometer will indicate different temperatures according to its relative position with respect to the direction of $\boldsymbol{q}$. This is not totally surprising because in non-equilibrium there is no longer equipartition, and therefore, thermometers which are sensitive to different degrees of freedom will indicate different values for the temperature. For instance, if we have a mixture of matter and radiation at different temperatures, a completely reflecting thermometer will indicate the temperature of matter, whereas a thermometer with perfectly black walls will read a value which is the average temperature of the mixture.

Another situation worthy of attention is found in fluids at uniform temperature subjected to a steady shear flow in the x direction. Since the non-equilibrium contributions to the pressure are of second order in the shear rate $\dot{\gamma}$, we must also go to this same order in the expression of the viscous pressure tensor, which will be given by $\mathbf{P}^v = -2\eta\mathbf{V} + \mu_{22}\mathbf{V}\cdot\mathbf{V}$. According to (2.46), the total pressure tensor will be written

$$\mathbf{P} = \begin{pmatrix} \pi & 0 & 0 \\ 0 & \pi & 0 \\ 0 & 0 & \pi \end{pmatrix} + \begin{pmatrix} \mu_{22}\eta^2\dot{\gamma}^2 & -\eta\dot{\gamma} & 0 \\ -\eta\dot{\gamma} & \mu_{22}\eta^2\dot{\gamma}^2 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{3.30}$$

For purely Newtonian fluids, $\mu_{22} = 0$, and for non-Newtonian fluids, the terms in μ_{22} are related to normal pressure effects (see Sect. 15.1). Ideal gases are Newtonian at low shear rates but exhibit normal pressure effects at higher values of $\dot{\gamma}$. By writing $\pi = p - a\dot{\gamma}^2$, the condition $\mathrm{Tr}\mathbf{P} = 3p$ imposes that

$$-3a\dot{\gamma}^2 + 2\mu_{22}\eta^2\dot{\gamma}^2 = 0, \tag{3.31}$$

which provides a relation between η and μ_{22}. According to (3.4), the entropy has the form

$$s(u, v, \mathbf{P}^v) = s_{\mathrm{eq}}(u, v) - \frac{\tau_2 v}{2\eta \mathrm{T}}(P_{12}^v)^2. \tag{3.32}$$

Taking into account that according to kinetic theory (see (4.44)), $\eta = p\tau_2$ and $pv =$ constant at constant internal energy, one has

$$\frac{\pi}{\theta} = \left(\frac{\partial s}{\partial v}\right)_{u,v\mathbf{P}^v} = \frac{p}{T} = nk_\mathrm{B}, \tag{3.33}$$

which is analogous to the result (3.27). From $\theta < T$, it follows that $\pi < p$; therefore $a > 0$ in (3.31) and henceforth $\mu_{22} > 0$ in virtue of (3.31). It turns out that the diagonal term of tensor $\mathbf{P}$ with the lowest value is precisely π. We comment further on this point in Sect. 8.4. Similar considerations apply to the equations of state for the chemical potential and imply, for instance, a shift of the critical point and the coexistence lines in the phase diagram of polymer solutions under a shear rate, and the displacement of chemical equilibrium under a flow or a heat flux. Some examples are analysed in Chap. 16.

3.4 Concavity Requirements and Stability

Now we turn our attention to the requirements stemming from the concavity of entropy, namely, the requirement that the second differential $\delta^2 s$ of the entropy must be negative definite. After integrating the generalised Gibbs equation (3.11) and expanding the entropy around the local equilibrium value up to the second order in the fluxes, one obtains

$$s(u, v, \boldsymbol{q}, p^v, \overset{0}{\mathbf{P}}{}^v) = s_\mathrm{eq}(u, v) - \frac{v\tau_1}{2\lambda T^2}\boldsymbol{q}\cdot\boldsymbol{q} - \frac{v\tau_0}{2\zeta T}p^v p^v - \frac{v\tau_2}{4\eta T}\overset{0}{\mathbf{P}}{}^v : \overset{0}{\mathbf{P}}{}^v. \tag{3.34}$$

When the dissipative fluxes are zero, one recovers the classical conditions for stability,

$$c_v = T(\partial s/\partial T)_v > 0, \quad \kappa_T = -(1/v)(\partial v/\partial p)_\mathrm{T} > 0, \tag{3.35a}$$

with c_v being the specific heat at constant volume and κ_T the isothermal compressibility. When the non-classical terms containing the fluxes are taken into account, the concavity of the entropy (3.34) implies that

$$\frac{v\tau_1}{\lambda T^2} > 0, \ \frac{v\tau_0}{\zeta T} > 0, \ \frac{v\tau_2}{2\eta T} > 0. \tag{3.35b}$$

Because T is positive, and since the second law requires that λ ζ, and η are all positive, it turns out from (3.35b) that the relaxation times τ_1, τ_0, and τ_2 must be positive, otherwise causality would be violated.

The property of concavity of entropy is equivalent to the requirement that the field equations form a symmetric hyperbolic system. Such a property ensures that the problem is well posed and that the characteristic speeds are real and finite. The relation between symmetric hyperbolicity and the existence of a concave function whose production has a definite sign, that is, the existence of an entropy function, has been examined from a general mathematical point of view by several authors (Friedrichs and Lax 1971; Boillat and Strumia 1988; Wilmanski 1998;

Muller and Ruggeri 1998). This result is important as it indicates that the condition of hyperbolicity implies the existence of an entropy function. Here we have adopted the reciprocal point of view: starting from the hypothesis of the existence of a generalised entropy, we have arrived at hyperbolic field equations.

Let us now show using simple examples, such as heat conduction and Couette viscous flow, that concavity is satisfied only for values of the fluxes smaller than some critical values when the reference state is a non-equilibrium steady state.

3.4.1 Heat Conduction in a Rigid Solid

Let us first consider heat conduction in a rigid solid for which $s = s(u, \boldsymbol{q})$. The second differential of the generalised entropy (2.38) is then given by

$$\delta^2 s = -\left(\frac{1}{c_v T^2} + \frac{1}{2} q^2 \frac{\partial^2 \alpha}{\partial u^2}\right)(\delta u)^2 - \alpha \delta \boldsymbol{q} \cdot \delta \boldsymbol{q} - 2\boldsymbol{q} \frac{\partial \alpha}{\partial u} \delta u \cdot \delta \boldsymbol{q}, \tag{3.36}$$

where use is made of (2.35) with $c_v = \partial u / \partial T$ and $\alpha = \tau_1 v / (\lambda T^2)$. If v, τ_1, c_v and λ are constant, one has $\partial \alpha / \partial u = -2\alpha (c_v T)^{-1}$ and $\partial^2 \alpha / \partial u^2 = 6\alpha (c_v T)^{-2}$. The expression for $\delta^2 s$ is definite negative if the matrix Δ of its coefficients, given by

$$\Delta = -\begin{pmatrix} \dfrac{1}{c_v T^2} + \dfrac{1}{2} \dfrac{\partial^2 \alpha}{\partial u^2} q^2 & \dfrac{\partial \alpha}{\partial u} \boldsymbol{q} \\ \dfrac{\partial \alpha}{\partial u} \boldsymbol{q} & \alpha \end{pmatrix}, \tag{3.37}$$

is negative. This requires that the diagonal components and the determinant of Δ are negative. The first condition is valid for all values of the heat flux. The second condition is

$$\frac{\alpha}{c_v T^2} + \left[\frac{\alpha}{2} \frac{\partial^2 \alpha}{\partial u^2} - \left(\frac{\partial \alpha}{\partial u}\right)^2\right] q^2 \geq 0; \tag{3.38}$$

This inequality is satisfied for values of q such that (see Problem 3.4)

$$q \leq \left(\frac{c_v}{\alpha}\right)^{1/2} = \rho c_v T \left(\frac{\lambda}{\rho c_v \tau_1}\right)^{1/2}, \tag{3.39}$$

where $[\lambda / (\rho c_v \tau_1)]^{1/2} = U$ is the maximum speed of the thermal waves, as shown in Sect. 9.1. Thus, thermodynamic stability is only guaranteed when the heat flux is lower than the critical value (3.39).

Furthermore, when this condition is satisfied, one avoids an unsatisfactory property of the telegrapher equation, namely, that an initial absolute temperature profile which is positive everywhere may take negative values during some time intervals (Criado-Sancho et al. 1993); this unpleasant result is not found with parabolic diffusion equations, where the positive character of the temperature field is always respected. In hyperbolic heat transport, one should impose as initial conditions not only a positive temperature profile but also that the heat flux is bounded everywhere by the critical value $\rho u U$.

3.4.2 Heat Conduction in Ideal Gases

A more general situation taking into account that the generalised entropy $s(u, v, \boldsymbol{q})$ depends also on v yields the following matrix for the coefficients of the second-order derivatives of s:

$$\delta^2 s = \begin{pmatrix} \dfrac{\partial^2 s_{\text{eq}}}{\partial u^2} - \dfrac{1}{2}\dfrac{\partial^2 \alpha}{\partial u^2}q^2 & \dfrac{\partial^2 s_{\text{eq}}}{\partial u \partial v} - \dfrac{1}{2}\dfrac{\partial^2 \alpha}{\partial u \partial v}q^2 & -\dfrac{\partial \alpha}{\partial u}q \\ \dfrac{\partial^2 s_{\text{eq}}}{\partial u \partial v} - \dfrac{1}{2}\dfrac{\partial^2 \alpha}{\partial u \partial v}q^2 & \dfrac{\partial^2 s_{\text{eq}}}{\partial v^2} - \dfrac{1}{2}\dfrac{\partial^2 \alpha}{\partial v^2}q^2 & -\dfrac{\partial \alpha}{\partial v}q \\ -\dfrac{\partial \alpha}{\partial u}q & -\dfrac{\partial \alpha}{\partial v}q & -\alpha \end{pmatrix}, \tag{3.40}$$

where, as in (3.36), α stands for $\alpha = \tau_1 v/(\lambda T^2)$. To obtain a more explicit expression, consider an ideal monatomic gas for which, according to the kinetic theory of gases, $\lambda = \frac{5}{2}(nk_B T^2/m)$ and therefore $\alpha = \frac{2}{5}mv(pk_B T^2)^{-1}$ (see (4.44)). Furthermore, the caloric and thermal equations of state are $u = \frac{3}{2}k_B T/m$ and $p = nk_B T$, where n is the number density of particles and m the mass of the particles. Simple calculations lead to

$$\delta^2 s = \begin{pmatrix} -\dfrac{2m}{3k_B T^2} - \dfrac{16m^2}{15n^2k_B^4T^5}q^2 & \dfrac{4m^2}{5nk_B^3T^4}q^2 & \dfrac{4m}{5n^2k_B^3T^4}q \\ \dfrac{4m^2}{5nk_B^3T^4}q^2 & -mn^2k_B - \dfrac{2m^2}{5k_B^2T^3}q^2 & -\dfrac{4m}{5nk_B^2T^3}q \\ \dfrac{4m}{5n^2k_B^3T^4}q & -\dfrac{4m}{5nk_B^2T^3}q & -\dfrac{2}{5n^2k_B^2T^3} \end{pmatrix}. \tag{3.41}$$

Necessary conditions for a matrix to be negative definite are that the diagonal terms are negative and the complete and partial determinants along the diagonal have alternate signs. The first condition is always fulfilled by (3.41), but not the latter. Such conditions state that the minor M formed by the first two columns and the first two rows must be positive. This quantity is found to be

$$M = \tfrac{2}{3}(m^2n^2/T^2) + \tfrac{4}{3}(m^3/k_B^3T^5)q^2 - \tfrac{16}{75}(m^4/n^2k_B^6T^8)q^4. \tag{3.42}$$

It is positive for q not exceeding $q_{c1} = 2.67nk_B T(k_B T/m)^{1/2} = 1.03\rho u v_{\text{rms}}$, with $\rho u = \frac{3}{2}nk_B T$ and v_{rms} being the root mean-square velocity given by

$v_{\mathrm{rms}} = (3k_{\mathrm{B}}T/m)^{1/2}$. This corresponds to a critical temperature gradient $\partial \ln T/\partial x = 1.85/\ell$, with $\ell = \tau v_{\mathrm{rms}}$ being the mean free path. The determinant of the matrix (3.41) is

$$\det \Lambda = -\tfrac{4}{15}(m^2/k_{\mathrm{B}}^2T^5) + \tfrac{8}{15}(m^3/n^2k_{\mathrm{B}}^5T^8)q^2. \tag{3.43}$$

It remains negative for heat fluxes smaller than $q_{c2} = 0.27\rho u v_{\mathrm{rms}}$. This second value puts a more severe limitation on the maximum allowable value of the temperature gradient, ensuring the validity of EIT. The limiting value is now $\partial \ln T/\partial x = 0.49/\ell$. Accordingly, $\det \Lambda$ will remain negative for perturbations of wavelength not smaller than $\ell_c = 2.04\ell$. The above result is interesting as it gives a hint about the domain of applicability of EIT, which appears to be well suited for wavelengths slightly greater than the mean free path, when $\boldsymbol{q}$ is the only non-equilibrium variable.

3.4.3 Shear Viscous Pressure in Viscous Fluids

Further information on the stability restrictions on the fluxes is provided by the study of an ordinary viscous fluid when heat effects are negligible. The entropy (3.4) is now given by

$$s(u, v, \overset{0}{\mathbf{P}}{}^v) = s_{\mathrm{eq}}(u, v) - \tau_2 v/(4\eta T)\,\overset{0}{\mathbf{P}}{}^v : \overset{0}{\mathbf{P}}{}^v. \tag{3.44}$$

The kinetic theory of gases shows that $\eta = p\tau$ and as a consequence $\tau_2 v/(4\eta T) = mv^2/(4k_{\mathrm{B}}T^2)$. By restricting the analysis to a plane Couette flow, for which $\overset{0}{\mathbf{P}}{}^v : \overset{0}{\mathbf{P}}{}^v = 2\eta^2\dot{\gamma}^2$, $\dot{\gamma}$ being the shear rate, a calculation parallel to the previous one yields

$$\Lambda = \begin{pmatrix} -\dfrac{2m}{3k_{\mathrm{B}}T^2} - \dfrac{4m^3v^2}{3k_{\mathrm{B}}^3T^4}\eta^2\dot{\gamma}^2 & \dfrac{4m^2v}{3k_{\mathrm{B}}^2T^3}\eta^2\dot{\gamma}^2 & \dfrac{4m^2v^2}{3k_{\mathrm{B}}^2T^3}\eta\dot{\gamma} \\ \dfrac{4m^2v}{3k_{\mathrm{B}}^2T^3}\eta^2\dot{\gamma}^2 & -mn^2k_{\mathrm{B}} - \dfrac{m}{k_{\mathrm{B}}T^2}\eta^2\dot{\gamma}^2 & -\dfrac{2mv}{k_{\mathrm{B}}T^2}\eta\dot{\gamma} \\ \dfrac{4m^2v^2}{3k_{\mathrm{B}}^2T^3}\eta\dot{\gamma} & -\dfrac{2mv}{k_{\mathrm{B}}T^2}\eta\dot{\gamma} & -\dfrac{mv^2}{k_{\mathrm{B}}T^2} \end{pmatrix}. \tag{3.45}$$

As before, the diagonal elements are always negative, whereas the first minor formed by the first two rows and the first two columns,

$$M = \tfrac{2}{3}(m^2n^2/T^2) + 2(m^2/k_{\mathrm{B}}^2T^4)(\eta\dot{\gamma})^2 - \tfrac{4}{9}(m^2/n^2k_{\mathrm{B}}^4T^6)(\eta\dot{\gamma})^4, \tag{3.46}$$

remains positive up to a critical value $(\eta\dot{\gamma})^2 = 4.81(nk_{\mathrm{B}}T)^2$. In view of the kinetic result $\eta = p\tau$, one has $(\dot{\gamma}\tau)_c = 2.19$. On the other hand, the determinant of (3.45) results in

$$\det \Delta = -\tfrac{1}{3}(mk_{\mathrm{B}}/T^4) + \tfrac{7}{9}(m/n^2k_{\mathrm{B}}^3T^6)(\eta\dot{\gamma}) - \tfrac{10}{9}(m/n^4k_{\mathrm{B}}^5T^8)(\eta\dot{\gamma})^2 \tag{3.47}$$

which is negative for $\dot{\gamma}\tau$ lower than $(\dot{\gamma}\tau)_c = 0.51$. It is thus concluded that (3.47) is negative for values of $\dot{\gamma}^{-1} > 1.96\tau$. This gives the domain of validity of the relaxational equation for the viscous pressure.

3.5 Problems

3.1. In a monatomic ideal gas, the thermal conductivity is given by $\lambda = \frac{5}{2}(nk_B^2 T/m)\tau_1$. (a) Determine θ^{-1} in the presence of a heat flux $\boldsymbol{q}$ by using (3.14). (b) Calculate the difference between θ and the local-equilibrium temperature T for Ar (atomic weight 40) at 0.1 atm and 300 K. (c) According to (3.23), obtain the generalised pressure π under a heat flux, and evaluate the difference between it and the local-equilibrium pressure p for Ar at 0.1 atm and 300 K.

3.2. (a) For an ideal monatomic gas, the internal energy is given by $\rho u = \frac{3}{2}nk_B T$, whether in equilibrium or not. Write ρu in terms of the generalised absolute temperature θ and the heat flux $\boldsymbol{q}$. (b) Show that, up to the second-order terms in $\boldsymbol{q}$, the caloric equation of state can be given in the form

$$\rho u(\theta, \boldsymbol{q}) = \rho u_{\text{eq}}(\theta) + a(\theta)\boldsymbol{q} \cdot \boldsymbol{q},$$

with $a(\theta) = (1/\theta)(\tau/\lambda) - \frac{1}{2}\mathrm{d}(\tau v/\lambda)/\mathrm{d}\theta$, and where $u_{\text{eq}}(\theta)$ is the value of u for $\boldsymbol{q} = 0$.

3.3. The thermal conductivity of a dielectric solid is $\lambda = \frac{1}{3}\rho c_v c_0^2 \tau_1$, with c_0 being the phonon speed, τ_1 the relaxation time due to resistive phonon collisions, c_v the heat capacity per unit mass, and ρ the mass density. In the Debye model, c_v is proportional to T^3 at low temperature. Determine the difference $\theta - T$ when the solid is subjected to a heat flux $\boldsymbol{q}$.

3.4. Show that inequality (3.38) is indeed satisfied for values of the heat flux lower than the critical value (3.39) for $\alpha = \tau_1 v/(\lambda T^2)$, with τ_1, v and λ being constant.

3.5. Consider a monatomic gas with internal energy U. Assume that the molecular motions may be organized in such a way that all the molecules have the same velocity in the same direction, so that the total molecular energy E is equal to U. Evaluate the energy flux when all the molecules are oriented in the same direction and compare its value with the value of the critical heat flux derived from (3.43).

3.6. For a monatomic gas at temperature T subject to a heat flux $\boldsymbol{q}$, the specific internal energy per unit mass is $u = \frac{3}{2}k_B T/m$ and its specific entropy is (2.38). Determine the internal energy u' of the gas in such a way that its equilibrium entropy $s_{\text{eq}}(u')$ is equal to the entropy $s(u, \boldsymbol{q})$. What would be the corresponding temperature T' of the gas? Compare T' with T and the generalised absolute temperature θ.

Part II
Microscopic Foundations

Chapter 4
The Kinetic Theory of Gases

The aim of this chapter is to provide a microscopic interpretation of extended irreversible thermodynamics (EIT) by means of the kinetic theory of gases. The interface between the macroscopic description and the kinetic theory is shown to be much wider in EIT than in the classical irreversible thermodynamics (CIT). As a consequence, the comparison provides more information and focuses our attention on a richer set of subtle topics in the extended case than in the classical situation.

Our purpose is to justify the hypotheses and the main results of EIT. To be explicit, we have to substantiate (a) the choice of the dissipative fluxes as extra independent variables in the description of systems out of equilibrium, (b) the evolution equations of the fluxes, the generalised Gibbs equation, and (c) the expression of the entropy flux. Moreover, the evolution equations for the fluxes as well as the relations between the transport coefficients appearing in these equations demand a sound justification.

The main part of this chapter addresses the study of the linear terms of the evolution equations. We have not systematically considered the non-linear terms, and will only occasionally insist on them. Our attitude is not dictated by convenience, but it has a more fundamental justification: as noted in Chap. 2, thermodynamics is generally not able to impose explicit restrictions on the non-linear terms.

This chapter concerns essentially ideal non-relativistic monatomic gases, whereas the corrections arising from the interaction potential in non-ideal gases are also examined up to the lowest order in the density. The study of the relativistic kinetic theory is postponed to Chap. 17.

4.1 The Basic Concepts of Kinetic Theory

We first consider ideal or highly diluted monatomic gases. The basis for the analysis is the distribution function $f(\boldsymbol{r}, \boldsymbol{c}, t)$, which accounts for the number of particles between $\boldsymbol{r}$ and $\boldsymbol{r} + \mathrm{d}\boldsymbol{r}$ with velocity between $\boldsymbol{c}$ and $\boldsymbol{c} + \mathrm{d}\boldsymbol{c}$ at time t. The evolution of $f(\boldsymbol{r}, \boldsymbol{c}, t)$ is described by the well-known Boltzmann equation, which takes into account the effects of binary collisions between particles, and neglects collisions involving more than two particles, a quite plausible hypothesis in dilute gases (Grad 1958; Chapman and Cowling 1970).

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_4,

The Boltzmann equation has the form

$$\frac{\partial f}{\partial t}+\boldsymbol{c}\cdot\frac{\partial f}{\partial \boldsymbol{r}}+\boldsymbol{F}\cdot\frac{\partial f}{\partial \boldsymbol{c}}=\int \mathrm{d}\tilde{\boldsymbol{c}}\int \mathrm{d}\Omega|\boldsymbol{c}-\tilde{\boldsymbol{c}}|\sigma(\boldsymbol{c}-\tilde{\boldsymbol{c}},\theta)\left[f'\tilde{f}'-f\tilde{f}\right]. \tag{4.1}$$

Here, f, $\tilde{f}$, f', and $\tilde{f}'$ stand for $f(\boldsymbol{r},\boldsymbol{c},t)$, $f(\boldsymbol{r},\tilde{\boldsymbol{c}},t)$, $f(\boldsymbol{r},\boldsymbol{c}',t)$, and $f(\boldsymbol{r},\tilde{\boldsymbol{c}}',t)$ respectively; $\boldsymbol{F}$ is the external force per unit mass acting on the particles; $\sigma(\boldsymbol{c}-\tilde{\boldsymbol{c}},\theta)$ is the differential cross-section of the collisions between the particles, one of them with initial velocity $\boldsymbol{c}$ and the other with initial velocity $\tilde{\boldsymbol{c}}$, which give as final velocities after collision $\boldsymbol{c}'$ and $\tilde{\boldsymbol{c}}'$; θ is the angle between $\boldsymbol{c}$ and $\boldsymbol{c}'$; $\mathrm{d}\Omega$ is the differential solid angle around θ.

We consider only one single species of molecules, without internal degrees of freedom. If different types of molecules are concerned, a separate distribution function for each type must be introduced, and the collision term will couple them.

The Boltzmann equation is a non-linear, integro-differential equation which is very difficult to solve. However, several general consequences can be drawn from it even without solving it explicitly. This arises as a consequence of an important and very useful symmetry property of the collision term. Let us write (4.1) as

$$\frac{\partial f}{\partial t}+\boldsymbol{c}\cdot\frac{\partial f}{\partial \boldsymbol{r}}+\boldsymbol{F}\cdot\frac{\partial f}{\partial \boldsymbol{c}}=J(f), \tag{4.2}$$

with $J(f)$ the collision term and let $\psi(\boldsymbol{c})$ be an arbitrary function of the molecular velocity $\boldsymbol{c}$. Then, the following relation is satisfied

$$\int \psi(\boldsymbol{c})J(f)\mathrm{d}\boldsymbol{c}=\frac{1}{4}\int\left[\psi(\boldsymbol{c})+\psi(\tilde{\boldsymbol{c}})-\psi(\boldsymbol{c}')-\psi(\tilde{\boldsymbol{c}}')\right]. \tag{4.3}$$

This equality is a consequence of the next three relations. First, it is immediately seen that

$$\int \psi(\boldsymbol{c})J(f)\mathrm{d}\boldsymbol{c}=\int \mathrm{d}\boldsymbol{c}\int \mathrm{d}\tilde{\boldsymbol{c}}\int \mathrm{d}\Omega|\boldsymbol{c}-\tilde{\boldsymbol{c}}|\sigma[f'\tilde{f}'-f\tilde{f}]\psi(\boldsymbol{c})=\int \psi(\tilde{\boldsymbol{c}})J(f)\mathrm{d}\boldsymbol{c}. \tag{4.4}$$

The equality is obvious, for in (4.4) $\boldsymbol{c}$ and $\tilde{\boldsymbol{c}}$ are dummy quantities, since they are integrated over all their possible values; hence an exchange between $\boldsymbol{c}$ and $\tilde{\boldsymbol{c}}$ is irrelevant.

A second equality is obtained after replacing $\boldsymbol{c}$ and $\tilde{\boldsymbol{c}}$ by $\boldsymbol{c}'$ and $\tilde{\boldsymbol{c}}'$; it yields

$$\begin{aligned}\int \psi(\boldsymbol{c}')J(f')\mathrm{d}\boldsymbol{c}'&=\int \mathrm{d}\boldsymbol{c}'\int \mathrm{d}\tilde{\boldsymbol{c}}'\int \mathrm{d}\Omega'|\boldsymbol{c}'-\tilde{\boldsymbol{c}}'|\sigma[f\,\tilde{f}-f'\,\tilde{f}']\psi(\boldsymbol{c}')\\&=-\int \mathrm{d}\boldsymbol{c}\int \mathrm{d}\tilde{\boldsymbol{c}}\int \mathrm{d}\Omega|\boldsymbol{c}-\tilde{\boldsymbol{c}}|\sigma[f'\,\tilde{f}'-f\,\tilde{f}]\psi(\boldsymbol{c})\\&=-\int \psi(\tilde{\boldsymbol{c}})J(f)\mathrm{d}\boldsymbol{c}.\end{aligned} \tag{4.5}$$

This equality results clearly from the properties $\mathrm{d}\boldsymbol{c}\,\mathrm{d}\tilde{\boldsymbol{c}} = \mathrm{d}\boldsymbol{c}'\,\mathrm{d}\tilde{\boldsymbol{c}}'$, $\boldsymbol{c} - \tilde{\boldsymbol{c}} = \boldsymbol{c}' - \tilde{\boldsymbol{c}}'$, and $\sigma = \sigma(\boldsymbol{c} - \tilde{\boldsymbol{c}}, \theta) = \sigma(\boldsymbol{c}' - \tilde{\boldsymbol{c}}', \theta') = \sigma'$. The first two of these equalities are valid for elastic binary collisions, while the third is satisfied when the intermolecular potential is invariant under spatial rotations and reflections, and under time reversal.

A third equality follows from the exchange of the dummy quantities $\boldsymbol{c}'$ and $\tilde{\boldsymbol{c}}'$:

$$\int \psi(\boldsymbol{c}')J(f')\mathrm{d}\boldsymbol{c}' = \int \psi(\tilde{\boldsymbol{c}}')J(\tilde{f}')\mathrm{d}\tilde{\boldsymbol{c}}'. \tag{4.6}$$

Now, by combining (4.4)–(4.6), the key relation (4.3) is obtained.

4.1.1 Balance Equations

The first important consequence of (4.3) is the possibility of deriving the hydrodynamic balance equations for mass, momentum, and energy from Boltzmann's equation. The mass density ρ, the mean velocity $\boldsymbol{v}$, and the internal energy u per unit mass are defined in terms of the distribution function as follows:

$$\rho(\boldsymbol{r},t) = \int mf(\boldsymbol{r},\boldsymbol{c},t)\mathrm{d}\boldsymbol{c}, \tag{4.7}$$

$$\rho(\boldsymbol{r},t)\boldsymbol{v}(\boldsymbol{r},t) = \int m\boldsymbol{c}f(\boldsymbol{r},\boldsymbol{c},t)\mathrm{d}\boldsymbol{c}, \tag{4.8}$$

$$\rho(\boldsymbol{r},t)u(\boldsymbol{r},t) = \int \frac{1}{2}m(\boldsymbol{c}-\boldsymbol{v})\cdot(\boldsymbol{c}-\boldsymbol{v})f(\boldsymbol{r},\boldsymbol{c},t)\mathrm{d}\boldsymbol{c}. \tag{4.9}$$

Evolution equations for these quantities are obtained from the evolution equation for f. In order to do this, one must consider the influence of the collision term. Note, however, that in view of (4.3) one may write

$$\int mJ(f)\mathrm{d}\boldsymbol{c} = \frac{1}{4}\int [m + m - m - m]J(f)\mathrm{d}\boldsymbol{c} = 0, \tag{4.10a}$$

$$\int m\boldsymbol{c}J(f)\mathrm{d}\boldsymbol{c} = \frac{1}{4}\int [m\boldsymbol{c} + m\tilde{\boldsymbol{c}} - m\boldsymbol{c}' - m\tilde{\boldsymbol{c}}']J(f)\mathrm{d}\boldsymbol{c} = 0, \tag{4.10b}$$

$$\int mc^2J(f)\mathrm{d}\boldsymbol{c} = \frac{1}{4}\int [mc^2 + m\tilde{c}^2 - mc'^2 - m\tilde{c}'^2]J(f)\mathrm{d}\boldsymbol{c} = 0. \tag{4.10c}$$

The vanishing of these integrals follows from the property that mass, momentum and kinetic energy are collisional invariants, i.e. they do not change in elastic binary collisions.

From definitions (4.7–4.9) and relations (4.10a–c), the balance equations for mass, momentum, and energy can be derived from the Boltzmann equation. Multiplying each term of (4.1) by m, $m\boldsymbol{c}$, and $\frac{1}{2}mc^2$ respectively and integrating over $\boldsymbol{c}$ it is found that

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}) = 0, \tag{4.11}$$

$$\frac{\partial (\rho \boldsymbol{v})}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}\boldsymbol{v} + \mathbf{P}) = \rho \boldsymbol{F}, \tag{4.12}$$

$$\frac{\partial}{\partial t}\left(\rho u + \frac{1}{2}\rho v^2\right) + \nabla \cdot \left[\rho\left(u + \frac{1}{2}v^2\right)\boldsymbol{v} + \mathbf{P}\cdot\boldsymbol{v} + \boldsymbol{q}\right] = \rho \boldsymbol{F}\cdot\boldsymbol{v}, \tag{4.13}$$

with $\mathbf{P}$ and $\boldsymbol{q}$ being defined as

$$\mathbf{P} = \int m\boldsymbol{C}\boldsymbol{C} f \,\mathrm{d}\boldsymbol{c}, \tag{4.14}$$

$$\boldsymbol{q} = \int \frac{1}{2} m C^2 \boldsymbol{C} f \,\mathrm{d}\boldsymbol{c}. \tag{4.15}$$

$\boldsymbol{C} = \boldsymbol{c} - \boldsymbol{v}$ is the relative velocity of the molecules with respect to the mean motion of the gas.

Equations (4.11–4.13) turn out to be the well-known balance equations of hydrodynamics, provided that one identifies $\mathbf{P}$ and $\boldsymbol{q}$ defined by (4.14) and (4.15) as the pressure tensor and the heat flux vector respectively.

Since at equilibrium f is an isotropic function of $\boldsymbol{C}$, the pressure tensor reduces to

$$\mathbf{P} = p\mathrm{U}, \tag{4.16}$$

with U the identity tensor and p, the equilibrium pressure, given by

$$p = \frac{1}{3}\int mC^2 f \,\mathrm{d}c. \tag{4.17}$$

It is found from the definition (4.9) of the internal energy that $p = \frac{2}{3}\rho u$. The macroscopic thermal equation of state for ideal gases leads then to the following definition of the absolute equilibrium temperature:

$$p = \frac{2}{3}\rho u = n k_{\mathrm{B}} T, \tag{4.18}$$

with n the number of particles per unit volume and k_{B} the Boltzmann constant.

4.1.2 The H-Theorem and the Second Law

Another important result from Boltzmann's equation is the so-called H-theorem, which is a kinetic version of the second law. We define η as follows:

$$\rho(\boldsymbol{r},t)\eta(\boldsymbol{r},t) = \int f(\boldsymbol{r},\boldsymbol{c},t)\ln f(\boldsymbol{r},\boldsymbol{c},t)\mathrm{d}\boldsymbol{c}. \tag{4.19}$$

The evolution equation for η may be derived by multiplying term by term the Boltzmann equation (4.1) by $\ln f$ and integrating over $\boldsymbol{c}$. In this way, one obtains

$$\frac{\partial(\rho\eta)}{\partial t} + \nabla \cdot (\boldsymbol{J}^{\eta} + \rho\eta\boldsymbol{v}) = \sigma^{\eta}, \tag{4.20}$$

with the flux $\boldsymbol{J}^{\eta}$ given by

$$\boldsymbol{J}^{\eta} = \int \boldsymbol{C} f \ln f \, \mathrm{d}\boldsymbol{c}. \tag{4.21}$$

The production term σ^{η} defined as

$$\sigma^{\eta} = \int J(f) \ln f \, \mathrm{d}\boldsymbol{c}, \tag{4.22}$$

can be written, in virtue of (4.3), as

$$\begin{aligned} \sigma^{\eta} &= \frac{1}{4} \int \mathrm{d}\boldsymbol{c} \int \mathrm{d}\tilde{\boldsymbol{c}} \int \mathrm{d}\Omega |\boldsymbol{c} - \tilde{\boldsymbol{c}}| \sigma [f' \tilde{f}' - f \tilde{f}][\ln f + \ln \tilde{f} - \ln f' - \ln \tilde{f}'] \\ &= \frac{1}{4} \int \mathrm{d}\boldsymbol{c} \int \mathrm{d}\tilde{\boldsymbol{c}} \int \mathrm{d}\Omega |\boldsymbol{c} - \tilde{\boldsymbol{c}}| \sigma [f' \tilde{f}' - f \tilde{f}] \ln[f \tilde{f}/(f' \tilde{f}')]. \end{aligned} \tag{4.23}$$

By inspecting the product of the quantities $[f' \tilde{f}' - f \tilde{f}]$ and $\ln[f \tilde{f}/(f' \tilde{f}')]$ one sees immediately that

$$\sigma^{\eta} \leq 0 \tag{4.24}$$

The equality sign holds only for $f' \tilde{f}' = f \tilde{f}$, i.e. for $J(f) = 0$, which corresponds to equilibrium situations.

The equilibrium distribution function is obtained by realizing that, since $f_{\mathrm{eq}} \tilde{f}_{\mathrm{eq}} = f'_{\mathrm{eq}} \tilde{f}'_{\mathrm{eq}}$, it follows that $\ln f_{\mathrm{eq}}$ is a collisional invariant and can therefore be expressed as a linear combination of m, $m\boldsymbol{c}$, and $\frac{1}{2} mc^2$:

$$\ln f_{\mathrm{eq}} = Am + \boldsymbol{B} \cdot m\boldsymbol{c} + D\frac{1}{2}mc^2. \tag{4.25}$$

The five constants A, $\boldsymbol{B}$, and D appearing in (4.25) can be determined in terms of ρ, $\boldsymbol{v}$, and T, taking into account the definitions (4.7–4.9) and (4.18). The result is the well-known Maxwell–Boltzmann distribution function

$$f_{\mathrm{eq}} = n \left(\frac{m}{2\pi k_{\mathrm{B}} T} \right)^{3/2} \exp\left[-\frac{mC^2}{2k_{\mathrm{B}} T} \right]. \tag{4.26}$$

The H-theorem, stating the negative character of σ^{η}, allows us to express the entropy in terms of the distribution function f. Indeed, it suggests that the entropy s per unit mass may be defined as $\rho s = -A'\rho\eta + B'$, where A' and B' are two constants. Their values can be determined by comparing the equilibrium value of s with the value of η when the equilibrium distribution function (4.26) is substituted in the definition (4.19). It turns out that $A' = k_{\mathrm{B}}$. The value of B' is not so important because generally only entropy changes are relevant. The above considerations suggest the following expressions for the entropy and the entropy flux respectively:

$$\rho s = -k_{\mathrm{B}} \int f \,\ln f \mathrm{d}\boldsymbol{c}, \tag{4.27}$$

$$\boldsymbol{J}^{s} = -k_{\mathrm{B}} \int \boldsymbol{C}\, f \ln f \mathrm{d}\boldsymbol{c}. \tag{4.28}$$

For completeness let us recall the expression of the equilibrium entropy for monatomic gases, the so-called Sackur–Tetrode formula:

$$\rho s = n k_{\mathrm{B}} \left\{ \frac{5}{2} + \ln \left[\frac{1}{n} \left(\frac{2\pi m k_{\mathrm{B}} T}{h^{2}} \right) \right]^{3/2} \right\}, \tag{4.29}$$

where h stands for Planck's constant.

4.2 Non-equilibrium Entropy and the Entropy Flux

Up to now, we have derived microscopic expressions for all the quantities of interest for our study. The microscopic definitions (4.27) and (4.28) give explicit expressions for the entropy and the entropy flux in non-equilibrium situations in terms of the non-equilibrium distribution function. The latter may be expanded according to

$$f = f_{\mathrm{eq}} \left[1 + \phi^{(1)} + \phi^{(2)} + \cdots \right], \tag{4.30}$$

where $\phi^{(1)}\, \phi^{(2)}, \ldots$ are expressed in terms of a small parameter, for instance the ratio of the relaxation time to the macroscopic time, the ratio of the mean free path to a characteristic length of the macroscopic inhomogeneities, the higher-order moments of the velocity distribution function, etc. The function f_{eq} is the equilibrium distribution function either in global or local equilibrium (in the first case, ρ, $\boldsymbol{v}$, and T would not depend on position and time, and in the second case they would depend on these variables).

The quantities $\rho = nm$, $\boldsymbol{v}$, and T are determined from the first five moments of the distribution function given by equations (4.7–4.9). This imposes on $\phi^{(i)}$ the closure conditions

$$\int f_{\mathrm{eq}}\phi^{(i)}\mathrm{d}\boldsymbol{c} = 0, \qquad \int f_{\mathrm{eq}}\phi^{(i)}\boldsymbol{C}\,\mathrm{d}\boldsymbol{c} = 0, \tag{4.31}$$
$$\int f_{\mathrm{eq}}\phi^{(i)}C^2\mathrm{d}\boldsymbol{c} = 0 \qquad (i = 1, 2, \ldots),$$

and when (4.30) is introduced into (4.27) and (4.28), one obtains up to second order

$$\rho s = \rho s_{\mathrm{eq}} - \frac{1}{2}k_{\mathrm{B}}\int f_{\mathrm{eq}}\phi^{(1)2}\mathrm{d}\boldsymbol{c} \tag{4.32}$$

and

$$\boldsymbol{J}^s = T^{-1}\boldsymbol{q} - \frac{1}{2}k_{\mathrm{B}}\int f_{\mathrm{eq}}\phi^{(1)2}\boldsymbol{C}\,\mathrm{d}\boldsymbol{c}. \tag{4.33}$$

Owing to the restrictions (4.31), $\phi^{(2)}$ does not contribute to the entropy up to the second order of approximation. Furthermore, it follows from the third of conditions (4.31) that the bulk viscous pressure for an ideal monatomic gas vanishes identically. The first terms on the right-hand side of (4.32) and (4.33) are the classical ones. The second terms are related to the non-classical corrections on which we shall focus our attention in the next section.

It must be noted that, in contrast to the exact solutions of the Boltzmann equation, approximate solutions like (4.30) do not necessarily satisfy the H-theorem beyond the linear approximation. The same problem arises in macroscopic theories when constitutive equations containing non-linear truncated approximations are used, as seen in (2.28). The requirement of a positive entropy production may provide a criterion on the range of validity of a given approximation, both in microscopic and in macroscopic theories. The positive entropy production requirement may also be useful to model the non-linear terms in such a way that entropy production is always positive.

A second point worth outlining is that the thermodynamic entropy is a function of macroscopic variables. Therefore, assuming the existence of a macroscopic entropy implies that one selects among the several possible microscopic distribution functions those depending parametrically on quantities which have a clear macroscopic meaning or, at least, which are macroscopically measurable and controllable. In principle, one can construct a wide range of microscopic distribution functions but their physical meaning is not necessarily clear. Here, we always refer to the so-called thermodynamic branch of approximate solutions of the Boltzmann equation Eu (1992, 1998), i.e. to those solutions satisfying the above-mentioned requirement.

4.3 Grad's Solution

Two important models, namely the Chapman–Enskog and Grad ones, have been proposed to solve the Boltzmann equation in non-equilibrium situations. In the Chapman–Enskog approach (Chapman and Cowling 1970), f is expressed in terms of the first five moments n, $\boldsymbol{v}$, and T and their gradients. Then, $\phi^{(1)}$ is proportional to $\nabla\boldsymbol{v}$ and ∇T, while $\phi^{(2)}$ includes terms in $\nabla\nabla\boldsymbol{v}$, $\nabla\nabla T$ and so on. In Grad's model (Grad 1958; Harris 1971; Woods 1994), f is expanded in terms of its moments with respect to the molecular velocity. Note that, in view of definitions (4.14–4.15), $\mathbf{P}$ and $\boldsymbol{q}$ are directly related to the moments of the velocity distribution function (the scalar viscous pressure p^v vanishes in an ideal gas). Therefore, the mean values of $\boldsymbol{q}$ and of $\overset{0}{\mathbf{P}}{}^v$ are considered in Grad's theory as independent variables, so that Grad's theory is closer to the macroscopic developments of EIT than Chapman–Enskog's. It can thus be asserted that both EIT and Grad's thirteen-moment method make use of the same independent variables.

In Grad's method, the non-equilibrium distribution function $f(\boldsymbol{r},\boldsymbol{c},t)$ is replaced by the infinite set of variables $\rho = mn(\boldsymbol{r},t)$, $\boldsymbol{v}(\boldsymbol{r},t)$, $T(\boldsymbol{r},t)$, $\boldsymbol{a}_n(\boldsymbol{r},t)$, where $\boldsymbol{a}_n$ stand for the successive higher-order moments of the distribution function. These moments are chosen in such a way that they are mutually orthogonal, and they are given by Hermite polynomials. In the thirteen-moment approximation, the development is limited to all the second-order moments and to some of the third-order moments, those related to the heat flux.

In the thirteen-moment approximation, the distribution function is written as

$$f = f_{\mathrm{eq}}[1 + \boldsymbol{A}\cdot\boldsymbol{C} + \overset{0}{\mathbf{B}}{}^v : \overset{0}{\boldsymbol{C}\boldsymbol{C}} + (\boldsymbol{C}\cdot\boldsymbol{C})(\boldsymbol{D}\cdot\boldsymbol{C})]. \tag{4.34}$$

The coefficients $\boldsymbol{A}(\boldsymbol{r},t)$, $\overset{0}{\mathbf{B}}{}^v(\boldsymbol{r},t)$ and $\boldsymbol{D}(\boldsymbol{r},t)$ are determined by introducing (4.34) into (4.14), (4.15), and the third of conditions (4.31). In order to help the reader, the general form of integrals appearing in these calculations is given in Appendix B. Such equations allow us to identify $\boldsymbol{A}$, $\overset{0}{\mathbf{B}}{}^v$, and $\boldsymbol{D}$ in terms of the heat flux $\boldsymbol{q}$ and the viscous pressure tensor $\overset{0}{\mathbf{P}}{}^v$:

$$\boldsymbol{A} = -\frac{m}{pk_{\mathrm{B}}T}\boldsymbol{q}, \quad \overset{0}{\mathbf{B}}{}^v = \frac{m}{2pk_{\mathrm{B}}T}\overset{0}{\mathbf{P}}{}^v, \quad \boldsymbol{D} = \frac{m^2}{5pk_{\mathrm{B}}^2T^2}\boldsymbol{q}. \tag{4.35}$$

As a consequence, f may be written explicitly as

$$f = f_{\mathrm{eq}}\left[1 + \frac{m}{2pk_{\mathrm{B}}T}\overset{0}{\boldsymbol{C}\boldsymbol{C}} : \overset{0}{\mathbf{P}}{}^v + \frac{2m}{5pk_{\mathrm{B}}^2T^2}\left(\frac{1}{2}mC^2 - \frac{5}{2}k_{\mathrm{B}}T\right)\boldsymbol{C}\cdot\boldsymbol{q}\right]. \tag{4.36}$$

After substitution of (4.36) into (4.32–4.33), the expressions for the entropy and entropy flux turn out to be

$$\rho s = \rho s_{\mathrm{eq}} - \frac{1}{4pT}\overset{0}{\mathbf{P}}{}^v : \overset{0}{\mathbf{P}}{}^v - \frac{m}{5pk_{\mathrm{B}}T^2}\boldsymbol{q}\cdot\boldsymbol{q}, \tag{4.37}$$

$$\boldsymbol{J}^s = \frac{1}{T}\boldsymbol{q} - \frac{2}{5pT}\overset{0}{\mathbf{P}}{}^v\cdot\boldsymbol{q}. \tag{4.38}$$

These results confirm the plausibility of the hypotheses of EIT stating that the entropy may depend on the dissipative fluxes and that the entropy flux contains extra contributions besides $\boldsymbol{q}/T$.

It remains to verify that the EIT expressions of the transport coefficients appearing in the non-classical parts of s and $\boldsymbol{J}^s$ are confirmed by the kinetic theory. Moreover, EIT predicts the existence of some relations between these coefficients and those found in the evolution equations for the fluxes.

To check these results, one needs the evolution equations for the fluxes. These can be obtained by inserting (4.36) into Boltzmann's equation. In the thirteen-moment approximation one is led to (Grad 1958)

$$\begin{aligned}(\overset{0}{\mathbf{P}}{}^{v})^{\cdot} = {} & -\frac{4}{5}(\overset{0}{\nabla\boldsymbol{q}})^{s} - 2p\,\overset{0}{\mathrm{V}} - \rho\gamma\,\overset{0}{\mathbf{P}}{}^{v} - \overset{0}{\mathbf{P}}{}^{v}\cdot(\nabla\boldsymbol{v}) - (\nabla\boldsymbol{v})\cdot(\overset{0}{\mathbf{P}}{}^{v})^{T} \\ & - \overset{0}{\mathbf{P}}{}^{v}(\nabla\cdot\boldsymbol{v}) + \frac{2}{3}[\overset{0}{\mathbf{P}}{}^{v} : (\nabla\boldsymbol{v})]\mathrm{U}, \end{aligned} \tag{4.39}$$

and

$$\begin{aligned}\dot{\boldsymbol{q}} = {} & -(k_{\mathrm{B}}T/m)\nabla\cdot\overset{0}{\mathbf{P}}{}^{v} - \frac{5}{2}(pk_{\mathrm{B}}/m)\nabla T - \frac{2}{3}\rho\gamma\boldsymbol{q} - \frac{7}{5}\boldsymbol{q}\cdot(\nabla\boldsymbol{v}) - \frac{2}{5}\boldsymbol{q}\cdot(\nabla\boldsymbol{v})^{T} \\ & - \frac{7}{5}\boldsymbol{q}(\nabla\cdot\boldsymbol{v}) - \frac{7}{2}(k_{\mathrm{B}}/m)\overset{0}{\mathbf{P}}{}^{v}\cdot\nabla T + \rho^{-1}\overset{0}{\mathbf{P}}{}^{v}\cdot(\nabla\cdot\overset{0}{\mathbf{P}}{}^{v}). \end{aligned} \tag{4.40}$$

The coefficient γ is given in terms of the collision integrals by

$$\gamma = \frac{2}{5}\sqrt{2\pi}\int_0^\infty x^6 e^{-x^2/2}\left[\int_0^\infty m^{-1}\sigma\left(\theta, x\sqrt{2k_{\mathrm{B}}T/m}\right)\sin^2\theta\,\cos^2\,\theta\mathrm{d}\theta\right]\mathrm{d}x \tag{4.41}$$

and is shown to be a positive quantity (Grad 1958).

We focus our attention on the linear terms of (4.39, 4.40) and therefore omit non-linear contributions, such as $\overset{0}{\mathbf{P}}{}^{v}\cdot(\nabla\boldsymbol{v})$ in (4.39) and $\overset{0}{\mathbf{P}}{}^{v}\cdot\nabla T$ in (4.40). It is true that for a fixed temperature gradient this term is linear in $\overset{0}{\mathbf{P}}{}^{v}$, but when we take perturbations around equilibrium, both $\overset{0}{\mathbf{P}}{}^{v}$ and ∇T can be considered as perturbations, and consequently such a term is non-linear. In the linear approximation, (4.39, 4.40) reduce to

$$\frac{1}{\rho\gamma}(\overset{0}{\mathbf{P}}{}^{v})^{\cdot} = -\left(\overset{0}{\mathbf{P}}{}^{v} + \frac{2p}{\rho\gamma}\overset{0}{\mathrm{V}}\right) - \frac{4}{5\rho\gamma}(\overset{0}{\nabla\boldsymbol{q}})^{s} \tag{4.42}$$

and

$$\frac{3}{2\rho\gamma}\dot{\boldsymbol{q}} = -\left(\boldsymbol{q} + \frac{15pk_{\mathrm{B}}}{4m\rho\gamma}\nabla T\right) - \frac{3k_{\mathrm{B}}T}{2m\rho\gamma}\nabla\cdot\overset{0}{\mathbf{P}}{}^{v}. \tag{4.43}$$

These relations may be directly compared with the linear evolution equations (2.72) and (2.70), respectively, derived from the macroscopic theory. One is then led to the identifications

$$\tau_1 = \frac{3}{2\rho\gamma}, \tag{4.44a}$$

$$\lambda = \frac{5pk_\mathrm{B}}{2m}\tau_1, \tag{4.44b}$$

$$-\lambda T^2 \beta = \frac{k_\mathrm{B}T}{m}\tau_1. \tag{4.44c}$$

$$\tau_2 = \frac{1}{\rho\gamma}, \tag{4.45a}$$

$$\eta = p\tau_2 \quad \text{(b)}, \tag{4.45b}$$

$$-2\eta T \beta = \frac{4}{5}\tau_2. \tag{4.45c}$$

Expressions of the form (2.70–2.72) (or (4.42–4.43)) could have been guessed by purely dimensional arguments, but thermodynamics brings supplementary information and imposes specific limitations. The first two are $\tau_1 > 0$ and $\tau_2 > 0$, as a consequence of $\gamma > 0$. Furthermore, a direct consequence of (4.44b) and (4.45b) is that $\lambda > 0$ and $\eta > 0$. The symmetry relations between the cross coefficients in (2.70–2.72) are confirmed by comparing the two independent expressions obtained for β in (4.44c) and (4.45c): they are seen to coincide and are given by

$$\beta = -\frac{2}{5pT}. \tag{4.46}$$

This expression for β is nothing but the factor $-2/(5pT)$ of the non-classical term of the entropy flux (4.38) and is the same as that predicted by the macroscopic theory. Note also that the relaxation times of $\boldsymbol{q}$ and $\overset{0}{\mathbf{P}}{}^v$ are not coincident but $\tau_1 = \frac{3}{2}\tau_2$.

We now turn our attention to the macroscopic Gibbs equation (2.44). After integration this yields

$$\rho s = \rho s_\mathrm{eq} - \frac{\tau_1}{2\lambda T^2}\boldsymbol{q}\cdot\boldsymbol{q} - \frac{\tau_2}{4\eta T}\overset{0}{\mathbf{P}}{}^v : \overset{0}{\mathbf{P}}{}^v. \tag{4.47}$$

Making use of the results given by (4.44c), (4.45c), and (4.46), we see that $\tau_1/(2\lambda T^2) = m/(5pk_\mathrm{B}T^2)$ and $\tau_2/(4\eta T) = 1/(4pT)$, from which it follows that (4.37) is strictly identical with the macroscopic result (4.47). Consequently, we can conclude that, within the linear range, there is a complete agreement between Grad's theory and the predictions of EIT, not only in regard to the choice of the variables and the expressions of the entropy and the entropy flux, but also concerning the expressions of the linearized evolution equations for the thermodynamic fluxes.

Expression (4.47) allows us to calculate the order of magnitude of the non-equilibrium correction with respect to the local-equilibrium entropy. In the absence of viscous effects, one has

$$\rho s = \rho s_{\mathrm{eq}} - \frac{\tau_1}{2\lambda T^2}\boldsymbol{q}\cdot\boldsymbol{q}. \tag{4.48}$$

To evaluate the range of temperature gradients for which the local-equilibrium hypothesis is acceptable, we write the non-equilibrium contribution to (4.48) as

$$\frac{\tau_1}{2\lambda T^2}\boldsymbol{q}\cdot\boldsymbol{q} = \frac{\tau_1\lambda}{2T^2}(\nabla T)^2 = \frac{5nk_{\mathrm{B}}^2 T}{4m}\tau_1^2\left(\frac{\nabla T}{T}\right)^2. \tag{4.49}$$

By defining the mean free path by $\ell = [3k_{\mathrm{B}}T/(2m)]^{1/2}\tau_1$, one may write the non-equilibrium correction as

$$\Delta(\rho s)_{\mathrm{neq}} = \frac{5nk_{\mathrm{B}}}{6}\ell^2\left(\frac{\nabla T}{T}\right)^2. \tag{4.50}$$

Moreover, according to the Sackur–Tetrode formula (4.29), the local-equilibrium entropy is of the order of $\rho s_{\mathrm{eq}} \approx nk_{\mathrm{B}}$. Thus the relative value of the non-equilibrium contribution with respect to the local-equilibrium value is of the order of

$$\frac{\Delta(\rho s)_{\mathrm{neq}}}{\rho s_{\mathrm{eq}}} \approx \ell^2\left(\frac{\nabla T}{T}\right)^2. \tag{4.51}$$

For gases like O_2 and N_2 at standard temperature and pressure, the mean free path ℓ is of the order of 10^{-4} cm, so that the relative non-equilibrium corrections will be less than 0.01% for temperature gradients lower than 10^4 K cm^{-1}. The conclusion is that in these situations the local-equilibrium entropy is a reasonable approximation. However, this agreement, achieved for steady state situations, does not necessarily imply that the local-equilibrium entropy remains a satisfactory concept in fast non-steady processes, for which $\boldsymbol{q}$ cannot be approximated by $\boldsymbol{q} = -\lambda\nabla T$, or for specific materials, such as polymer solutions, where viscous effects play a dominant role.

It must be noted that the moment expansion of Grad lacks a smallness parameter allowing to control its domain of validity. The problem may be circumvented by introducing another "flux variable", like the conjugate to the flux in Gibbs' equation (see Box 2.2). In Sect. 4.7 we will present a wider approach taking into account an infinite number of higher-order moments. It is also interesting to observe that, since all the moments are mutually orthogonal, the incorporation of higher-order moments does not alter the value of the first thirteen ones; therefore, the specification of the first thirteen moments does not mean a univocal microscopic solution of the Boltzmann equation. The relations between Grad's method and hydrodynamics have been thoroughly analysed by Gorban et al. (2004) and Gorban and

Karlin (2005) by means of the method of invariant manifolds; on the other side, Garzó and Santos (2003) have systematically studied ideal and interacting gases in several kinds of flows. We refer to the books by these authors for interesting overviews of new ideas and recent developments in kinetic theory and its connection with hydrodynamics and thermodynamics beyond the classical regime.

4.4 The Relaxation-Time Approximation

Since the Boltzmann equation is very complicated, simpler kinetic equations have been proposed in the literature. A very simple model is the well-known relaxation-time approximation, which is used here to analyse the thermodynamics of steady states.

In the relaxation-time approximation, the evolution equation of the distribution function is modelled by

$$\frac{\partial f}{\partial t} + \boldsymbol{c} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \boldsymbol{F} \cdot \frac{\partial f}{\partial \boldsymbol{c}} = -\frac{1}{\tau}(f - f_{\mathrm{eq}}). \tag{4.52}$$

For steady non-equilibrium situations in the absence of external forces, it is found that

$$f = (1 + \tau \boldsymbol{c} \cdot \nabla)^{-1} f_{\mathrm{eq}}, \tag{4.53}$$

a formal expression to which an operative meaning can be attached by expanding it in powers of $\tau \boldsymbol{c} \cdot \nabla$. In the simple case of temperature and velocity gradients, the first-order and second-order corrections to the equilibrium distribution function are

$$\phi^{(1)} = -\frac{\tau}{k_{\mathrm{B}} T^2} \left(\frac{1}{2} m C^2 - \frac{5}{2} k_{\mathrm{B}} T \right) \boldsymbol{C} \cdot \nabla T - \frac{\tau}{k_{\mathrm{B}} T} m \overset{0}{\boldsymbol{C}\boldsymbol{C}} : (\overset{0}{\nabla \boldsymbol{v}}) + \mathrm{NL} \tag{4.54}$$

and

$$\phi^{(2)} = -\frac{\tau^2}{k_{\mathrm{B}} T^2} \left(\frac{1}{2} m C^2 - \frac{5}{2} k_{\mathrm{B}} T \right) \overset{0}{\boldsymbol{C}\boldsymbol{C}} \cdot \nabla\nabla T - \frac{\tau^2}{k_{\mathrm{B}} T} m \overset{0}{\boldsymbol{C}\boldsymbol{C}\boldsymbol{C}} : (\overset{0}{\nabla\nabla \boldsymbol{v}}) + \mathrm{NL}, \tag{4.55}$$

where NL stands for non-linear terms involving gradient products. The introduction of (4.54) into (4.32) gives the following expression of the entropy:

$$\begin{aligned} \rho s = \rho s_{\mathrm{eq}} &- \frac{\tau}{2T^2} \left[\frac{\tau}{k_{\mathrm{B}} T^2} \left\langle \left(\frac{1}{2} m C^2 - \frac{5}{2} k_{\mathrm{B}} T \right)^2 C_1^2 \right\rangle \right] (\nabla T)^2 \\ &- \frac{\tau}{2T} \left[\frac{\tau}{k_{\mathrm{B}} T} \left\langle m^2 C_1^2 C_2^2 \right\rangle \right] (\overset{0}{\nabla \boldsymbol{v}})^s : (\overset{0}{\nabla \boldsymbol{v}})^s \end{aligned} \tag{4.56}$$

and from (4.33) one finds for the entropy flux

$$\boldsymbol{J}^s = \frac{1}{T}\boldsymbol{q} - \frac{\tau^2}{k_\mathrm{B}T^3}\left\langle\left(\frac{1}{2}mC^2 - \frac{5}{2}k_\mathrm{B}T\right)mC_1^2C_2^2\right\rangle \overset{0}{(\nabla\boldsymbol{v})}{}^s \cdot \nabla T, \tag{4.57}$$

where C_1, C_2 are components of $\boldsymbol{C}$, and the quantity $\langle a\rangle$ stands for

$$\langle a\rangle = \int a(\boldsymbol{c})f_\mathrm{eq}(\boldsymbol{c})\mathrm{d}\boldsymbol{c}. \tag{4.58}$$

By inserting (4.54–4.55) into (4.30) we obtain a distribution function which can be substituted into (4.14–4.15) and taking into account that $\langle(\frac{1}{2}mC^2 - \frac{5}{2}k_\mathrm{B}T)\boldsymbol{C}\cdot\boldsymbol{C}\rangle = 0$, the expressions for the heat flux and the pressure tensor are of the form

$$\begin{aligned}\boldsymbol{q} &= -\frac{\tau}{k_\mathrm{B}T^2}\left\langle\left(\frac{1}{2}mC^2 - \frac{5}{2}k_\mathrm{B}T\right)^2 C_1^2\right\rangle\nabla T - \frac{\tau^2}{2T}\left\langle\left(\frac{1}{2}mC^2 - \frac{5}{2}k_\mathrm{B}T\right)mC_1^2C_2^2\right\rangle \\ &\quad\times\nabla\cdot\overset{0}{(\nabla\boldsymbol{v})}{}^s, \qquad (4.59)\\ \overset{0}{\mathbf{P}}{}^v &= -\frac{\tau}{k_\mathrm{B}T}\left\langle m^2C_1^2C_2^2\right\rangle\overset{0}{(\nabla\boldsymbol{v})}{}^s - \frac{\tau^2}{k_\mathrm{B}T^2}\left\langle\left(\frac{1}{2}mC^2 - \frac{5}{2}k_\mathrm{B}T\right)^2 mC_1^2C_2^2\right\rangle\nabla\nabla T.\end{aligned}$$

A limitation of the relaxation-time approximation is that the relaxation times of both fluxes coincide. Compare (4.59) with (2.70–2.72) in a steady state, with $\boldsymbol{q}$ and $\overset{0}{\mathbf{P}}{}^v$ substituted by their first-order expressions $\boldsymbol{q}^{(1)} = -\lambda\nabla T$ and $\overset{0}{\mathbf{P}}{}^{v(1)} = -2\eta\overset{0}{\mathrm{V}}$. In this way one obtains a confirmation of the relation between the cross terms predicted by the thermodynamic theory and the relation of these coefficients with those of the second-order term in the entropy flux (4.57). Furthermore, the expression (4.56) for the entropy may equivalently be written as

$$\rho s = \rho s_\mathrm{eq} - \frac{\tau_1\lambda}{2T^2}(\nabla T)\cdot(\nabla T) - \frac{\tau_2\eta}{T}\overset{0}{(\nabla\boldsymbol{v})}{}^s : \overset{0}{(\nabla\boldsymbol{v})}{}^s. \tag{4.60}$$

This is nothing but expression (3.4) when the fluxes are replaced by their first-order steady-state approximations. It is also interesting to observe that the entropy (4.60) does not coincide with the local-equilibrium entropy even in the steady case.

The agreement between the kinetic theory of gases and the macroscopic predictions undoubtedly reinforces the consistency of EIT. Although our analysis is limited to the linear range, the agreement between EIT and kinetic theory is much wider than the agreement of the latter with the usual local-equilibrium thermodynamics. It should be kept in mind that the previous comparisons have been achieved within the Boltzmann theory, which concerns only two-body collisions. A comparison at a higher level, where higher-order collisions are included, raises some notable features (Dufty and McLennan 1974; Ernst et al. 1976; Reichl 1980).

Computer experiments and careful microscopic studies of the correlation functions have shown that many-body processes play an important role in determining the long-time behaviour of correlation functions. Thus, whereas Boltzmann's equation leads to an exponential decay of the fluctuations, hydrodynamic arguments predict for a d-dimensional system a potential decay of the form $t^{-d/2}$. An appropriate thermodynamic extension to these situations remains a challenging problem.

4.5 Dilute Non-ideal Gases

The treatment of non-ideal gases is more complex, owing to intermolecular interactions which contribute both to the viscous pressure tensor and to the heat flux vector (Rice and Gray 1965; Green 1969). For simplicity, we deal here only with the viscous effects. In kinetic theory, the pressure tensor is split into a kinetic and a potential part

$$\mathbf{P} = \mathbf{P}_c + \mathbf{P}_p, \tag{4.61}$$

given respectively by

$$\mathbf{P}_c = \int m\boldsymbol{C}\boldsymbol{C} f_1 \mathrm{d}\boldsymbol{c} \tag{4.62}$$

and

$$\mathbf{P}_p = -\frac{1}{2}n^2 \int \phi'(R) R^{-1} \boldsymbol{R}\boldsymbol{R} g(R) \mathrm{d}\boldsymbol{R}. \tag{4.63}$$

The kinetic part $\mathbf{P}_c$ is expressed in terms of the one-particle distribution function $f_1(\boldsymbol{r}, \boldsymbol{c})$ while the potential part $\mathbf{P}_p$ depends on the two-particle distribution function $f_2(\boldsymbol{r}_1, \boldsymbol{c}_1, \boldsymbol{r}_2, \boldsymbol{c}_2)$. In (4.63), $\boldsymbol{R} = \boldsymbol{r}_1 - \boldsymbol{r}_2$ is the relative position of molecule 1 with respect to molecule 2, $\phi(R)$ the interaction potential, with a prime indicating the spatial derivative with respect to R; and $g(R)$ is the pair-correlation function defined in terms of f_2 as

$$n^2 g(R) = \int f_2(\boldsymbol{r}_1, \boldsymbol{c}_1, \boldsymbol{r}_2, \boldsymbol{c}_2) \mathrm{d}\boldsymbol{c}_1 \mathrm{d}\boldsymbol{c}_2. \tag{4.64}$$

Defining the thermodynamic equilibrium pressure as one-third of the trace of $\mathbf{P}$ at equilibrium, it follows from (4.61–4.63) that

$$p = nk_\mathrm{B}T - \frac{1}{6}n^2 \int \phi'(R) g_\mathrm{eq}(R) R \mathrm{d}\boldsymbol{R}, \tag{4.65}$$

with $g_\mathrm{eq}(R)$ being the equilibrium pair correlation function.

Since the relaxation times of the one-particle distribution f_1 and the pair-correlation function g do not necessarily coincide, one should not regard $\mathbf{P}^v$ as one single physical quantity, but rather as the sum of two independent variables, $\mathbf{P}_c^v$ and $\mathbf{P}_p^v$.

4.5.1 Entropy and Evolution Equations

The thermodynamic phenomenological description of the non-ideal gas may be summarized as follows. The entropy has the form

$$\rho s = \rho s_{\mathrm{eq}} - \frac{\tau_c}{4\eta_c T}\overset{0}{\mathbf{P}}{}^v_c : \overset{0}{P}{}^v_c - \frac{\tau_p}{4\eta_p T}\overset{0}{P}{}^v_p : \overset{0}{P}{}^v_p - \frac{\tau_0}{2\zeta T} p^v_p p^v_p, \tag{4.66}$$

since p^v_c vanishes identically, as remarked in Sect. 4.2. The relaxation times and viscosities are defined through the evolution equations for their respective fluxes:

$$\frac{\mathrm{d}}{\mathrm{d}t}\overset{0}{\mathbf{P}}{}^v_c = -\frac{1}{\tau_c}(\overset{0}{\mathbf{P}}{}^v_c + 2\eta_c \overset{0}{\mathbf{V}}), \tag{4.67a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\overset{0}{\mathbf{P}}{}^v_p = -\frac{1}{\tau_p}(\overset{0}{\mathbf{P}}{}^v_p + 2\eta_p \overset{0}{\mathbf{V}}), \tag{4.67b}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}p^v_p = -\frac{1}{\tau_0}(p^v_p + \zeta\nabla\cdot\boldsymbol{v}). \tag{4.67c}$$

This is the simplest generalisation of the scheme proposed for ideal monatomic gases. A decomposition of the viscous pressure tensor in a sum of partial viscous pressure tensors is given in Chap. 16, where polymers are considered.

Our purpose is to explore the consistency of the thermodynamic scheme (4.66–4.67a–c) from a microscopic point of view. Therefore we need an expression for the entropy in terms of f_1 and f_2. This is supplied by (Green 1969)

$$\rho s = -k_{\mathrm{B}}\int f_1(1)\ln f_1(1)\mathrm{d}\Gamma_1 - \tfrac{1}{2}k_{\mathrm{B}}\int f_2(1,2)\ln\frac{f_2(1,2)}{f_1(1)f_1(2)}\mathrm{d}\Gamma_{12}, \tag{4.68}$$

where $\mathrm{d}\Gamma_1 = \mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{c}_1$ and $\mathrm{d}\Gamma_{12} = \mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{c}_1\mathrm{d}\boldsymbol{r}_2\mathrm{d}\boldsymbol{c}_2$. An explicit form for the entropy in terms of f_1 and g can be obtained by assuming that $f_2(1,2) = f_1(1)f_1(2)g(1,2)$. This result is exact at equilibrium and valid up to the first order in the shear rate for a wide class of interaction potentials. Within this approximation and setting $f_1 = f$ one has

$$\rho s = -k_{\mathrm{B}}\int f\ln f\mathrm{d}\boldsymbol{c} - \tfrac{1}{2}n^2k_{\mathrm{B}}\int g\ln g\mathrm{d}\boldsymbol{R}. \tag{4.69}$$

In analogy with Boltzmann's equation, the evolution equations for f and g can be written as

$$\frac{\partial f}{\partial t} + \boldsymbol{c}\cdot\frac{\partial f}{\partial \boldsymbol{r}} = J_c(f), \tag{4.70a}$$

$$\frac{\partial g}{\partial t} + \boldsymbol{R}\cdot(\nabla\boldsymbol{v})\cdot\nabla_{\boldsymbol{R}}g = J_p(g), \tag{4.70b}$$

where ∇_R stands for the gradient with respect to the relative position $\boldsymbol{R}$ between two molecules. It is not necessary to know the specific form of collision operators J_c and J_p on the right-hand sides of Eq. 4.70. The only result of interest is that at equilibrium $J_c(f_{\mathrm{eq}}) = 0$ and $J_p(g_{\mathrm{eq}}) = 0$, with f_{eq} and g_{eq} given by

$$f_{\mathrm{eq}} \approx \exp\left[-\frac{mC^2}{2k_{\mathrm{B}}T}\right], \quad g_{\mathrm{eq}} \approx \exp\left[-\frac{w(R)}{k_{\mathrm{B}}T}\right]. \tag{4.71}$$

The last expression defines an effective potential $w(R)$ which coincides with the interaction potential $\phi(R)$ only up to a first-order approximation in the density.

Now, by analogy with (4.34), one expands the non-equilibrium distribution functions f and g in terms of the moments of $\boldsymbol{C}$ and $\boldsymbol{R}$, respectively:

$$f = f_{\mathrm{eq}}[1 + \overset{0}{\boldsymbol{CC}} : \overset{0}{\mathbf{A}}(\boldsymbol{r},t)], \tag{4.72a}$$

$$g = g_{\mathrm{eq}}[1 + \overset{0}{\boldsymbol{RR}} : \overset{0}{\mathbf{B}}(\boldsymbol{r},t) + R^2 b(\boldsymbol{r},t)]. \tag{4.72b}$$

Here $\overset{0}{\mathbf{A}}$ and $\overset{0}{\mathbf{B}}$ are traceless symmetric tensors and b is a scalar, which may be related to $\overset{0}{\mathbf{P}}{}^v_c$, $\overset{0}{\mathbf{P}}{}^v_p$, and p^v_p by introducing (4.72) into (4.62–4.63). Note that because of the third of conditions (4.31) the expansion of f is limited to the traceless term $\overset{0}{\boldsymbol{CC}}$. It is found that

$$\overset{0}{\mathbf{P}}{}^v_c = \frac{2m}{15}\langle C^4\rangle\, \overset{0}{\mathbf{A}}, \tag{4.73a}$$

$$\overset{0}{\mathbf{P}}{}^v_p = \frac{n^2}{15}\langle \phi'(R)R^3\rangle\, \overset{0}{\mathbf{B}}, \tag{4.73b}$$

$$p^v_p = -\frac{n^2}{6}\langle \phi'(R)R^3\rangle b, \tag{4.73c}$$

with $\langle\cdots\rangle$ being the corresponding equilibrium average.

Furthermore, one can derive an expression for the entropy by substituting (4.72) into (4.69). Making $f = f_{\mathrm{eq}}(1+\psi_c)$ and $g = g_{\mathrm{eq}}(1+\psi_p)$, one obtains up to second order

$$\rho s = \rho s_{\mathrm{eq}} - \tfrac{1}{2}k_{\mathrm{B}}\int f_{\mathrm{eq}}\psi_c^2 \mathrm{d}\boldsymbol{c} - \tfrac{1}{4}k_{\mathrm{B}}n^2\int g_{\mathrm{eq}}\psi_p^2 \mathrm{d}\boldsymbol{R}. \tag{4.74}$$

Relations (4.73) allow to express the entropy in terms of the dissipative fluxes, namely:

$$\rho s = \rho s_{\mathrm{eq}} - \frac{\alpha_{cc}}{2T}\overset{0}{\mathbf{P}}{}^v_c : \overset{0}{\mathbf{P}}{}^v_c - \frac{\alpha_{pp}}{2T}\overset{0}{\mathbf{P}}{}^v_p : \overset{0}{\mathbf{P}}{}^v_p - \frac{\alpha_0}{2T}(p^v_p)^2, \tag{4.75}$$

with

$$\alpha_{cc} = \frac{15k_{\mathrm{B}}T}{2m^2}\frac{1}{\langle C^4\rangle}, \tag{4.76a}$$

$$\alpha_{pp} = \frac{15k_{\mathrm{B}}T}{n^2}\frac{\langle R^4\rangle}{\langle \phi'(R)R^3\rangle^2}, \tag{4.76b}$$

$$\alpha_0 = \frac{18k_{\mathrm{B}}T}{n^2}\frac{\langle R^4\rangle}{\langle \phi'(R)R^3\rangle^2}. \tag{4.76c}$$

4.5.2 Microscopic Identification of Coefficients

Expression (4.75) confirms the result that the entropy depends on $\overset{0}{\mathbf{P}}{}^{v}_{c}$, $\overset{0}{\mathbf{P}}{}^{v}_{p}$, and p^v_p. The relation between the coefficients α_{cc},α_{pp}, and α_0 and their microscopic analogues are derived from the evolution equations for the fluxes. Introducing (4.72) into (4.70), and multiplying the resulting equations term by term by $\boldsymbol{CC}$, $\boldsymbol{RR}$, and R^2 respectively, one is led, after integration with respect to $\boldsymbol{C}$ and $\boldsymbol{R}$, to

$$\frac{2}{15}\langle C^4\rangle\frac{\partial \overset{0}{\mathbf{A}}}{\partial t} + \frac{2m}{15k_{\mathrm{B}}T}\langle C^4\rangle \overset{0}{\mathbf{V}} = -\frac{1}{\tau_c}\overset{0}{\mathbf{V}} + \mathrm{NL}, \tag{4.77a}$$

$$\frac{2}{15}\langle R^4\rangle\frac{\partial \overset{0}{\mathbf{B}}}{\partial t} - \frac{2}{15k_{\mathrm{B}}T}\langle w'(R)R^3\rangle \overset{0}{\mathbf{V}} = -\frac{1}{\tau_p}\overset{0}{\mathbf{B}} + \mathrm{NL}, \tag{4.77b}$$

$$\langle R^4\rangle\frac{\partial b}{\partial t} - \frac{1}{3k_{\mathrm{B}}T}\langle w'(R)R^3\rangle\nabla\cdot\boldsymbol{v} = -\frac{1}{\tau_0}b + \mathrm{NL}. \tag{4.77c}$$

In (4.77) NL stands for non-linear terms, while the relaxation times τ_c, τ_p, and τ_0 are related to the collision operators J_c and J_p of (4.70) by

$$-\frac{1}{\tau_c} = \langle C_1C_2J_c(C_1C_2)\rangle, \quad -\frac{1}{\tau_p} = \langle R_1R_2J_p(R_1R_2)\rangle, \quad -\frac{1}{\tau_0} = \langle R^2J_p(R^2)\rangle. \tag{4.78}$$

Here we do not require the explicit expressions for the relaxation times. In the more general case, the relaxation times form a fourth-rank tensor; however, for simplicity we consider only the particular case for which they reduce to scalar quantities. After expressing $\overset{0}{\mathbf{A}}$, $\overset{0}{\mathbf{B}}$ and b in terms of the fluxes according to (4.73), one obtains from (4.77) the evolution equations for the fluxes. The ratios $\frac{1}{2}\tau/\eta$ may be derived directly from the ratio of the coefficients of the terms $\mathrm{d}\overset{0}{\mathbf{P}}{}^{v}/\mathrm{d}t$ and the corresponding terms in $\overset{0}{\mathbf{V}}$, as immediately seen by inspection of (4.67).

Comparison of (4.77a) with the ratio

$$\frac{\tau_c}{2\eta_c} = \frac{15k_\mathrm{B}T}{m^2}\frac{1}{\langle C^4\rangle}, \tag{4.79a}$$

obtained from (4.76a) confirms the thermodynamic result $\alpha_{cc} = \frac{1}{2}\tau_c/\eta_c$. From (4.76b and c) one obtains

$$\frac{\tau_p}{2\eta_p} = \frac{15k_\mathrm{B}T}{n^2}\frac{\langle R^4\rangle}{\langle\phi' R^3\rangle\langle w' R^3\rangle}, \tag{4.79b}$$

$$\frac{\tau_0}{\zeta} = \frac{18k_\mathrm{B}T}{n^2}\frac{\langle R^4\rangle}{\langle\phi' R^3\rangle\langle w' R^3\rangle}. \tag{4.79c}$$

Thus, the analogous thermodynamic predictions $\alpha_{pp} = \frac{1}{2}\tau_p/\eta_p$ nd $\alpha_0 = \tau_0/\zeta$ are also confirmed, but only at first order in the density. This is so because the generalised potential $w(R)$ defined in (4.71b) and the interaction potential $\phi(R)$ (and consequently w' and ϕ') are identical only at this order of approximation: in this case, the ratios (4.79b) coincide with their respective counterparts in (4.76), but not at higher orders in the density.

The restriction of the latter identifications to first-order terms in the density is not an important drawback, since the products $\alpha_{pp}\overset{0}{\mathbf{P}}{}^v_p : \overset{0}{\mathbf{P}}{}^v_p$ and $\alpha_0(p^v)^2$ in the entropy (4.75) are of order n^2, so that the differences between α_{pp} and $\frac{1}{2}\tau_p/\eta_p$ and α_0 and $\alpha_0 = \tau_0/\zeta$ are of order n^3 in the expression of entropy. Such terms cannot be included in the present study because the definition (4.69) of entropy is valid up to order n^2 only. To incorporate terms in n^3 demands a description in terms of f_3, the three-particle distribution function in (4.68), which is beyond the scope of the present book. Up to the order of approximation tested here, it can thus be claimed that the macroscopic predictions of EIT are in agreement with the kinetic approach.

The results of EIT are also confirmed by the kinetic theory for gases consisting of molecules with internal degrees of freedom (Rodriguez et al. 1987) and for dilute solutions of dimers and polymers (Camacho and Jou 1990) (see also Chap. 16). The interested reader is referred to the original papers for the analysis of these systems.

4.6 Non-linear Transport

Eu (1992, 1998) has developed a modified version of the moment method with the purpose of deriving non-linear evolution equations. Instead of using, like Grad, an expansion of the form

$$f = f_0\left[1 + \sum\nolimits_i a^{(i)}H^{(i)}(\boldsymbol{C})\right], \tag{4.80}$$

where $H^{(i)}(\boldsymbol{C})$ are Hermite polynomials expressing the moments of the distribution function, Eu proposes a canonical form

$$f_{\mathrm{E}} \approx \exp\left[-\frac{1}{2}\beta m C^2 - \sum\nolimits_i Y^{(i)} H^{(i)}(\boldsymbol{C})\right], \tag{4.81}$$

in which the expansion coefficients $Y^{(i)}$ are depending on $\boldsymbol{r}$ and t. The above expression for the distribution function is similar to that used in the so-called maximum-entropy approaches, which will be discussed in Sect. 6.3, but in Eu's formalism the coefficients $Y^{(i)}$ are required to satisfy some supplementary conditions which guarantee the positiveness of the entropy production at each step of the approximation. He also introduces a new thermodynamic quantity, the so-called calortropy Ψ (see Sect. 3.1), defined as

$$\rho\Psi = -k_{\mathrm{B}} \int f_{\mathrm{E}}(\ln f_{\mathrm{E}} - 1)\mathrm{d}\boldsymbol{C}, \tag{4.82}$$

rather than the Boltzmann definition for the entropy, and which plays in Eu's approach a central role.

From his modified moment method, Eu is able to determine specific forms for the non-linear terms of the evolution equations, which are important in several fields, such as rheology and electronics. We present here a brief analysis which provides explicit information about non-linearities in transport equations. Starting from (4.81), it can be seen that the distribution function will take the form

$$f_E = f_{eq} \exp[-X_1 \cdot q - \overset{0}{X}_2 : \overset{0}{P}{}^v], \tag{4.83}$$

with q and $\overset{0}{\mathcal{P}}{}^v$ the microscopic operators for the respective macroscopic heat flux and pressure tensor; $\boldsymbol{X}_1$ and $\underset{2}{\overset{0}{\boldsymbol{X}}}$ are macroscopic quantities, which in the simplest version of EIT, can be identified as

$$\boldsymbol{X}_1 = -\frac{\tau_1}{2k_{\mathrm{B}}\lambda T^2}\boldsymbol{q}, \quad \overset{0}{\mathbf{X}}_2 = -\frac{\tau_2}{4k_{\mathrm{B}}\eta T}\overset{0}{\mathbf{P}}{}^v. \tag{4.84}$$

The entropy production is given by

$$\sigma^s = -k_{\mathrm{B}} \int \ln f_{\mathrm{E}} J(f_{\mathrm{E}})\mathrm{d}\boldsymbol{c}, \tag{4.85}$$

with $J(f_{\mathrm{E}})$ the collision operator defined in (4.2). It is convenient, for further purposes, to introduce a dimensionless form of (4.85), namely

$$\bar{\sigma}^s = \frac{\tau_{\mathrm{E}}}{k_{\mathrm{B}} n}\sigma^s, \tag{4.86}$$

where $\tau_{\mathrm{E}} = [(2k_{\mathrm{B}}T/m)^{1/2} n d^2]^{-1}$ is of the order of the collision time. Here d is the molecular diameter.

From the property (4.3) of the collision operator $J(f_{\mathrm{E}})$ and the fact that $\ln f_{\mathrm{E}}$ is composed of collisional invariants, one can write (4.86) as

$$\bar{\sigma}^s = \tfrac{1}{4} \int (x - x') J(f_{\mathrm{E}}) \mathrm{d}\boldsymbol{c}, \tag{4.87}$$

with

$$\boldsymbol{x} = \overset{0}{\mathbf{X}}_2 : [\overset{0}{\mathcal{P}^v}(\boldsymbol{c}) + \overset{0}{\mathcal{P}^v}(\tilde{c})] + \boldsymbol{X}_1 \cdot [\mathcal{Q}(c) + \mathcal{Q}(\tilde{c})] \tag{4.88}$$

and $\boldsymbol{x}'$ the corresponding value of $\boldsymbol{x}$ after the collision. In view of the form of (4.83) for the distribution function and that of $J(f)$ in (4.2), (4.87) can be rewritten as (Eu 1992)

$$\bar{\sigma}^s = \chi \sinh \chi, \tag{4.89}$$

with

$$\chi = \tfrac{1}{2} \langle\langle (\boldsymbol{x} - \boldsymbol{x}')^2 \rangle\rangle^{1/2} = (\bar{\sigma}_0^s)^{1/2}, \tag{4.90}$$

where $\bar{\sigma}_0^s$ is the expression (2.50) of the entropy production derived in Chap. 2.

The important result is that (4.89) is positive definite; however, in contrast to $\bar{\sigma}_0^s$, it is not a simple quadratic form. The essential difference between the conventional and the modified moment methods is that in the conventional case the entropy production is not proved to be positive definite beyond the second order of approximation, while in the modified moment approach it is rigorously positive definite at any order of approximation.

Let us rewrite the entropy production as follows

$$\sigma^s = \sigma_0^s \frac{\sinh \chi}{\chi}. \tag{4.91}$$

For small values of the fluxes, χ is small and (4.91) reduces to σ_0^s. Expression (4.91) is useful for determining the expressions for the non-linear thermal conductivity λ and shear viscosity η. From the form of σ_0^s derived in Chap. 2, it is inferred that

$$\sigma^s = \left(\frac{1}{\lambda_0 T^2} \boldsymbol{q} \cdot \boldsymbol{q} + \frac{1}{2\eta_0 T} \overset{0}{\mathbf{P}^v} : \overset{0}{\mathbf{P}^v} \right) \frac{\sinh \chi}{\chi}; \tag{4.92}$$

this suggests that we should define a non-linear λ and a non-linear η through

$$\lambda(\boldsymbol{q}, \overset{0}{\mathbf{P}^v}) = \lambda_0 \frac{\chi}{\sinh \chi}, \quad \eta(\boldsymbol{q}, \overset{0}{\mathbf{P}^v}) = \eta_0 \frac{\chi}{\sinh \chi}, \tag{4.93}$$

where λ_0 and η_0 are the limits of λ and η for small values of the fluxes, and χ stands for

$$\chi = \left[\frac{\tau_{\mathrm{E}}}{n k_{\mathrm{B}}} \left(\frac{1}{\lambda_0 T^2} \boldsymbol{q} \cdot \boldsymbol{q} + \frac{1}{2\eta_0 T} \overset{0}{\mathbf{P}^v} : \overset{0}{\mathbf{P}^v} \right) \right]^{1/2}, \tag{4.94}$$

in view of (4.86) and (4.90).

To be more explicit consider the generalised viscosity (4.93) in the absence of heat flux. It takes the form

$$\eta(\overset{0}{\mathbf{P}}{}^{v}) = \eta_0 \frac{[\tau_{\mathrm{E}}/(2nk_{\mathrm{B}}T\eta_0)\,\overset{0}{\mathbf{P}}{}^{v} : \overset{0}{\mathbf{P}}{}^{v}]^{1/2}}{\sinh[\tau_{\mathrm{E}}/(2nk_{\mathrm{B}}T\eta_0)\,\overset{0}{\mathbf{P}}{}^{v} : \overset{0}{\mathbf{P}}{}^{v}]^{1/2}}. \tag{4.95}$$

For a plane Couette flow parallel to the x_1 axis, $\overset{0}{\mathbf{P}}{}^{v} : \overset{0}{\mathbf{P}}{}^{v} = 2(P_{12}^{v})^2$, where $P_{12}^{v} = -\eta(\dot{\gamma})\dot{\gamma}$ with $\dot{\gamma}$ the shear rate; in this case, (4.95) reduces to

$$\eta(\dot{\gamma}) = \eta_0 \frac{\sinh^{-1}(\tau^*\dot{\gamma})}{\tau^*\dot{\gamma}} = \eta_0 \frac{\ln\left\{\tau^*\dot{\gamma} + \left[1 + (\tau^*\dot{\gamma})^2\right]^{1/2}\right\}}{\tau^*\dot{\gamma}}, \tag{4.96}$$

with $\tau^* = [\tau_{\mathrm{E}}\eta_0/(nk_{\mathrm{B}}T)]^{1/2}$. Expression (4.96) is the well-known Eyring formula, which describes shear thinning, i.e. the decrease of the apparent viscosity η with increasing shear rate.

With regard to heat transport, the first of relations (4.93) predicts a reduction of the heat flux for very large values of the temperature gradient. This phenomenon, which is imperceptible under usual circumstances, becomes crucial in laser-driven plasmas devised to achieve controlled thermonuclear fusion. This reduction plays a very important role in the transport of laser energy from the deposition region to the ablative surface (Clause and Balescu 1982; Eu 1992).

The consequences of non-linear transport coefficients for the velocity and the temperature profiles in Lennard-Jones fluids have been analysed in detail by Eu and co-workers in a variety of situations (Eu 1992, 1998). Their results are in good agreement with molecular dynamics and experimental data. Non-linear effects are especially important at very low densities, because τ varies as n^{-1}, and at very high density, where the viscosity η_0 increases exponentially with density. Both situations have been examined by Eu, who has shown that EIT provides a unified way to treat problems ranging from rarefied Knudsen gases to dense fluids.

Other non-linear extensions have been proposed where the dependence of the entropy on the fluxes is not limited to second order. An exact solution of the Boltzmann equation has been derived for Maxwell molecules under a heat flux (Santos and Brey 1991), which confirms the basic idea that the generalised entropy will depend on the fluxes, but shows a complicated dependence of the entropy on $\boldsymbol{q}$.

Other non-linearities may arise from the non-dissipative terms occurring in the entropy flux; as a matter of fact, the β coefficient in the expression for the entropy flux may depend, in principle, on the scalar invariants of the fluxes. Thermodynamics does not provide special restrictions on these coefficients in the non-linear domain. However, valuable information may be obtained if one requires that the non-dissipative part of the evolution equations be Hamiltonian, or, in other words, susceptible of being written in terms of Poisson brackets (Grmela and Öttinger 1997; Öttinger 2005). This hypothesis is quite reasonable, because both particle mechanics at the microscopic level and the macroscopic behaviour of a perfect fluid are Hamiltonian. Moreover, since the equations of EIT can be written in the form of Poisson brackets (see Chap. 1), this opens the way to the use of the powerful techniques of symplectic geometry. The formulation in terms of Poisson brackets appears therefore to be an interesting complement to the thermodynamic results.

4.7 Beyond the Thirteen-Moment Approximation: Continued-Fraction Expansions of Transport Coefficient

In the previous sections, one has selected as the extra variables the fluxes of heat, momentum, and matter. However, there exists no restriction on extending the space of variables by including a whole hierarchy of new quantities obeying linear or even non-linear evolution equations. Now, the question arises whether it is sufficient to base a mesoscopic description exclusively on the conserved variables plus the usual dissipative fluxes (or a small number of additional fluxes) or, on the contrary, whether one should include an infinite number of variables. As recalled earlier, Grad's method does not introduce a smallness parameter; therefore, it is difficult to find any rigorous justification to truncate the expansion at the thirteen-moment level, as it is shown in Sect. 4.3.

These questions have raised doubts about the foundations of EIT. The need to take into account higher-order fluxes has become increasingly urgent as shown in the analyses by Velasco and García-Colin (1991, 1993). In this section we propose a way out, which consists in including a priori an infinite number of fluxes in the description; in a second step most of these extra variables are eliminated by introducing an effective relaxation time which takes their contribution into account. Such a reduction in the number of variables is needed as we wish to compare with experimental results, which are usually described by a limited number of variables. As an illustration, we consider the effect of introducing higher-order moments in heat conduction. The results can be directly extended to viscous flows, electrical conduction or any other transport phenomenon.

So far, we have taken as non-equilibrium variable the heat flux $\boldsymbol{q}$; we now wish to incorporate higher-order variables, each one being defined as the flux of the preceding one. To be explicit, we take as variables $\boldsymbol{J}^{(1)}$, $\boldsymbol{J}^{(2)}, \ldots, \boldsymbol{J}^{(n)}$, where $\boldsymbol{J}^{(n)}$, a tensor of order n, is the flux of $\boldsymbol{J}^{(n-1)}$. This is not an academic game: at least two arguments can be put forward in favour of this extension. First, it follows from the kinetic theory that the relaxation times of $\boldsymbol{q}$ and P^{v} are of the order of magnitude of the collision time. Since the relaxation times of the higher-order fluxes cannot be much shorter than the collision time, all of them are of the same order. Therefore, using only the first-order fluxes as independent variables is probably not satisfactory to describe high-frequency processes; indeed, when the frequency becomes high enough to be comparable to the inverse of the relaxation time of the first-order fluxes, the higher-order fluxes behave themselves like independent variables and must be incorporated in the formalism. The second point is that, up to now, the analysis has been mostly limited to an exponential relaxation for the dynamics of the fluxes. The inclusion of higher-order fluxes opens the way to more complicated dynamics.

In microscopic terms, $\boldsymbol{J}^{(1)} = \boldsymbol{q}$ is a part of the third-order moment of the velocity distribution function and $\boldsymbol{J}^{(n)}$ is, correspondingly, a part of its $(n + 2)$ th-order moment. Up to the nth-order moment, the Gibbs equation takes the form

$$\mathrm{d}s = T^{-1}\mathrm{d}u - \alpha_1 v \boldsymbol{J}^{(1)} \cdot \mathrm{d}\boldsymbol{J}^{(1)} - \cdots - \alpha_n v \boldsymbol{J}^{(n)} \otimes \mathrm{d}\boldsymbol{J}^{(n)}, \tag{4.97}$$

and the entropy flux can be written as

$$\boldsymbol{J}^s = \beta_0 \boldsymbol{J}^{(1)} + \beta_1 \boldsymbol{J}^{(2)} \cdot \boldsymbol{J}^{(1)} + \cdots + \beta_{n-1} \boldsymbol{J}^{(n)} \otimes \boldsymbol{J}^{(n-1)}. \tag{4.98}$$

The symbol $\otimes$ denotes the contraction of the corresponding tensors, and the coefficient β_0 may be identified by comparison with the classical theory as $\beta_0 = T^{-1}$. We have limited ourselves to the simplest form of the entropy and the entropy flux and have not taken into account coupled contributions of the form $\boldsymbol{J}^{(3)} : \boldsymbol{J}^{(1)}\boldsymbol{J}^{(1)}$, and similarly, in (4.97–4.98). This approximation is sufficient for the present purposes.

The entropy production is easily derived from (4.97–4.98) and is given by

$$\begin{aligned}\sigma^s = &-\left[-\nabla T^{-1} + \alpha_1 \dot{\boldsymbol{J}}^{(1)} - \beta_1 \nabla \cdot \boldsymbol{J}^{(2)}\right] \cdot \boldsymbol{J}^{(1)} \ldots \\ &-\sum_{n=3}^{N} \boldsymbol{J}^{(n-1)} \otimes \left[\alpha_{n-1} \dot{\boldsymbol{J}}^{(n-1)} - \beta_{n-1} \nabla \cdot \boldsymbol{J}^{(n)} - \beta_{n-2} \nabla \boldsymbol{J}^{(n-2)}\right].\end{aligned} \tag{4.99}$$

The above expression suggests the following set of evolution equations for the $\boldsymbol{J}^{(n)}$:

$$\nabla T^{-1} - \alpha_1 \dot{\boldsymbol{J}}^{(1)} + \beta_1 \nabla \cdot \boldsymbol{J}^{(2)} = \mu_1 \boldsymbol{J}^{(1)}, \tag{4.100a}$$

$$\beta_{n-1} \nabla \boldsymbol{J}^{(n-1)} - \alpha_n \dot{\boldsymbol{J}}^{(n)} + \beta_n \nabla \cdot \boldsymbol{J}^{(n+1)} = \mu_n \boldsymbol{J}^{(n)}, \tag{4.100b}$$

with $\mu_n \geq 0$, as required from the positiveness of the entropy production. Defining τ_n as $\tau_n = \alpha_n / \tau_n$ and writing ∇T^{-1} in terms of ∇T, the set of equations (4.100) can be written as follows

$$\tau_1 \dot{\boldsymbol{J}}^{(1)} = -(\dot{\boldsymbol{J}}^{(1)} + \lambda \nabla T) + \frac{\beta_1 \tau_1}{\alpha_1} \nabla \cdot \boldsymbol{J}^{(2)}, \tag{4.101a}$$

$$\tau_n \dot{\boldsymbol{J}}^{(n)} = -\boldsymbol{J}^{(n)} + \frac{\beta_n \tau_n}{\alpha_n} \nabla \cdot \boldsymbol{J}^{(n+1)} + \frac{\beta_{n-1} \tau_n}{\alpha_n} \nabla \boldsymbol{J}^{(n-1)} \; (n = 2, 3, \ldots, N). \tag{4.101b}$$

Since $\boldsymbol{J}^{(n)}$ is the flux of $\boldsymbol{J}^{(n-1)}$, this implies, by the very definition of a flux requiring that $\dot{\boldsymbol{J}}^{(n-1)} = -\nabla \cdot \boldsymbol{J}^{(n)} + \cdots$, that the coefficient of $\nabla \cdot \dot{\boldsymbol{J}}^{(n)}$ in the equation for $\dot{\boldsymbol{J}}^{(n-1)}$ must be equal to -1. As a consequence, $\beta_n = -\alpha_n$ is a relation which reduces considerably the number of independent parameters. Indeed, we have a set of $3N$ coefficients α_n β_n and τ_n, but the above relation between β_n and α_n reduces them to $2N$ independent coefficients in the macroscopic theory. Furthermore, the theory of fluctuations predicts that $\alpha_n = k_\mathrm{B}\langle \delta J^{(n)} \delta J^{(n)} \rangle^{-1}$, so that we are left with N independent coefficients at the level of the fluctuation theory. In addition, the kinetic theory allows one to express τ_n in terms of molecular interactions, from which it follows that the formalism contains no free parameters.

In the $(\omega, k)-$ Fourier space the hierarchy of equations (4.101) may be written as a generalised transport law with (ω, k) -dependent coefficients

$$\tilde{\boldsymbol{J}}^{(1)}(\omega, k) = -\mathrm{i}k\lambda(\omega, k)\tilde{T}(\omega, k), \tag{4.102}$$

where $\tilde{\boldsymbol{J}}^{(1)}(\omega, k)$ and $\tilde{T}(\omega, k)$ are the Fourier transforms of $\boldsymbol{J}^{(1)} \equiv \boldsymbol{q}(\boldsymbol{r}, t)$ and $T(\boldsymbol{r}, t)$ while $\lambda(\omega, k)$ stands for

$$\lambda(\omega, k) = \cfrac{\lambda_0}{1 + \mathrm{i}\omega\tau_1 + \cfrac{k^2 l_1^2}{1+\mathrm{i}\omega\tau_2 + \cfrac{k^2 l_2^2}{1+\mathrm{i}\omega\tau_3 + \cfrac{k^2 l_3^2}{1+\mathrm{i}\omega\tau_4}}}}, \tag{4.103}$$

with $l_n^2 = \beta_n^2 (\mu_n \mu_{n+1})^{-1} > 0$. The result (4.103) allows us to define a k-dependent thermal conductivity $\lambda(k)$ in the steady state. Compact expressions for $\lambda(k)$ may be obtained in special cases:

(a) if l_n are given by $l_n^2 = \alpha_{n+1} l^2$, with $\alpha_n = n^2[(2n+1)(2n-1)]^{-1}$ (Hess 1977), the continued-fraction expansion for $\lambda(k)$ given by (4.103) may, in the limiting case $\omega = 0$, be written as

$$\lambda(k) = \frac{3\lambda_0}{(lk)^2}\left[\frac{lk}{\tan^{-1}(lk)} - 1\right]; \tag{4.104a}$$

(b) when $l_n^2 = \frac{1}{4} l^2$, which represents a model for two-dimensional systems (Hess 1977), it is found that for $\omega = 0$

$$\lambda(k) = \frac{2\lambda_0}{(lk)^2}\left[\sqrt{1 + (lk)^2} - 1\right]. \tag{4.104b}$$

Expressions of transport coefficients in the form of a continued-fraction expansion, such as (4.103), are well known in non-equilibrium statistical mechanics (Nagano et al. 1980) and they have proved very useful in the analysis of critical phenomena, where non-local effects become important and where the usual polynomial expansions of the generalised transport coefficients in terms of powers of k fail to converge.

Introducing (4.103) into the energy balance equation $\rho c \dot{T} = -\nabla \cdot \boldsymbol{q}$ yields the dispersion relation

$$-\mathrm{i}\omega = \frac{\chi k^2}{1+\mathrm{i}\omega\tau_1+\frac{k^2l_1^2}{1+\mathrm{i}\omega\tau_2+\frac{k^2l_2^2}{1+\mathrm{i}\omega\tau_3+\frac{k^2l_3^2}{1+\mathrm{i}\omega\tau_4}}}}. \tag{4.105}$$

The value of the phase speed $v_p = \omega/\mathrm{Re}\,k$ depends on the order of approximation considered in (4.105). For instance, up to third-order and in the high-frequency limit, one obtains

$$v_{p1}^2(\infty) = \frac{\chi}{\tau_1}, \tag{4.106a}$$

$$v_{p2}^2(\infty) = \frac{\chi}{\tau_1} + \frac{l_1^2}{\tau_1\tau_2}, \tag{4.106b}$$

$$v_{p3}^4(\infty) = \left(\frac{\chi}{\tau_1} + \frac{l_1^2}{\tau_1\tau_2} + \frac{l_2^2}{\tau_2\tau_3}\right) v_{p3}^2(\infty) - \frac{\chi}{\tau_1}\frac{l_2^2}{\tau_2\tau_3}. \tag{4.106c}$$

For ideal gases, the convergence of (4.105) is seen to be slow, and therefore it is necessary to use an asymptotic expression including an infinite number of higher-order fluxes. A proposed scheme is the following. Let us define $H_n(\omega,k)$ by $H_n(\omega,k) = \lambda_n(\omega,k)/\lambda_0$, where $\lambda_n(\omega,k)$ is the nth-order approximant to $\lambda(\omega,k)$ in (4.103). In the asymptotic limit, it is found that

$$H_\infty(\omega,k) = \frac{1}{1 + i\omega\tau_\infty + l_\infty^2 k^2 H_\infty(\omega,k)}, \tag{4.107}$$

with τ_∞ and l_∞ being the limits of τ_n and l_n for high n. This scheme has proved to be sufficiently accurate for a wide variety of problems in physics (Giannozzi et al. 1988). Solving (4.107) with respect to $H_n(\omega,k)$ results in

$$H_\infty(\omega,k) = \frac{-(1+\mathrm{i}\omega\tau_\infty) \pm \sqrt{(1+\mathrm{i}\omega\tau_\infty)^2 + 4k^2l_\infty^2}}{2k^2l_\infty^2}. \tag{4.108}$$

The dispersion equation (4.105) thus becomes $\mathrm{i}\omega = -\chi k^2 H_\infty(\omega,k)$ which leads in the high-frequency limit to

$$\mathrm{i}\omega = \frac{\chi}{2l_\infty^2}\left(\mathrm{i}\omega\tau_\infty \pm \sqrt{4l_\infty^2k^2 - \omega^2\tau_\infty^2}\right), \tag{4.109}$$

while the corresponding phase speed is

$$v_{p\infty}^2 = \frac{\chi}{\tau_\infty - (l_\infty^2/\chi)}. \tag{4.110}$$

By identifying this expression for the phase velocity with the standard expression $v_p = (\chi/\tau_{\mathrm{eff}})^{1/2}$, one may introduce a 'renormalized' or 'effective' relaxation time by

$$\tau_{1\text{eff}} = \tau_\infty - (l_\infty^2/\chi). \tag{4.111}$$

The interest of this procedure is that it takes account of the presence of all the fluxes although one single flux, the first-order one, is used in the analysis; the key point is that its relaxation time is no longer given by τ_1 but rather by $\tau_{1\text{eff}}$ defined by relation (4.111).

Such an approach finds a natural application in nano-materials wherein non-local effects are dominant and wherein some heat carriers may travel through the medium without undergoing collisions, as it will be shown in Chap. 10.

An analogous development for the viscous pressure tensor would yield the following expression for the effective relaxation times of the corresponding variables

$$\tau_{2\text{eff}} = \tau_2 - (l_\infty'^2/\nu), \tag{4.112}$$

ν being the kinematic viscosity, and ν the corresponding correlation length. It may be shown by Hess (1977) that

$$l_\infty^2 = \frac{3k_\mathrm{B}T}{4m}\tau_1^2, l_\infty'^2 = \frac{3k_\mathrm{B}T}{4m}\tau_2^2. \tag{4.113}$$

By recalling that $\chi = 5k_\mathrm{B}T/(3m)\tau_1$ and $\nu = (k_\mathrm{B}T/m)\tau_2$, it is found from (4.111) and (4.112) that

$$\tau_{1\text{eff}} = \frac{11}{20}\tau_{1\text{Grad}}, \tau_{2\text{eff}} = \frac{1}{4}\tau_{2\text{Grad}}, \tag{4.114}$$

where $\tau_{1\text{Grad}}$ and $\tau_{2\text{Grad}}$ are the respective relaxation times in the thirteen-moment approximation. These values for the effective times are comparable to their respective values obtained by fitting the experimental data for ultrasound velocity which are $\tau_{1\,\text{exp}} = 0.40\tau_{1\text{Grad}}$, $\tau_{2\,\text{exp}} = 0.29\tau_{2\text{Grad}}$ (Anile and Pluchino 1984).

It can thus be stated that the introduction of the whole set of higher-order fluxes and their elimination through the definition of an effective relaxation time is able to yield results which are in better agreement with the experimental results than a simple theory restricted a priori to the first thirteen moments. The above procedure presents the advantage that it does not ignore a priori all the other fluxes. At high frequencies more and more fluxes contribute to the value of the phase speed of dissipative signals according to (4.106). By considering only the first-order fluxes as independent variables, one obtains nevertheless a satisfactory qualitative understanding of high-frequency phenomena, in contrast with the classical theory of irreversible processes, which predicts unrealistic results. However, to achieve a better quantitative agreement with experiments, the introduction of higher-order fluxes is needed. Furthermore, the possibility of recovering the continued-fraction expansion for transport coefficients from EIT provides a closer connection with microscopic theories than classical irreversible thermodynamics. The ability to gain specific information about the memory functions from thermodynamic arguments is an important feature, because of the extreme difficulty of deriving explicit results from statistical mechanics, where the problem is generally circumvented by mathematical modelling.

One should finally note that since the evolution equations of EIT contain more variables than those of classical descriptions, they require more boundary conditions. This problem has been examined in the kinetic theory of rarefied gases (Waldmann and Vestner 1975; Roldughin 1995) and more recently from a macroscopic point of view (Struchtrup 2003).

4.8 Problems

4.1. (a) Show how to obtain the results (4.37) and (4.38) from (4.32–4.33) and (4.36). (b) By following the procedure leading to (4.30–4.33), determine the non-equilibrium contributions to the entropy and the entropy flux up to the fourth order in ϕ.

4.2. Assuming $f(\boldsymbol{r},\boldsymbol{c},t) = f_{\mathrm{eq}}(\boldsymbol{c})[1+\phi(\boldsymbol{r},\boldsymbol{c},t)]$ with $\phi(\boldsymbol{r},\boldsymbol{c},t) \ll 1$, derive the linearized form of the Boltzmann collision operator. Study the H-theorem in this approximation.

4.3. The shear viscosities for He and Ar at 273 K and 1 atm are respectively $1.87 \times 10^{-5}\,\mathrm{kg\,m^{-1}\,s^{-1}}$ and $2.11 \times 10^{-5}\,\mathrm{kg\,m^{-1}\,s^{-1}}$. (a) Calculate the collision time τ_2 for both gases. (b) If $\tau_1 = \frac{3}{2}\tau_2$, evaluate the thermal conductivity of both gases, if their respective atomic weights are 4 and 40.

4.4. An expression for the relaxation time is $\tau^{-1} = \sqrt{2}n\sigma_0\langle v\rangle$, where n is the number of molecules per unit volume; $\langle v\rangle = [8k_{\mathrm{B}}T/(\pi m)]^{1/2}$ the mean speed of the molecules, and σ_0 the collision cross-section, which for rigid spheres of diameter d is given by $\sigma_0 = \pi d^2$. (a) Determine the dependence of the viscosity and the thermal conductivity on n and T. (b) Using the data of Problem 4.3, evaluate the atomic diameters of He and Ar. (c) From dimensional arguments, find the dependence of the collision cross-section σ_0 on n and T when the interaction between the particles is described by a potential of the form $V(r) \sim r^{-s}$, with s being a constant. Show that η and λ behave as $T^{(s+4)/(2s)}$.

4.5. A monatomic gas composed of molecules of atomic diameter $2 \times 10^{-10}\,\mathrm{m}$ is subjected to a plane Couette flow at 273 K and 1 atm. (a) Determine the relaxation time τ_2 and calculate the shear viscosity at low shear rates. (b) A non-linear analysis of the Boltzmann equation yields for the shear-rate dependent viscosity the expression

$$\eta(\dot{\gamma}) = \eta_0 \frac{\sinh^{-1}(\tau\dot{\gamma})}{\tau\dot{\gamma}},$$

with τ being a relaxation time which may be identified as τ_2 and η_0 the shear viscosity for low shear rates (see (4.96)). Evaluate the shear viscosity for $\tau\dot{\gamma} = 0.5$.

4.6. Show that the kinetic equation for the distribution function in the relaxation-time approximation

$$\frac{\partial f}{\partial t} + \boldsymbol{c} \cdot \nabla f = -\frac{1}{\tau}(f - f_{\mathrm{eq}})$$

satisfies an H-theorem. Find the expression of the corresponding entropy production.

4.7. Find the evolution equations of $\mathbf{P}^v$ and $\boldsymbol{q}$ from the kinetic equation for the distribution function in the relaxation-time approximation.

4.8. Grad proposed to expand the non-equilibrium distribution function in Hermite polynomials of the dimensionless molecular velocity $\overline{\boldsymbol{C}} = [m/(k_{\mathrm{B}}T)]^{1/2}\boldsymbol{C}$:

$$f = f_{\mathrm{eq}}[1 + \sum_n (1/n!) a_i^{(n)}(\boldsymbol{r}, t) H_i^{(n)}(\boldsymbol{C})],$$

where the $H_i^{(n)}$ are tensors of order n, with subscripts i denoting a collection of n labels ($i = \{i_1, i_2, \ldots, i_n\}$), and f_{eq} is the local-equilibrium distribution function. The coefficients $a_i^{(n)}$ are also tensors of order n, given by $a_i^{(n)} = (m/\rho) \int f\, H_i^{(n)} \mathrm{d}\boldsymbol{C}$. The first three polynomials are $H_i^{(1)} = \overline{C}_i$, $H_{ij}^{(2)} = \overline{C}_i \overline{C}_j - \delta_{ij}$, $H_{ijk}^{(3)} = \overline{C}_i \overline{C}_j \overline{C}_k - (\overline{C}_i \delta_{jk} + \overline{C}_j \delta_{ki} + \overline{C}_k \delta_{ij})$. (a) Show that $a_i^{(1)} = 0$, $a_{ij}^{(2)} = (1/p) P_{ij}^v$, and $a_{ijk}^{(3)} = (1/p)(m/k_{\mathrm{B}}T)^{1/2} S_{ijk}$, with $S_{ijk} = \int \overline{C}_i \overline{C}_j \overline{C}_k f\, \mathrm{d}C$. (b) Show that

$$\sum_{r=1}^{3} a_{\mathrm{irr}}^{(3)} = \frac{2}{p}\left(\frac{m}{k_{\mathrm{B}}T}\right)^{1/2} q_i .$$

(c) The Hermite polynomials $H_i^{(n)}$ and $H_j^{(m)}$ are orthogonal, i.e. their product $\int f_{\mathrm{eq}} H_j^{(m)} H_i^{(n)}\, \mathrm{d}\boldsymbol{C}$ is zero unless $n = m$ and i is a permutation of j. Show that the non-equilibrium entropy has the form

$$s = s_{\mathrm{eq}} - \frac{1}{2} k_{\mathrm{B}} \sum_n \alpha_n a_i^{(n)} a_i^{(n)} .$$

Find the form of α_n in terms of the products of $H_i^{(n)}$(summation over all permutations of the set of subindices i is assumed in the expression for f and s) (see Velasco, García-Colín (1993)).

4.9. To clarify the asymptotic expressions used in Sect. 4.7 for transport coefficients, (a) show that the continued fraction

$$R = \frac{a}{1 + \frac{a}{1 + \frac{a}{1 + \cdots}}}$$

tends, in the asymptotic limit of an infinite expansion, to

$$R_\infty = \frac{1}{2}\left(\sqrt{1+4a}-1\right).$$

(*Hint:* Note that in this limit, R_∞ must satisfy $R_\infty = a/(1+R_\infty)$). (b) From this result, show relation (4.104b). (c) Using the method outlined in this problem, and assuming that all the relaxation times and correlation lengths are equal, prove (4.107) and (4.108).

Chapter 5
Fluctuation Theory

Up to now we have developed a thermodynamic formalism and have derived evolution equations for the dissipative fluxes. In the Part III of this book, these equations are used to interpret experimental data or applied to situations which are beyond the scope of the classical irreversible thermodynamics. In this chapter, we focus our attention on the generalised Gibbs equation, which is the central result of extended irreversible thermodynamics (EIT). Our aim is to show that the generalised entropy plays an essential role in the description of fluctuations around equilibrium states of not only the conserved variables but the dissipative fluxes, too.

The main reason to study the fluctuations is that it provides a link between entropy and probability and that it allows one to compute the non-classical coefficients of the entropy in terms of the equilibrium distribution function. The line of thought involving fluctuations is somewhat intermediate between the macroscopic and the microscopic descriptions: this is the reason why some authors refer to it as a mesoscopic theory. In fact, some other modern approaches to non-equilibrium thermodynamics beyond local equilibrium introduce, as additional variables of the theory, the second moments of the fluctuations out of equilibrium instead of the fluxes (see for instance Keizer 1987). However, to take into account this alternative possibility one must consider fluctuations around non-equilibrium states, which will be examined in Chap. 6.

Still another reason to consider fluctuations is that their study around equilibrium states has led to one of the most important results of classical non-equilibrium thermodynamics, namely, the Onsager reciprocal relations, the derivation of which is reviewed in Sect. 5.6.

5.1 Einstein's Formula: Second Moments of Equilibrium Fluctuations

The basic question to be answered is: How far is it possible to extend the relation between entropy and probability when the classical entropy is replaced by a generalised one? One way to solve this problem is to have non-equilibrium ensembles in the Gibbsian sense and this has been the line of thinking of some authors. However,

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_5,

the construction of such ensembles in general situations remains an open problem, which is discussed in chap. 6.

In the present chapter, we follow an intermediate way based on the Einstein relation for the probability of fluctuations. For isolated systems, the probability of fluctuations of thermodynamic variables with respect to their equilibrium reference values is related to the change in entropy ΔS associated with the fluctuation

$$\Delta S = S - S(\text{equilibrium}) \tag{5.1}$$

where S is the total entropy of a system of mass M and volume V. The relation between the probability and the entropy change was proposed by Einstein by inverting the well known Boltzmann–Planck formula for the entropy,

$$S = k_\mathrm{B} \ln W, \tag{5.2}$$

with W the probability of the macrostate and k_B the Boltzmann constant. In this way one is led to

$$W \approx \exp(\Delta S / k_\mathrm{B}). \tag{5.3}$$

If the fluctuations are small, the quantity ΔS may be expanded:

$$\Delta S \approx (\delta S)_\mathrm{eq} + \frac{1}{2}\left(\delta^2 S\right)_\mathrm{eq}, \tag{5.4}$$

δS and $\delta^2 S$ being the first and second differentials of the entropy. Recalling that, for an isolated system, the entropy is maximum in equilibrium, it follows that $(\delta S)_\mathrm{eq} = 0$ and $\left(\delta^2 S\right)_\mathrm{eq} \le 0$. Introduction of these results into (5.3) leads to the Einstein's formula

$$W \approx \exp\left(\frac{1}{2}\delta^2 S / k_\mathrm{B}\right). \tag{5.5}$$

This relation is easily understood for isolated systems. Of course, the total energy and the total volume of an isolated system cannot fluctuate. Consider, however, an isolated system composed of two subsystems in thermal and mechanical contact. The internal energy and the volume may be distributed between both subsystems in different ways, one of which corresponds to the equilibrium situation defined by the equality of the temperatures and pressures of both subsystems. The fluctuations considered here refer to those in the distribution of internal energy and volume between both subsystems.

However (5.5) is a particular case of a more general expression formulated for non-isolated systems. When the surroundings are incorporated, Einstein suggested expressing the probability of fluctuations as

$$W \approx \exp(-\Delta \mathcal{A} / k_\mathrm{B} T_0), \tag{5.6}$$

where $\mathcal{A}$, the availability, is a new quantity defined as

$$\mathcal{A} = U - T_0 S + p_0 V, \tag{5.7}$$

in which T_0 and p_0 are the constant temperature and pressure of the surroundings. Note that $\mathcal{A}$ is not a property of the system alone but of the system in a given environment. It can be shown that $\Delta\mathcal{A}$ measures the maximum amount of useful work which can be extracted from the system during exchanges with the surroundings (Callen 1985; Landau and Lifshitz 1980). If the system and surroundings are in thermal and mechanical equilibrium, $T = T_0$ and $p = p_0$, the change in $\mathcal{A}$ is given by

$$\Delta\mathcal{A} = \Delta U - T\Delta S + p\Delta V = \Delta G, \tag{5.8}$$

G being the Gibbs function, and (5.6) takes the form

$$W \approx \exp(-\Delta G/k_{\mathrm{B}}T). \tag{5.9}$$

Similarly, for a system at fixed V and T, $\Delta\mathcal{A} = \Delta\Phi$, with Φ the Helmholtz free energy, and the probability of fluctuations becomes

$$W \approx \exp(-\Delta\Phi/k_{\mathrm{B}}T). \tag{5.10}$$

Expressions (5.9) and (5.10) are valid for large and small fluctuations. Restricting our study to small fluctuations, $\Delta\mathcal{A}$ can be expanded in a series as follows:

$$\Delta\mathcal{A} \approx \delta\mathcal{A}_{\mathrm{eq}} + \frac{1}{2}\left(\delta^2\mathcal{A}\right)_{\mathrm{eq}} + \cdots,$$

where the first-order term is zero at equilibrium because G (or Φ), at fixed T and p (or fixed V and T), are minimum in equilibrium. This allows us to write

$$W \approx \exp\left[-\frac{1}{2}\delta^2 G/(k_{\mathrm{B}}T)\right], \; W \approx \exp\left[-\frac{1}{2}\delta^2\Phi/(k_{\mathrm{B}}T)\right]. \tag{5.11}$$

These equations are analogous to (5.5) and may still be written as (5.5); indeed, it is easy to see that $\delta^2\Phi$ at constant T is proportional to $\delta^2 S$. To do so, remember that $\Phi = U - TS$; to study the fluctuations of U at constant T, U is the independent variable and S is a function of U. Thus, one has $\delta^2\Phi = -T\delta^2 S$ and from (5.11) one recovers (5.5) but with $\delta^2 S$ computed at constant T and V. Similarly, it is easy to see that $\delta^2 G = -T\delta^2 S$ which, combined with (5.11), again leads to (5.5) but with $\delta^2 S$ computed at constant T and p. We have dealt explicitly with this variety of situations to emphasize that (5.5) is not only applicable to isolated systems but to many other situations, provided that one keeps in mind that different quantities are to be fixed depending on the external constraints placed on the system.

Now, we shall use the generalised entropy of EIT to obtain information about the fluctuations around equilibrium states. The second differential of the generalised entropy may be derived directly from the Gibbs equation (2.44), and when this expression is introduced into (5.5) one obtains

$$W(\delta u, \delta v, \delta p^v, \delta \boldsymbol{q}, \delta \overset{0}{\mathbf{P}}{}^v) \approx \exp\left\{ \frac{M}{2k_\mathrm{B}} \left[(T^{-1})_u (\delta u)^2 + 2(T^{-1})_v \delta u \delta v + (T^{-1}p)_v (\delta v)^2 \right.\right.$$
$$\left.\left. - \frac{v\tau_0}{\zeta T} \delta p^v \delta p^v - \frac{v\tau_1}{\lambda T^2} \delta \boldsymbol{q} \cdot \delta \boldsymbol{q} - \frac{v\tau_2}{2\eta T} \delta \overset{0}{\mathbf{P}}{}^v : \delta \overset{0}{\mathbf{P}}{}^v \right] \right\} \tag{5.12}$$

where the subscripts u and v stand for partial derivatives with respect to u and v respectively. Note that the terms coupling the fluctuations of u and v to those of the fluxes are proportional to the average value of the fluxes, which is zero at equilibrium. In Chap. 6 we will consider fluctuations around non-equilibrium steady states, where these terms do not longer vanish.

To obtain the second moments of the fluctuations from (5.12), it must be recalled that for a multivariant Gaussian distribution function

$$W \approx \exp\left[-\frac{1}{2} E_{ij} \delta x_i \delta x_j \right] \tag{5.13}$$

the second moments are given by

$$\langle \delta x_i \delta x_j \rangle = (E^{-1})_{ij}, \tag{5.14}$$

where the brackets $\langle \ldots \rangle$ enote the average over the probability distribution (5.13). Since in equilibrium the fluctuations of the classical variables u and v are uncoupled with the fluctuations of the fluxes, as seen in (5.12), the second moments of the fluctuations of u and v may be obtained from (5.12) and (5.14) by taking into account that the matrix corresponding to the second derivatives of the entropy with respect to these variables is

$$E_{uv} = -\frac{M}{k_\mathrm{B}} \begin{pmatrix} (T^{-1})_u & (T^{-1})_v \\ (T^{-1})_v & (T^{-1}p)_v \end{pmatrix}. \tag{5.15}$$

By inversing the matrix and introducing the result in (5.14), one obtains

$$\langle \delta u \delta u \rangle = k_\mathrm{B} c_p T^2 - 2k_\mathrm{B} T^2 p v \alpha + k_\mathrm{B} T^2 p^2 v \kappa_T, \tag{5.16a}$$
$$\langle \delta u \delta v \rangle = k_\mathrm{B} T^2 v \alpha - k_\mathrm{B} T p v \kappa_T, \tag{5.16b}$$
$$\langle \delta v \delta v \rangle = k_\mathrm{B} T v \kappa_T, \tag{5.16c}$$

where c_p is the specific heat at constant pressure, α the coefficient of thermal expansion, and κ_T the isothermal compressibility. Similarly, the second moments of the fluctuations of the fluxes are given by

$$\langle \delta q_i \delta q_j \rangle = k_B \lambda T^2 (\tau_1 V)^{-1} \delta_{ij}, \tag{5.17a}$$

$$\langle \delta p^v \delta p^v \rangle = k_B \zeta T (\tau_0 V)^{-1}, \tag{5.17b}$$

$$\langle \delta P^v_{ij} \delta P^v_{ij} \rangle = k_B \eta T (\tau_2 V)^{-1} \Delta_{ijkl}, \tag{5.17c}$$

with δ_{ij} the Kronecker symbol and $\Delta_{ijkl} = \left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{kl}\right)$.

Expressions (5.17a–c) are worth of further examination. They relate the dissipative coefficients λ, ζ, and η to the fluctuations of the fluxes with respect to equilibrium. These relations may be interpreted in two different ways: either by stating that the dissipative coefficients determine the strength of the fluctuations or saying that the fluctuations determine the dissipative coefficients. The latter point of view has been exploited in the Green–Kubo relations for the dissipative coefficients, which are one of the cornerstones of modern non-equilibrium statistical mechanics. Expressions (5.17a–c) for the second moments of the fluctuations allow us also to compute the non-classical coefficients of the Gibbs equation (3.11) from the equilibrium distribution function and the microscopic expressions of the dissipative fluxes. In Sect. 6.7), it is shown how to generalise these results to fluctuations around non-equilibrium steady states.

Here we will make evident the connection of (5.17a–c) with the well-known Green–Kubo formulae. To this end, recall the Green–Kubo relations for thermal conductivity and shear viscosity (Reich 1982):

$$\lambda = \frac{V}{k_B T} \int_0^\infty \langle \delta q_i(0) \delta q_i(t) \rangle \mathrm{d}t, \tag{5.18a}$$

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle \delta P^v_{ij}(0) \delta P^v_{ij}(t) \rangle \mathrm{d}t \quad (i \neq j), \tag{5.18b}$$

respectively. In (5.18a–b) the brackets $\langle ... \rangle$gtand for equilibrium average and no summation is implied over repeated indices. At this point, it must be underlined that (5.18) are valid for all kinds of dynamics; in particular, if the evolution of the fluctuations of the fluxes is described by the Maxwell–Cattaneo relaxational equations (2.64–2.66), then, after integration, (5.18) reduce to

$$\lambda = \frac{\tau_1 V}{k_B T^2} \langle \delta q_i(0) \delta q_i(0) \rangle, \tag{5.19a}$$

$$\eta = \frac{\tau_2 V}{k_B T} \langle \delta P^v_{ij}(0) \delta P^v_{ij}(0) \rangle, \tag{5.19b}$$

which are nothing else than the results expressed by (5.17a–c).

The Green–Kubo relations have generated a wide interest in connection with the study of the evolution of the dissipative fluxes in statistical mechanics. This point is worth emphasizing, because one of the objectives of EIT is just the determination of evolution equations for the dissipative fluxes, but from a macroscopic point of view. This provides an interesting point of contact between the macroscopic and the microscopic approaches.

5.2 Ideal Gases

In this section we compute the coefficients appearing in the non-classical part of the generalised entropy by using the expressions for the second moments derived in the previous section and the equilibrium distribution function for ideal gases.

As seen in Chap. 4 the kinetic definitions for $\boldsymbol{q}$ and $\mathbf{P}^v$ are

$$\boldsymbol{q} = \int \frac{1}{2} m C^2 \boldsymbol{C} f \, \mathrm{d}\boldsymbol{c} \tag{5.20}$$

and

$$P^v = \int \left(m \boldsymbol{C}\boldsymbol{C} - \frac{1}{3} p U \right) f \, \mathrm{d}\boldsymbol{c}, \tag{5.21}$$

where f is the distribution function, $\boldsymbol{c}$ the velocity of a molecule, $\boldsymbol{v}$ the mean velocity, $\boldsymbol{C} = \boldsymbol{c} - \boldsymbol{v}$ the molecular velocity relative to the mean motion, m the mass of a molecule, U the identity tensor, and p the thermodynamic pressure.

The fluctuations of $\boldsymbol{q}$ near equilibrium are due to the fluctuations δf of the distribution function and the fluctuations $\delta \boldsymbol{v}$ of the mean velocity. Up to first-order terms in the fluctuations one has

$$\delta \boldsymbol{q} = \int \frac{1}{2} m C^2 \boldsymbol{C} \delta f \, \mathrm{d}\boldsymbol{c} - \left[\int \tfrac{1}{2} m C^2 f_{\mathrm{eq}} \mathrm{d}\boldsymbol{c} \right] \delta \boldsymbol{v} - \left[\int m \boldsymbol{C}\boldsymbol{C} f_{\mathrm{eq}} \mathrm{d}\boldsymbol{c} \right] \cdot \delta \boldsymbol{v}. \tag{5.22}$$

For an ideal gas at equilibrium, the second and third integrals on the right-hand side of (5.22) give respectively $\rho u \delta \boldsymbol{v}$ and $p\delta boldsymbol v$, and hence

$$\delta \boldsymbol{q} = \int \frac{1}{2} m C^2 \boldsymbol{C} \delta f \, \mathrm{d}\boldsymbol{c} - \rho h \delta \boldsymbol{v}, \tag{5.23}$$

where $h = u + (p/\rho)$ is the enthalpy per unit mass, which for a classical monatomic ideal gas takes the form $h = \frac{5}{2} k_{\mathrm{B}} T/m$.

Since $\delta \boldsymbol{v}$ is, by definition, taken from

$$\rho \delta \boldsymbol{v} = \int m \boldsymbol{C} \delta f \, \mathrm{d}\boldsymbol{c}, \tag{5.24}$$

the fluctuation of the heat flux given by (5.23) can be written as

$$\delta \boldsymbol{q} = \int \left(\frac{1}{2} m C^2 - \tfrac{5}{2} k_{\mathrm{B}} T \right) \boldsymbol{C} \delta f \, \mathrm{d}\boldsymbol{c}. \tag{5.25}$$

Using this expression, frequently called the subtracted heat flux, to compute the second moments of the fluctuations, one finds that

$$\langle \delta \boldsymbol{q} \delta \boldsymbol{q} \rangle = \int \mathrm{d}\mathbf{c} \int \mathrm{d}\boldsymbol{c}' \left(\frac{1}{2} m C^2 - \frac{5}{2} k_{\mathrm{B}} T \right) \boldsymbol{C} \left(\frac{1}{2} m C'^2 - \frac{5}{2} k_{\mathrm{B}} T \right) \boldsymbol{C}' \langle \delta f(\boldsymbol{C}) \delta f(\boldsymbol{C}') \rangle. \tag{5.26}$$

For the fluctuations of the non-diagonal components of the viscous pressure tensor, an analogous derivation yields

$$\delta \mathbf{P}^v = \int m\boldsymbol{C}\boldsymbol{C}\delta f \,\mathrm{d}\boldsymbol{c}, \tag{5.27}$$

from which

$$\langle \delta P^v_{ij}\delta P^v_{kl}\rangle = \int \mathrm{d}c \int \mathrm{d}\boldsymbol{c}' m C_i C_j m C'_k C'_l \langle \delta f(\boldsymbol{C})\delta f(\boldsymbol{C}')\rangle. \tag{5.28}$$

The expression for the second moments of the fluctuations of the distribution function may be obtained (Landau and Lifshitz 1980) from Einstein's formula (5.5). When Boltzmann's definition of entropy (4.27), namely

$$S = -k_\mathrm{B} V \int f \ln f \mathrm{d}\boldsymbol{c}, \tag{5.29a}$$

where V is the volume of the system, is introduced into (5.5), one obtain

$$\Pr(\delta f) \approx \exp\left[-\frac{1}{2}\frac{V}{f_\mathrm{eq}(\mathbf{r},\boldsymbol{c},t)}(\delta f(\boldsymbol{r},\boldsymbol{c},t))^2\right]. \tag{5.29b}$$

$$\langle \delta f(\boldsymbol{r},\boldsymbol{c},t)\delta f(\boldsymbol{r}',\boldsymbol{c}',t)\rangle = \frac{1}{V} f_\mathrm{eq}(\boldsymbol{r},\boldsymbol{c})\delta(\boldsymbol{r}-\boldsymbol{r}')\delta(\boldsymbol{c}-\boldsymbol{c}') \tag{5.30}$$

and consequently (5.26) and (5.28) reduce to

$$\langle \delta \boldsymbol{q}\delta \boldsymbol{q}\rangle = \frac{1}{V}\int \mathrm{d}\boldsymbol{c}\left(\frac{1}{2}mC^2 - \frac{5}{2}k_\mathrm{B}T\right)^2 \boldsymbol{C}\boldsymbol{C} f_\mathrm{eq}, \tag{5.31a}$$

$$\langle \delta P^v_{ij}\delta P^v_{kl}\rangle = \frac{1}{V}\int \mathrm{d}\boldsymbol{c} m^2 C_i C_j C_k C_l f_\mathrm{eq} \tag{5.31b}$$

Introducing the Maxwell–Boltzmann distribution function,

$$f_\mathrm{eq} = n\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} \exp\left(-\frac{mC^2}{2k_\mathrm{B}T}\right), \tag{5.32}$$

into (5.31a and b) and substituting the corresponding results in (5.17a and c), one obtains for the ratios τ_1/λ and τ_2/η:

$$\tau_1 v/(\lambda T^2) = \tfrac{2}{3}(p^2T)^{-1}, \ \tau_2 v/(2\eta T) = \tfrac{1}{2}v(pT)^{-1}. \tag{5.33}$$

The present theory may also be applied to degenerate ideal gases. In this case, the entropy reads (Landau and Lifshitz 1980)

$$S = -k_B V \int [f \ln(f/y) \mp y\,(1 \pm f/y) \ln(1 \pm f/y)]\mathrm{d}\boldsymbol{c}, \tag{5.34}$$

where the upper sign applies for Bose–Einstein statistics and the lower one for Fermi–Dirac statistics; the quantity y stands for $y = (2s+1)/h^3$ for particles with spin s and mass m different from zero and $y = 2s/h^3$ for particles with vanishing mass. Here, h is the Planck constant. Combining the Einstein formula (5.5) with (5.34), one obtains for the second moments of the fluctuations of the distribution function

$$\langle \delta f(\boldsymbol{r}, \boldsymbol{c}, t)\delta f(\boldsymbol{r}', \boldsymbol{c}', t)\rangle = -\frac{1}{V}\left(\frac{\partial f}{\partial \alpha}\right)_{\mathrm{eq}} \delta(\boldsymbol{r} - \boldsymbol{r}')\delta(\boldsymbol{c} - \boldsymbol{c}'), \tag{5.35}$$

$$f_{\mathrm{eq}} = \frac{y}{\exp(\alpha + \boldsymbol{x}^2) \mp 1}, \tag{5.36}$$

with $\boldsymbol{x} = [m/(2k_{\mathrm{B}}T)]^{1/2}\boldsymbol{C}$ and $\alpha = -\mu/(k_{\mathrm{B}}T)$, μ being the chemical potential. The expressions for $\boldsymbol{q}$ and $\mathbf{P}^v$ are identical with those of the preceding case, but now, of course, the expressions for the enthalpy h and pressure p are those corresponding to degenerate gases.

The results are consequently given in terms of the functions $I_n(\alpha)$ defined as

$$I_n^{\pm}(\alpha) = \int_0^{\infty} \frac{x^n}{\exp(\alpha + x^n) \pm 1}\mathrm{d}x, \tag{5.37}$$

$$\frac{\tau_1 v}{\lambda T^2} = \left\{\frac{5}{3}\frac{k_{\mathrm{B}}T^{7/2}}{mA}\left[\frac{7}{5}\frac{k_{\mathrm{B}}T}{m}I_6(\alpha) - \frac{5}{3}\frac{k_{\mathrm{B}}T^{5/2}}{m\rho A}I_4^2(\alpha)\right]\right\}^{-1}, \tag{5.38}$$

and

$$\frac{\tau_2 v}{2\eta T} = \frac{3mA}{4k_{\mathrm{B}}T^{7/2}I_4(\alpha)}, \tag{5.39}$$

with $A^{-1} = 4\pi 2^{1/2} y R^{3/2} m$ and R being the gas constant. These results coincide with those derived by Liu and Müller (1983) by a different method. In the limit of high values of α, (5.38, 5.39) reduce to (5.33).

The results of this section are in agreement with those of the kinetic theory of ideal gases discussed in Chap. 4. The interest of the theory of fluctuations is outlined by (5.33) and (5.38–5.39), which show that it is possible to calculate the extra terms of entropy from equilibrium statistical mechanics without appealing to a non-equilibrium kinetic theory.

For obtaining results in the case of dilute real gases it must be taken into account the interaction effects between particles. This leads to several corrections to the coefficients $\tau_1 v/(\lambda T^2)$ and $\tau_2 v/(2\eta T)$, which have been evaluated by Jou (1989) up to the first order in a virial expansion.

5.3 Fluctuations and Hydrodynamic Stochastic Noise

Expressions (5.16) can also be related to the classical formulae of Landau and Lifshitz (1982) for hydrodynamic stochastic noise. This is achieved by assuming that this noise arises from fast fluctuations of the dissipative fluxes; by using an ad hoc version of the Onsager–Machlup formulation (1953), they were able to obtain expressions for the second moments of the noise. Whereas in the usual theory the stochastic noise appears as a purely mathematical entity, in EIT it receives a more precise physical meaning, as shown below.

To make explicit the relation between rapid fluctuations and noise, we calculate the time correlation functions from (5.17) and (2.66)–(2.68); it is found that

$$\langle \delta q_i(0)\delta q_j(t)\rangle = k_{\mathrm{B}}\lambda T^2(\tau_1 V)^{-1}\delta_{ij}\exp(-t/\tau_1), \tag{5.40a}$$

$$\langle \delta P^v_{ij}(0)\delta P^v_{ij}(t)\rangle = k_{\mathrm{B}}\eta T(\tau_2 V)^{-1}\Delta_{ijkl}\exp(-t/\tau_2). \tag{5.40b}$$

In the limit of vanishing relaxation times, we recover the classical formulae of Landau and Lifshitz, since in this limit $\tau^{-1}\exp(-t/\tau) \to 2\delta(t)$, $\delta(t)$ being the Dirac delta function. Accordingly, in this limit we recover not only the classical deterministic formulation of linear irreversible thermodynamics but its fluctuating hydrodynamics counterpart too (Keizer 1983). In a strict sense, $\delta \boldsymbol{q}$ and $\delta \overset{0}{P}{}^v$ may be considered as noises only in the limit of vanishing τ. In general, one should include a white noise $\boldsymbol{f}$ in the evolution equations of these variables; for instance, one could write (see Problem 5.6)

$$\delta\dot{\boldsymbol{q}} + \tau^{-1}\delta\boldsymbol{q} = \boldsymbol{f} \tag{5.41a}$$

being $\boldsymbol{f}$ a Gaussian noise with second moments given by

$$\langle f_i(t)f_j(t')\rangle = \frac{2\lambda k_{\mathrm{B}}T^2}{\tau^2}\delta_{ij}\delta(t-t'). \tag{5.41b}$$

When $\tau \to 0$, $\delta\boldsymbol{q}$ tends to $\tau\boldsymbol{f}$ and it may be considered as a true stochastic noise, rather than the fluctuation of a basic variable.

Let us also mention that by writing $\boldsymbol{q} = -\lambda\nabla T + \delta\boldsymbol{q}$ and allowing ∇T to fluctuate, this formalism leads to spatial correlations of the temperature fluctuations (see Problem 5.7); this was proposed by several authors as a possible origin of the $1/f$ noise (Sato 1978) but we do not enter here into this specialized subject.

5.4 The Entropy Flux

The next step is to calculate the coefficients appearing in the entropy flux in terms of the moments of fluctuations (Jou and Pavón 1985). The procedure is not straightforward and the final result not so direct and appealing as for the coefficients occurring in the expression of the generalised entropy.

Assume that the fluctuation in the distribution function, $\delta f = f - f_{\mathrm{eq}}$, is given by

$$\delta f = f_{\mathrm{eq}}(\delta\lambda\cdot\boldsymbol{\mathcal{Q}} + \delta\overset{0}{\lambda}{}^{v} : \overset{0}{\boldsymbol{\mathcal{P}}}{}^{v}), \tag{5.42}$$

with $\boldsymbol{\mathcal{Q}}$ and $\overset{0}{\boldsymbol{\mathcal{P}}}{}^{v}$ the microscopic operators corresponding to the fluxes and $\delta\lambda$ and $\delta\overset{0}{\lambda}{}^{v}$ parameters which are to be related to the fluctuations of the fluxes. This expression is the simplest one leading to non-zero values for $\delta\mathbf{q}$ and $\delta\overset{0}{P}{}^{v}$

According to (5.42), we have the following relations between $\delta\lambda$, $\delta\overset{0}{\lambda}{}^{v}$ and $\delta\boldsymbol{q}$, $\delta\overset{0}{\mathbf{P}}{}^{v}$

$$\delta\boldsymbol{q} = \int \boldsymbol{\mathcal{Q}}\delta f\,\mathrm{d}\boldsymbol{c} = \left(\int \mathcal{Q}_1^2 f_{\mathrm{eq}}\mathrm{d}c\right)\delta\lambda, \tag{5.43a}$$

$$\delta\overset{0}{\mathbf{P}}{}^{v} = \int \overset{0}{\boldsymbol{\mathcal{P}}}{}^{v}\delta f\,\mathrm{d}c = 2[\int (\overset{0}{\mathcal{P}}{}^{v}_{12})^2 f_{\mathrm{eq}}\mathrm{d}c]\delta\overset{0}{\lambda}{}^{v}, \tag{5.43b}$$

wherein we have assumed that only the component q_1 of $\boldsymbol{q}$ and P^{v}_{12} of $\mathbf{P}^{v}$, with $P^{v}_{12} = P^{v}_{21}$, are non-vanishing.

Introduction of (5.42) into expression (5.29a) of entropy and in the corresponding expression for the entropy flux

$$\boldsymbol{J}^{s} = -k_{\mathrm{B}}\int f\ln f\boldsymbol{C}\mathrm{d}\boldsymbol{c} \tag{5.44}$$

yields, up to second order in the fluctuations of the fluxes,

$$\Delta S = S - S_{\mathrm{eq}} = -\frac{1}{2}k_{\mathrm{B}}V\int f_{\mathrm{eq}}(\boldsymbol{\mathcal{Q}}\cdot\delta\lambda + \overset{0}{\boldsymbol{\mathcal{P}}}{}^{v} : \delta\overset{0}{\lambda}{}^{v})^2\mathrm{d}\boldsymbol{c}, \tag{5.45a}$$

$$\Delta\boldsymbol{J}^{s} = \boldsymbol{J}^{s} - T^{-1}\boldsymbol{q} = -\frac{1}{2}k_{\mathrm{B}}\int f_{\mathrm{eq}}(\boldsymbol{\mathcal{Q}}\cdot\delta\lambda + \overset{0}{\boldsymbol{\mathcal{P}}}{}^{v} : \delta\overset{0}{\lambda}{}^{v})^2\boldsymbol{C}\mathrm{d}c. \tag{5.45b}$$

These expressions can be recast in the form

$$\Delta S = -\frac{1}{2}k_{\mathrm{B}}V\left[\int f_{\mathrm{eq}}\mathcal{Q}_1^2\mathrm{d}\boldsymbol{c}\right]\delta\lambda\cdot\delta\lambda - \frac{1}{2}k_{\mathrm{B}}V\left[2\int f_{\mathrm{eq}}(\mathcal{P}^{v}_{12})^2\mathrm{d}\boldsymbol{c}\right]\delta\overset{0}{\lambda}{}^{v} : \delta\overset{0}{\lambda}{}^{v} \tag{5.46a}$$

$$\Delta\boldsymbol{J}^{s} = -\frac{1}{2}k_{\mathrm{B}}\left[4\int f_{\mathrm{eq}}\mathcal{Q}_1\mathcal{P}^{v}_{12}C_2\mathrm{d}\boldsymbol{c}\right]\delta\overset{0}{\lambda}{}^{v}\cdot\delta\lambda, \tag{5.46b}$$

which, according to (5.43), may be rewritten as

$$\Delta S = \frac{1}{2}k_\mathrm{B}V\left[\int f_\mathrm{eq}\mathcal{Q}_1^2\mathrm{d}\boldsymbol{c}\right]^{-1}\delta\boldsymbol{q}\cdot\delta\boldsymbol{q} - \tfrac{1}{2}k_\mathrm{B}V\left[2\int f_\mathrm{eq}(\mathcal{P}_{12}^v)^2\mathrm{d}\boldsymbol{c}\right]^{-1}\delta\overset{0}{\mathbf{P}^v}:\delta\overset{0}{\mathbf{P}^v} \tag{5.47a}$$

$$\Delta\boldsymbol{J}^s = -k_\mathrm{B}\frac{\int\mathcal{Q}_1\mathcal{P}_{12}^vC_2f_\mathrm{eq}\mathrm{d}\boldsymbol{c}}{\int\mathcal{Q}_1^2f_\mathrm{eq}\mathrm{d}\boldsymbol{c}\int(\mathcal{P}_{12}^v)^2f_\mathrm{eq}\mathrm{d}\boldsymbol{c}}\delta\overset{0}{\mathbf{P}^v}\cdot\delta\boldsymbol{q}. \tag{5.47b}$$

By comparing (5.47a and b) with their corresponding macroscopic expressions

$$\Delta S = -\frac{1}{2}\rho V(\alpha_1\delta\boldsymbol{q}\cdot\delta\boldsymbol{q} + \alpha_2\delta\overset{0}{\mathbf{P}^v}:\delta\overset{0}{\mathbf{P}^v}) \tag{5.48a}$$

$$\Delta\boldsymbol{J}^s = \beta\delta\overset{0}{\mathbf{P}^v}\cdot\delta\mathbf{q}, \tag{5.48b}$$

we find that

$$\alpha_1 = k_\mathrm{B}\left[\int\mathcal{Q}^2f_\mathrm{eq}\mathrm{d}\boldsymbol{c}\right]^{-1},\ \alpha_2 = k_\mathrm{B}\left[2\int\left(\mathcal{P}_{12}^v\right)^2f_\mathrm{eq}\mathrm{d}\boldsymbol{c}\right]^{-1}, \tag{5.49}$$

$$\beta = -k_\mathrm{B}\frac{\int C_2(\mathcal{P}_{12}^v)\mathcal{Q}_1f_\mathrm{eq}\mathrm{d}\mathbf{c}}{\int\mathcal{Q}^2f_\mathrm{eq}\mathrm{d}\boldsymbol{c}\int(\mathcal{P}_{12}^v)^2f_\mathrm{eq}\mathrm{d}\boldsymbol{c}}. \tag{5.50}$$

Relations (5.49) are identical to those previously given by (5.19), whereas (5.50) is new and expresses the coefficient β in the entropy flux as a function of fluctuations. Writing the denominator in terms of the dissipative coefficients and using the relations (5.16) for the relaxation times, one obtains the more compact form

$$\beta = -\frac{\tau_1\tau_2}{k_\mathrm{B}\lambda\eta T^3}\int C_2(\mathcal{P}_{12}^v)\mathcal{Q}f_\mathrm{eq}\mathrm{d}\boldsymbol{c}. \tag{5.51}$$

This is a particular case of a formula derived by Ernst(1970) from the kinetic theory by means of projection-operator methods. More general expressions of β in terms of correlation functions of fluxes have been given by several authors (Wong et al. 1978; Brey 1983). Application of (5.51) to ideal – either classical or degenerate – gases is straightforward and yields

$$\beta = -\frac{2}{3}pT, \tag{5.52}$$

a well-known result in kinetic theory, as shown in Chap. 4. The corresponding expression of β for dilute real gases is derived by Jou (1989).

5.5 Application to a Radiative Gas

It is easy to apply the above formalism to a radiation gas or a mixture of radiation (photons, neutrinos, gravitons) and a material fluid (Jou and Pavón 1985). The latter is assumed to thermalize in a short time, whereas the mean free time of radiation

τ is supposed to be much longer. Such systems are of interest in cosmological and astrophysical problems.

In this case, we may interpret $\boldsymbol{q}$ and $\overset{0}{\mathbf{P}}{}^{v}$ s

$$\delta \boldsymbol{q} = \boldsymbol{c}\delta e_{\text{rad}}, \tag{5.53}$$

and

$$\delta \overset{0}{\mathbf{P}}{}^{v} = (1/c^2)\boldsymbol{cc}\delta e_{\text{rad}}, \tag{5.54}$$

where $\boldsymbol{c}$ is the velocity vector (whose magnitude is the speed of light) and δe_{rad} is the fluctuation of the radiation energy per unit volume. When the Stefan–Boltzmann law $e_{\text{rad}} = aT^4$, with a the black-body constant, is used for a radiative gas, the only non-zero element of the matrix (5.15) is $\left(T^{-1}\right)_u$ and the expression (5.16a) may be written as

$$\langle \delta e_{\text{rad}} \delta e_{\text{rad}} \rangle = 4k_{\text{B}} a T^5 V^{-1} \tag{5.55}$$

By introducing this result into (5.17) and (5.50), it is found that

$$\lambda = \frac{\tau V}{k_{\text{B}} T^2} \langle \delta q_1 \delta q_1 \rangle = \frac{4}{3} c^2 a T^3 \tau, \tag{5.56a}$$

$$\eta = \frac{\tau V}{k_{\text{B}} T^2} \langle \delta P_{12}^{v} \delta P_{12}^{v} \rangle = \frac{4}{5} a T^4 \tau, \tag{5.56b}$$

$$\beta = -\frac{\tau^2 V}{k_{\text{B}} \lambda \eta T^3} \langle \delta q_1 \delta P_{12}^{v} C_2 \rangle = -\frac{1}{4aT^4}, \tag{5.56c}$$

which coincide with the results derived in the relativistic kinetic theory (Israel and Stewart 1979). In the above model, it was supposed that the relaxation times of $\boldsymbol{q}$ and $\overset{0}{\mathbf{P}}{}^{v}$ coincide.

Concerning the bulk viscous pressure, one must take into account that $\delta p^v = \Omega \delta e_{\text{rad}}$, with $\Omega = [\partial P_{\text{tot}}/\partial(\rho e)]_v - \frac{1}{3}$, P_{tot} being the total scalar pressure of the fluid, and ρ its proper density. One then obtains for the bulk viscosity

$$\zeta = (\tau V/k_{\text{B}} T)\langle \delta p^v \delta p^v \rangle = 4\Omega^2 a T^4 \tau. \tag{5.57}$$

An interesting point provided by the theory of fluctuations is a reduction of the number of independent parameters. In the macroscopic theory developed in Chap. 2, we have eight parameters, namely τ_1, τ_0, τ_2, λ, ζ, η, β, and β'. Equations (5.16) and (5.51) and its analogue for β' provide five relations between these parameters, so that we are left with just three independent parameters, for instance τ_1, τ_0, and τ_2. In this way, the macroscopic extended irreversible thermodynamics plus fluctuation theory give much more information than the classical theory with the same number of free parameters.

5.6 Onsager's Relations

Up to now, we have mainly considered static aspects of the fluctuations. The analysis of the evolution of fluctuations leads to the Onsager–Casimir reciprocal relations (Onsager 1931; Casimir 1945), which are of key importance in non-equilibrium thermodynamics. Here we shall reproduce the classical derivation of Onsager–Casimir relations. Another presentation based on extended thermodynamics will be given in Sect. 14.2.

Assume that the entropy is a function of several variables $A_1, \ldots, A_n$ and denote by α_β their deviation from the average equilibrium value $\langle A_\beta \rangle$, $\alpha_\beta = A_\beta - \langle A_\beta \rangle$. Thus, the entropy arising from the fluctuations α_β is

$$S = S_{\mathrm{eq}} - \frac{1}{2} G_{\beta\gamma} \alpha_\beta \alpha_\gamma, \tag{5.58}$$

with

$$G_{\beta\gamma} = -\left(\frac{\partial^2 S}{\partial \alpha_\beta \partial \alpha_\gamma} \right)_{\mathrm{eq}}. \tag{5.59}$$

Summation with respect to repeated subindices is understood. It follows from Einstein's relation (5.5) that the second moments of the fluctuations are given by

$$\langle \alpha_\beta \alpha_\gamma \rangle = k_{\mathrm{B}} (G^{-1})_{\beta\gamma}. \tag{5.60}$$

Onsager assumed that the decay of spontaneous fluctuations of the system is described by the same phenomenological laws that describe the evolution of the perturbations produced by external causes. He supposed, furthermore, that such laws are linear, so that the evolution of α_β is governed by

$$\frac{\mathrm{d}\alpha_\beta}{\mathrm{d}t} = -M_{\beta\gamma} \alpha_\gamma. \tag{5.61}$$

Onsager(1931) took as fluxes the time derivatives of the fluctuations α_β and as corresponding thermodynamic forces the derivatives of the entropy with respect to α_β:

$$J_\beta = \frac{\mathrm{d}\alpha_\beta}{\mathrm{d}t}, \quad X_\beta = \left(\frac{\partial S}{\partial \alpha_\beta} \right) = -G_{\beta\gamma} \alpha_\gamma. \tag{5.62}$$

With these definitions of J_β and X_β, the time derivative of the entropy is a bilinear form in the fluxes and the forces

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -G_{\beta\gamma} \alpha_\gamma \frac{\mathrm{d}\alpha_\beta}{\mathrm{d}t} = J_\beta X_\beta, \tag{5.63}$$

while the evolution equations (5.61) can be casted in the form of linear phenomenological relations between fluxes and forces, namely

$$J_\beta = L_{\beta\gamma} X_\gamma. \tag{5.64}$$

Indeed, it suffices to introduce the definitions (5.62) into (5.64) to obtain

$$\frac{\mathrm{d}\alpha_\beta}{\mathrm{d}t} = -L_{\beta\gamma} G_{\gamma\eta} \alpha_\eta. \tag{5.65}$$

Comparison with (5.61) leads to the identification

$$\mathbf{L} = \mathbf{M} \cdot \mathbf{G}^{-1}. \tag{5.66}$$

In a steady state, one has for any couple of variables α_β and α_γ

$$\langle \alpha_\beta(0)\alpha_\gamma(t)\rangle = \langle \alpha_\beta(0+\tau)\alpha_\gamma(t+\tau)\rangle \tag{5.67}$$

Since this equality is valid for any values of t and τ; in particular, for $\tau = -t$, one has

$$\langle \alpha_\beta(0)\alpha_\gamma(t)\rangle = \langle \alpha_\beta(-t)\alpha_\gamma(0)\rangle. \tag{5.68}$$

Assume that the variable A_β has a well-defined time-reversal parity, i.e. that under the transformations $t \to -t$, $\boldsymbol{p} \to -\boldsymbol{p}$, with $\boldsymbol{p}$ the momentum of the particles, it behaves as $\alpha_\beta(-t) = \varepsilon_\beta \alpha_\beta(t)$, with $\varepsilon_\beta = +1$ for even variables, such as mass and energy, and $\varepsilon_\beta = -1$ for odd variables, such as momentum or heat flux. As a consequence, (5.68) becomes

$$\langle \alpha_\beta(0)\alpha_\gamma(t)\rangle = \varepsilon_\beta \varepsilon_\gamma \langle \alpha_\beta(t)\alpha_\gamma(0)\rangle. \tag{5.69}$$

Note that (5.69) implies that equal-time correlations between even and odd variables vanish in equilibrium. Relation (5.69) is of fundamental importance in deriving the Onsager–Casimir relations: it expresses the microscopic reversibility of the system.

Moreover, direct integration of the evolution equation (5.61) yields

$$\alpha_\beta(t) = \exp[-\mathbf{M}t]_{\beta\gamma} \alpha_\gamma(0) \tag{5.70}$$

For small values of t one may expand (5.70) and keep only first-order terms in t. Then (5.69) takes the form

$$\langle \alpha_\beta(0)[\delta_{\gamma\eta} - M_{\gamma\eta}t]\alpha_\eta(0)\rangle = \varepsilon_\beta \varepsilon_\gamma \langle [\delta_{\beta\eta} - M_{\beta\eta}t]\alpha_\eta(0)\alpha_\gamma(0)\rangle \tag{5.71}$$

which yields

$$M_{\gamma\eta}\langle \alpha_\beta(0)\alpha_\eta(0)\rangle = \varepsilon_\beta \varepsilon_\gamma M_{\beta\eta}\langle \alpha_\eta(0)\alpha_\gamma(0)\rangle. \tag{5.72}$$

Expressing the second moments in terms of the matrix $\mathbf{G}$ of the second derivatives of the entropy, (5.72) can be written as

$$M_{\gamma\eta}(G^{-1})_{\beta\eta} = \varepsilon_\beta \varepsilon_\gamma M_{\beta\eta}(G^{-1})_{\eta\gamma}. \tag{5.73}$$

In view of the relation (5.66) between **L** and **M**, and since **G** is a symmetric matrix, it follows from (5.73) that

$$L_{\gamma\beta} = \varepsilon_\beta \varepsilon_\gamma L_{\beta\gamma} \tag{5.74}$$

which are the well known Onsager–Casimir reciprocal relations (1.82).

The present analysis has the advantage of exhibiting explicitly the main assumptions which underlie the derivation of Onsager–Casimir relations, namely, linear evolution equations and the hypothesis that the behaviour of fluctuations is described on the average by the macroscopic transport laws. In the presence of a magnetic field $\mathcal{B}$, the operation of time-reversal will only change the internal magnetic field arising from the motion of the particles, which is automatically reversed under time reversal. Because of the Lorentz force, which is proportional to the vector product of the velocities and the magnetic field strength, the external magnetic field $\boldsymbol{\mathcal{B}}$ must be inverted in order that the reversal motion follows the same path as in the direct motion. The same comment applies when the system rotates as a whole with angular velocity ω; the sign of the angular velocity must be changed because the Coriolis force is proportional to the vector product of the linear velocities of the particles and the angular velocity of the system. Therefore, in the presence of an external magnetic field $\boldsymbol{\mathcal{B}}$ and rotation ω, the Onsager–Casimir relations read

$$L_{\gamma\beta}(\boldsymbol{\mathcal{B}}, \omega) = \varepsilon_\beta \varepsilon_\gamma L_{\beta\gamma}(-\boldsymbol{\mathcal{B}}, -\omega). \tag{5.75}$$

The importance and the limitations of the Onsager–Casimir relations have been stressed in Chap. 1.

5.7 Experimental Observations of Fluctuations of the Fluxes and Flux Fluctuation Theorem

Fluctuations become especially relevant for systems in the small-number limit, like in nanotechnology, single-molecule studies of ion channels and molecular motors, and biological cells. In these cases, fluctuations of the diffusion flux across a channel will show considerable deviations with respect to the average value described by Fick's law. Moreover, the new techniques of microfluidics and nanotechnology have made possible a direct measurement of the fluctuations of the diffusion flux.

Seitaridou et al. (2007) have measured the flux of particles in a microfluidic system with colloidal particles and they have found that the distribution function of the values of the flux is Gaussian. This result is similar to that of EIT, accordingly the probability of fluctuations of the diffusion flux J is given by

$$\Pr(\delta J) \propto \exp\left[-\frac{\tau}{2D' k_{\mathrm{BT}}(\delta J)^2}\right] \tag{5.76}$$

with $D' = D(\partial\mu/\partial c)^{-1}$, D being the diffusion flux, τ the relaxation time of the diffusion flux, and μ the chemical potential.

Seitaridou et al. (2007) assume independent particles, one-dimensional diffusion and jump rates stationary in time. The correspondent probability distribution function is Gaussian with second moments proportional to $p(1-p)N$, p being the probability that a particle jumps in an operational time interval Δt, and N the total number of particles. The measured fluctuations of the diffusion flux were found in good agreement with the theoretical predictions.

The mentioned authors have also established the so-called "flux fluctuation theorem" i.e. the relative probability of the flux J to have a direction opposite to the one predicted by Fick's law, with a matter flow from higher to lower concentration (this direction will be the called forward direction). Seitaridou et al. found that the ratio between the probability of having a forward flux $(\boldsymbol{J})$ and the probability of having a backward flux $(-\boldsymbol{J})$ of the same modulus is given by

$$\frac{\Pr(J)}{\Pr(-J)} = \exp\left\{\frac{2\langle J\rangle}{\langle(\delta J)^2\rangle}\cdot J\right\}. \tag{5.77}$$

For large flux values, the probability of a backward flux is exponentially negligible.

Though derived from different arguments, it is interesting to note that this result can be directly obtained from the expression of the extended non-equilibrium entropy, by considering an average flux $\langle\boldsymbol{J}\rangle$ and by comparing the entropy of a forward and backward instantaneous fluxes $\boldsymbol{J}$ and $-\boldsymbol{J}$ respectively. It is convenient to use as a potential for the fluctuations the Legendre transform of the non-equilibrium entropy with respect to the diffusion flux, namely,

$$\tilde{s} \equiv s(u,\boldsymbol{J}) - \left(\frac{\partial S}{\partial \boldsymbol{J}}\right)\cdot\boldsymbol{J} = s_{\mathrm{eq}}(u) - \frac{1}{2}\alpha\boldsymbol{J}\cdot\boldsymbol{J} + \alpha\langle\boldsymbol{J}\rangle\cdot\boldsymbol{J}, \tag{5.78}$$

whose extreme value with respect to $\boldsymbol{J}$ is found at $\boldsymbol{J} = \langle\boldsymbol{J}\rangle$; α is defined by $\alpha = \tau/(D'T)$, as mentioned in (5.76).

Using Boltzmann's relation between probability and entropy, we may write

$$\Pr(+\boldsymbol{J}) \propto \exp\left[\frac{1}{k_{\mathrm{B}}}\left(s_{\mathrm{eq}} - \frac{1}{2}\alpha\boldsymbol{J}\cdot\boldsymbol{J} + \alpha\langle\boldsymbol{J}\rangle\cdot\boldsymbol{J}\right)\right], \tag{5.79a}$$

$$\Pr(-\boldsymbol{J}) \propto \exp\left[\frac{1}{k_{\mathrm{B}}}\left(s_{\mathrm{eq}} - \frac{1}{2}\alpha\boldsymbol{J}\cdot\boldsymbol{J} - \alpha\langle\boldsymbol{J}\rangle\cdot\boldsymbol{J}\right)\right], \tag{5.79b}$$

from which follows relation (5.77), after recalling that $\left\langle(\delta\boldsymbol{J})^2\right\rangle = k_{\mathrm{B}}/\alpha$. This derivation is interesting because (5.77) is not only valid for the diffusion flux, but also for other fluxes, as heat flux, electric current or viscous pressure. Ghosh et al. (2006) derived relation (5.77) by using the maximum entropy approach under the conditions of an average number of particles and an average diffusion flux, thus leading to a thermodynamic potential (which they called "calibre", following Jaynes) which depends on the diffusion flux.

Expressions analogous to (5.77), relating the probability of forward and backward processes in non-equilibrium steady states have been the subject of several studies. One of them consists in exploring the entropy changes in forward and backward direction respectively $\Pr(\Delta S)/\Pr(-\Delta S)$ (Evans and Searles 2002).

5.8 Problems

5.1. When the relaxation time of the distribution function is not a constant but a function of the peculiar (or relative) velocity $\boldsymbol{C}$, the Green–Kubo relations for the thermal conductivity and the shear viscosity yield

$$\lambda = (k_\mathrm{B}T^2)^{-1}V\langle\tau(C)\mathcal{Q}_x(C)\mathcal{Q}_x(C)\rangle,$$
$$\eta = (k_\mathrm{B}T^2)^{-1}V\langle\tau(C)\mathcal{P}^v_{xy}(C)\mathcal{P}^v_{xy}(C)\rangle,$$

with $\mathcal{Q}_x = (\frac{1}{2}mC^2 - \frac{5}{2}k_\mathrm{B}T)C_x$ and $\mathcal{P}^v_{xy} = mC_xC_y$. (a) Show that these expressions coincide with those derived from the relaxation-time approximation of the kinetic theory when τ depends on C. (b) Compare the values of λ and of η obtained when τ is assumed to be a constant and when $\tau(C)$ varies as C^{-1}.

5.2. Consider a non-ideal monatomic gas whose particles interact through a potential $\phi(\boldsymbol{r}_{ij})$ which depends only on the distance $\boldsymbol{r}_{ij}$ between the molecules, $\boldsymbol{r}_{ij}$ being the vector from particle i to particle j. The pressure tensor $\mathbf{P}$ is $\mathbf{P} = \mathbf{P}_c + \mathbf{P}_p$, with $\mathbf{P}_c$ and $\mathbf{P}_p$ being kinetic and potential contributions, as obtained from (5.62) and (5.63). The entropy of the system is given by (5.69). (a) Show that

$$\langle\delta P^v_{c12}\delta P^v_{c12}\rangle = k_\mathrm{B}T\eta_c/\tau_c,$$
$$\langle\delta P^v_{p12}\delta P^v_{p12}\rangle = k_\mathrm{B}T\eta_p/\tau_p,$$

with η_c and η_p the kinetic and potential contributions to the shear viscosity, and τ_c and τ_p the respective relaxation times of $\overset{0}{\mathbf{P}}{}^v_c$ and $\overset{0}{\mathbf{P}}{}^v_p$. (b) Show that

$$\langle\delta P^v_{c12}\delta P^v_{c12}\rangle = k_\mathrm{B}pT,$$
$$\langle\delta P^v_{c12}\delta P^v_{c12}\rangle = k_\mathrm{B}pT\left(\frac{4}{15}Y_1 + \frac{1}{15}Y_2\right),$$

with Y_1 and Y_2 given by

$$Y_1 = 2\pi n/(k_\mathrm{B}T)\int g_\mathrm{eq}\phi' r^3 dr,\ Y_2 = 2\pi n/(k_\mathrm{B}T)\int g_\mathrm{eq}\phi'' r^4 dr,$$

where g_eq is the equilibrium pair-correlation function. (*Hint:* use expression (4.69) for the entropy of a dilute gas with interactions),

5.3. The internal energy and the entropy of a photon gas at equilibrium are $U = aT^4V$ and $S = \frac{4}{3}aT^3V$, with $a = \frac{8}{15}\pi^5 k_B^4/(c^3h^3)$. (a) Using the first of expressions (5.56), show that the entropy of a photon gas under a radiative heat flux q is, up to the second order,

$$S = \frac{4}{3}a^{1/4}U^{3/4}V^{1/4} - \frac{3}{8}a^{1/4}U^{-5/4}V^{9/4}q^2.$$

(b) Obtain an expression for $\theta - T$ for this system, with θ the non-equilibrium absolute temperature defined in Sect. 3.2.

5.4. The photon mean free path in photon–electron mixtures is given by $\ell = (n\sigma_T)^{-1}$, with n being the number of electrons per unit volume and σ_T the Thomson scattering cross-section $\left(\sigma_T = \frac{8}{3}\pi e^4/\left(m_e^2c^4\right) = 6.65 \times 10^{-29}\mathrm{m}^2\right)$. According to (5.56) and neglecting the collisions of photons with protons, because of their much smaller scattering cross-section, evaluate the photon mean free path, the thermal conductivity, and the shear viscosity of a radiative gas at 3,000 K composed of photons and electrons (and protons) with $n = 4 \times 10^3\,\mathrm{m}^{-3}$.

5.5. In a mixture of radiation and non-relativistic matter, the pressure is $p = \frac{1}{4}aT^4 + nk_BT$ and the energy density $\varepsilon = aT^4 + \frac{3}{2}nk_BT + nm_0c^2$, with n being the number of particles per unit volume and m_0 the rest mass of the particles. Taking into account that $(\partial p/\partial\varepsilon)_n = (\partial p/\partial T)_n(\partial pT/\partial\varepsilon)_n$, obtain the bulk viscosity of the mixture from expression (5.57). Show that in the ultrarelativistic limit (i.e. vanishing n) the bulk viscosity is zero.

5.6. Assume that $\boldsymbol{a}(t)$ denotes a set of random variables satisfying a Langevin-like equation

$$\dot{\boldsymbol{a}} + \mathbf{H}\cdot\boldsymbol{a} = \boldsymbol{f}$$

with $\mathbf{H}$ a constant matrix and $\boldsymbol{f}$ a white noise such that

$$\langle \boldsymbol{f}(t)\rangle = 0,$$
$$\langle \boldsymbol{f}(t')\boldsymbol{f}^T(t)\rangle = \gamma\delta(t-t').$$

(a) Show that the matrix γ must satisfy the fluctuation–dissipation relation

$$\mathbf{H}\cdot\sigma + \sigma\cdot\mathbf{H}^T = \gamma$$

with $\sigma(t) = \langle\delta\boldsymbol{a}(t)\delta\boldsymbol{a}^T(t)\rangle$. (b) Prove relation (5.41b).

5.7. In a rigid heat conductor, the generalised entropy $s(u,\boldsymbol{q})$ is written as

$$s(u,\boldsymbol{q}) = s_{\mathrm{eq}}(u) - \tau(2\rho\lambda T^2)^{-1}\boldsymbol{q}\cdot\boldsymbol{q}.$$

In a steady state, where $\boldsymbol{q} = -\lambda\nabla T$, it is given as

$$s(u,\nabla u) = s_{\mathrm{eq}}(u) - \tau\lambda(2\rho c_v^2T^2)^{-1}\nabla u\cdot\nabla u,$$

where $u = c_v T$ and c_v is the specific heat capacity at constant volume considered here as a constant. In terms of energy fluctuations, the second differential of the entropy reads

$$\delta^2 s = \frac{1}{c_v T^2}(\delta u)^2 - \left(\frac{\tau\lambda}{2\rho c_v^2 T^2}\right)\nabla\delta u \cdot \nabla\delta u.$$

Show that

$$\langle \delta u(\boldsymbol{r})\delta u(\boldsymbol{r}+\boldsymbol{r}')\rangle = k_{\mathrm{B}} c_v T^2 (\xi^2 r')^{-1}\exp(-r'/\xi),$$

where ξ stands for $(\tau\lambda/\rho c_v)^{1/2}$ and has the meaning of a correlation length. Note that in the limit $\xi \to 0$ the well-known result $\langle \delta u(\boldsymbol{r})\delta u(\boldsymbol{r}+\boldsymbol{r}')\rangle = k_{\mathrm{B}} c_v T^2 \delta(r')$ is recovered. (*Hint*: Calculate the second moments of the Fourier components $|\delta u_k|$.) (See H. Sato, Physica B **97** (1979) 194 for an application to $1/f$ noise.)

5.8. Show how to obtain (5.52) from (5.51) for a monatomic ideal gas by following the procedure indicated in Sect. 5.2. Check that the result is the same for classical and quantum gases.

5.9. Assume that third-order terms of the form $\overset{0}{\mathbf{P}}{}^v : \overset{0}{\boldsymbol{qq}}$ were included in the extended entropy, such that

$$s = s_{\mathrm{eq}} - \frac{1}{2}\alpha_1 \boldsymbol{q}\cdot\boldsymbol{q} - \frac{1}{2}\alpha_2 \overset{0}{\mathbf{P}}{}^v : \overset{0}{\mathbf{P}}{}^v - \alpha'' \overset{0}{\mathbf{P}}{}^v : \overset{0}{\boldsymbol{qq}}\,.$$

(a) Prove that according to fluctuation theory (Callen 1985), the coefficient of the third-order terms may be expressed as a function of the third-order moments of the fluctuations of the corresponding fluxes as

$$\alpha'' = -k_{\mathrm{B}}^{-2}\alpha_2\alpha_1^2\langle \delta q_x \delta P^v_{xy}\delta q_y\rangle.$$

(b) By using this expression and following the procedure indicates in Sect. 5.2 show that for an ideal monatomic gas this coefficient is

$$\alpha'' = -\frac{9}{25}m(n^2 k_{\mathrm{B}}^3 T^4)^{-1}.$$

(See Jou, Casas-Vázquez (1983))

5.10. An analogous third-order coupling between viscous pressure and diffusion flux as that considered between viscous pressure tensor and heat flux in problem 5.9 is interesting in the analysis of the structure factor of polymer solutions under shear flow (see Criado-Sancho et al. (1999)). Following the procedure indicated in the Problem 5.9, find the expression to the corresponding coefficient in terms of third-order moments of fluctuations and evaluate it.

5.11. The fluctuations of the diffusion flux may be examined in a simple one-dimensional model composed of two reservoirs with N_1 and N_2 particles, respectively (Ghosh et al. (2006)). We discretize the time in intervals Δt, and assume that the probability that a particle jumps from one reservoir to the other in the time interval Δt is p, independent of time. We assume that all jumps are independent from each other.

(a) Show that the average net flux of particles from reservoir 1 to 2 is

$$\langle J(t) \rangle = p\frac{N_1(t) - N_2(t)}{\Delta t}.$$

Rewriting $N_1 - N_2 = (c_1 - c_2)\,\Delta x$, with c_i the concentration of particles per unit length in subsystem i and Δx the spatial separation of the systems, and defining $D = p(\Delta x)^2/\Delta t$ as the diffusion coefficient, check that the above expression for the particle flux corresponds to Fick's law.

(b) Show that the variance of the fluctuations of the diffusion flux is

$$\left\langle (\delta J)^2 \right\rangle = p(1-p)\frac{N}{(\Delta t)^2}$$

with $N = N_1 + N_2$.

(c) Show that for a high number of particles, the probability of fluctuations of J for given N_1 and N_2 is

$$\Pr(J) = \frac{1}{\sqrt{2\pi p(1-p)N}} \exp\left\{ -\frac{[J - p(N_1 - N_2)]^2}{2p(1-p)N} \right\}$$

Note that fluctuations around equilibrium correspond to $N_1 = N_2$.

Chapter 6
Information Theory

Information theory was first introduced in statistical mechanics by Jaynes in 1957 (see Jaynes 1963) and from then on has found many applications (Levine and Tribus 1979; Grandy 1988; Zubarev et al. 1997; Eu 1998; Luzzi et al. 2001, 2002). Here we discuss the main basic points underlying the theory and apply them to the analysis of the foundations of extended irreversible thermodynamics (EIT). There is a strong analogy between EIT and some formulations of information theory because information is measured by means of a generalised entropy depending on the various (equilibrium and non-equilibrium) constraints acting on the system. Moreover, information theory is not limited to the quadratic order of approximation and opens therefore an avenue to highly non-linear descriptions.

One of the problems in the information theory is the physical identification of the multipliers which are introduced for taking account of the constraints. At equilibrium, the nature of these Lagrange multipliers is elucidated by comparing the microscopic expression for the differential of the entropy with the macroscopic Gibbs equation. One problem out of equilibrium is to find the corresponding macroscopic Gibbs equation with an unambiguous identification of the non-classical parameters related to non-equilibrium constraints. EIT is the only theory which, at the present time, provides such a Gibbs equation.

For simplicity, we focus our analysis on steady states, which are the most direct generalisation of equilibrium states. Usually, information is incorporated in the study of the behaviour of the variables to obtain predictions about their most probable future evolution; this leads in a natural way to the formulation of the transport equations (Robertson 1967; Schlögl 1980; Luzzi et al. 2001). Here we are more interested in enlarging the concept of Gibbs ensembles to non-equilibrium states, thus providing a further basis for the understanding of the non-equilibrium entropy and the equations of state of EIT.

6.1 Basic Concepts

Consider a system of N particles characterized by their positions and momenta, $\Gamma_N = \{\boldsymbol{r}_1, \boldsymbol{p}_1, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_N\}$. Assume that we have instruments measuring the local mean values $\langle \boldsymbol{A}_i \rangle$ of a set of extensive observables $\boldsymbol{A}_i(\Gamma_N)$. The problem is to

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_6,

obtain the probability density $f_N(\Gamma_N)$ which maximizes the information about the system compatible with some measured quantities. In other words, the objective is to determine the probability density which maximizes the global entropy S defined by

$$S = -k_{\mathrm{B}}(h^{3N}N!)^{-1}\int f_N(\Gamma_N)\ln f_N(\Gamma_N)\mathrm{d}\Gamma_N, \tag{6.1}$$

subject to the constraint

$$(h^{3N}N!)^{-1}\int f_N(\Gamma_N)\mathrm{d}\Gamma_N = 1, \tag{6.2a}$$

$$(h^{3N}N!)^{-1}\int f_N(\Gamma_N)\boldsymbol{A}_i(\Gamma_N)\mathrm{d}\Gamma_N = \langle \boldsymbol{A}_i\rangle \quad (1 = 1, 2, \ldots), \tag{6.2b}$$

with specified values for the mean values $\langle \boldsymbol{A}_i\rangle$ of the observables $\boldsymbol{A}_i$ at any point $\boldsymbol{r}$. In (6.1–6.2a) $\mathrm{d}\Gamma_N = \mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{p}_1\cdots\mathrm{d}\boldsymbol{r}_N\mathrm{d}\boldsymbol{p}_N$ is the volume element in the phase space, h the Planck constant, and k_{B} the Boltzmann constant.

The choice of a correct set of observables plays an important role in the formalism; an incomplete set of variables leads to an unsatisfactory distribution function. The choice of variables depends both on theoretical arguments and on the degree of experimental accurateness one wants to ascribe. Information theory requires an adequate selection of the set of variables to give rise to satisfactory predictions and, therefore, does not correspond to a purely subjective choice of the variables. The choice of variables in non-equilibrium situations remains a problem which needs further developments (Vasconcellos et al. 1991; Luzzi et al. 1998, 2001).

According to the well-known Lagrange procedure, to achieve the maximization of S subject to constraints (6.2a), one has to maximize the quantity

$$S - (k_{\mathrm{B}}h^{3N}N!)^{-1}\int f_N\left\{\lambda_0 + \sum\nolimits_i [\boldsymbol{A}_i(\Gamma_N) - \langle \boldsymbol{A}_i\rangle]\cdot\boldsymbol{\lambda}_i\right\}\mathrm{d}\Gamma_N, \tag{6.3a}$$

where the $\boldsymbol{\lambda}_i$ are the Lagrange multipliers corresponding to the quantities $\boldsymbol{A}_i$ and the middot indicates a scalar product. In inhomogeneous systems, $\langle \boldsymbol{A}_i\rangle$ depend on the position and consequently the Lagrange multipliers λ_i must be also functions of the position. Since $\langle \boldsymbol{A}_i\rangle$ have fixed values and are not subject to variation, maximization of (6.3a) is equivalent to maximize

$$-k_{\mathrm{B}}\int\left[f_N\ln f_N + f_N\lambda_0 + f_N\sum\nolimits_i \lambda_i\cdot\boldsymbol{A}_i(\Gamma_N)\right]\mathrm{d}\Gamma_N, \tag{6.3b}$$

In (6.3), λ_0 is the Lagrange multiplier accounting for normalization, and in what follows subscript i starts with $i = 1$. In EIT the quantities $\boldsymbol{A}_i$ are identified with the internal energy, the particle density and the fluxes. For instance, a simple situation would consist of a closed system with internal energy U subjected to a heat flow Q; in this case, the constraints are U and Q (Fig. 6.1).

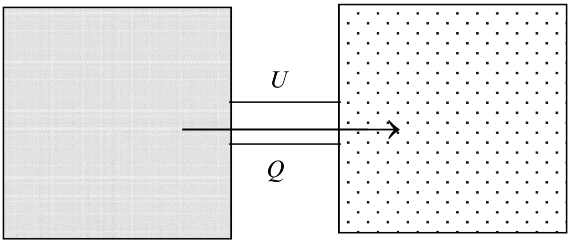


Fig. 6.1 A closed system is placed between two thermal reservoirs at different temperatures. The constraints on the system are the mean values of the energy U and heat flux Q

Expression (6.3b) is an extremum under the condition that f_N satisfies

$$\frac{\delta}{\delta f_N}\left[f_N \ln f_N + f_N \lambda_0 + f_N \sum\nolimits_i \boldsymbol{\lambda}_i \cdot \boldsymbol{A}_i(\Gamma_N)\right] = 0, \tag{6.4}$$

with δ being a functional derivative. This yields

$$f_N = Z^{-1} \exp\left[-\sum\nolimits_i \boldsymbol{\lambda}_i \cdot \boldsymbol{A}_i(\Gamma_N)\right], \tag{6.5}$$

where

$$Z = \left(h^{3N} N!\right)^{-1} \int \exp\left[-\sum\nolimits_i \boldsymbol{\lambda}_i \cdot \boldsymbol{A}_i(\Gamma_N)\right] \mathrm{d}\Gamma_N \tag{6.6}$$

is a generalised partition function that follows from the normalization condition for f_N.

The Lagrange multipliers are derived from the constraints (6.2a). The latter may be written in the compact form

$$-\frac{\partial \ln Z}{\partial \boldsymbol{\lambda}_i} = \langle \boldsymbol{A}_i \rangle, \tag{6.7}$$

as follows from definition (6.6) of Z and relations (6.2a). Introduction of the distribution density (6.5) in the definition (6.1) for the entropy results in

$$S = k_\mathrm{B}\left[\ln Z + \sum\nolimits_i \lambda_i \cdot \langle \boldsymbol{A}_i \rangle\right]. \tag{6.8}$$

In equilibrium, one may take as observable quantity the energy U of the system, $A(\Gamma_N) = \mathcal{H}(\Gamma_N)$, where $\mathcal{H}(\Gamma_N)$ is the microscopic Hamiltonian operator with $\langle \mathcal{H}(\Gamma_N) \rangle = U$. The distribution function (6.5) is then the one corresponding to the canonical ensemble

$$f_N = Z^{-1} \exp\left[-\beta \mathcal{H}(\Gamma_N)\right], \tag{6.9}$$

where we have written $\lambda_1 = \beta$, as it is usual in statistical mechanics. If in addition to the energy the number of particles is chosen as an observable quantity with a specified mean value, the distribution function takes the form

$$f_N = Z^{-1} \exp\left[-\beta \mathcal{H}(\Gamma_N) - \alpha N'\right], \tag{6.10}$$

with N' being the microscopic particle-number operator.

Up to now, the Lagrange multipliers α and β of (6.9) or (6.10) are not assigned a physical meaning. In view to their physical interpretation, let us take the differential expression of (6.8), namely

$$\mathrm{d}S = k_\mathrm{B} \sum_i \boldsymbol{\lambda}_i \cdot \mathrm{d}\langle \boldsymbol{A}_i \rangle + k_\mathrm{B} \sum_i \langle \boldsymbol{A}_i \rangle \cdot \mathrm{d}\boldsymbol{\lambda}_i + k_\mathrm{B} \mathrm{d} \ln Z = k_\mathrm{B} \sum_i \boldsymbol{\lambda}_i \cdot \mathrm{d}\langle \boldsymbol{A}_i \rangle. \tag{6.11}$$

The second equality follows from differentiating the expression (6.6) for Z with respect to the Lagrange multipliers, which results in $\mathrm{d} \ln Z = -\sum_i \langle \boldsymbol{A}_i \rangle \cdot \mathrm{d}\boldsymbol{\lambda}_i$. By identification of (6.11) with the Gibbs equation of classical thermodynamics,

$$\mathrm{d}S = T^{-1} \mathrm{d}U - \mu T^{-1} \mathrm{d}N, \tag{6.12}$$

one is led to the identifications

$$\beta = 1/(k_\mathrm{B} T), \quad \alpha = -\mu/(k_\mathrm{B} T),$$

with T being the absolute temperature and μ the chemical potential.

In a non-equilibrium state characterized by $\mathbf{P}^v$ and $\boldsymbol{q}$ as additional variables, one should write

$$\mathrm{d}S = k_\mathrm{B} \beta \mathrm{d}U + k_\mathrm{B} \alpha \mathrm{d}N + k_\mathrm{B} \boldsymbol{\lambda}_{\mathbf{P}^v} : \mathrm{d}\mathbf{P}^v + k_\mathrm{B} \lambda_{\boldsymbol{q}} \cdot \mathrm{d}\boldsymbol{q}. \tag{6.13}$$

Note that the Lagrange multipliers $\boldsymbol{\lambda}_{\mathbf{P}^v}$ and $\boldsymbol{\lambda}_q$ do not have any analogue in classical thermodynamics and therefore cannot be identified in an equilibrium theory. In EIT, such a Gibbs equation is given by (3.11) and after comparison with (6.13) allows us to identify the Lagrange multipliers, up to second order in the fluxes, as

$$\beta = \frac{1}{k_\mathrm{B}\theta}, \ \alpha = -\frac{\mu}{k_\mathrm{B}\theta}, \ \lambda_{\mathbf{P}^v} = -\frac{\tau_2 V}{2 k_\mathrm{B} \eta T} \mathbf{P}^v, \ \lambda_{\boldsymbol{q}} = -\frac{\tau_1 V}{k_\mathrm{B} \lambda T^2} \boldsymbol{q}. \tag{6.14}$$

The main point of interest of the foregoing analysis is the possibility of computing an entropy depending on the constraints acting on the system. In non-equilibrium steady states, typical constraints are the thermodynamic fluxes and forces, which thus may be introduced as variables in expression (6.8) for the entropy. Whether the above fluxes allow describing the system with sufficient details cannot be answered a priori, but by comparison with experiments.

It is worth noting that an expression for the entropy flux may be obtained in a way similar to that leading to (6.11) (Domínguez and Jou 1995b). The entropy flux is defined as

$$\boldsymbol{J}^s = -\frac{k_\mathrm{B}}{h^{3N}N!}\int f_N \ln f_N \sum_k (\boldsymbol{v}_k - \langle \boldsymbol{v}\rangle)\,\mathrm{d}\Gamma_N, \tag{6.15}$$

with $\boldsymbol{v}_k$ the velocity of particle k and $\langle \boldsymbol{v}\rangle$ the average velocity. Introducing into (6.15) the expression (6.5) for f_N and denoting by $\mathbf{J}^{A_i}$ the flux of the variable $\boldsymbol{A}_i$, namely

$$\mathbf{J}^{A_i} = -\frac{k_\mathrm{B}}{h^{3N}N!}\int f_N \boldsymbol{A}_i \sum_k (\boldsymbol{v}_k - \langle \boldsymbol{v}\rangle)\mathrm{d}\Gamma_N, \tag{6.16}$$

one finds in a direct way

$$\boldsymbol{J}^s = k_\mathrm{B}\sum_k \lambda_i \cdot \mathbf{J}^{A_i}. \tag{6.17}$$

Note that $\boldsymbol{\lambda}_i$ has the same tensorial rank as $\boldsymbol{A}_i$ whereas $\mathbf{J}^{A_i}$ is one rank higher, and thus their internal product is indeed a vector. When energy and particle fluxes are considered, the entropy flux (6.17) reduces to the classical expression $\boldsymbol{J}^s = (1/T)\boldsymbol{q} - (\mu/T)\boldsymbol{J}$, but will contain more terms if other fluxes are considered.

It is important to emphasize that the distribution function (6.5) is not the exact one, but an approximate distribution function which gives exact results for the variables taken as constraints, but not for other variables. To have a self-consistent description, one should introduce as constraints all the *slow* variables (i.e. all the variables whose time scale are of order of the time scale of observation) for internal consistency (Luzzi et al. 2002). Furthermore, expression (6.5) lacks information about the dissipation and the microscopic dynamics of the system, i.e. about the dynamics of the *fast* variables not included as constraints in the maximum-entropy description. A general approach along these lines is the so-called MaxEnt-NESOM (Non-Equilibrium Statistical Operator Method), which has been applied to several problems, but goes beyond the level of this book; the interested reader is referred to Luzzi et al. (2001, 2002).

Note that the information-theoretical methods do not specify which variables are necessary for the description of the system. In principle one should include all the variables decaying with a relaxation time comparable to the experimental time. Therefore, it is imperious to be careful in using a truncation procedure. Indeed, some systems are described by a hierarchy of variables whose relaxation times differ widely and whose higher-order variables tend to zero very fastly. In other systems, such as ideal gases, instead, all the non-conserved variables decay with almost the same value of the relaxation time, and that would indicate that, in principle, an infinite number of relaxation variables should be taken into account, and not only a finite number of them.

In this chapter we have limited our considerations to non-equilibrium steady states. Dynamical equations may also be obtained by following several approaches, such as those of Robertson (1967), Zubarev et al. (1997), the non-equilibrium statistical operator method (Luzzi et al. 2001, 2002), or the generalised projection operator of (Ichiyanagi 1990, 1991). However, the compatibility of the evolution equations with the H-theorem is, in many situations, a subject of controversy (Banach 1987; Nettleton 1990; Eu 1991).

6.2 Ideal Gas Under Heat Flux and Viscous Pressure

As a first application consider an ideal monatomic gas out of equilibrium subjected to a heat flux and a viscous pressure. This problem or closely related ones have been dealt with by several authors (Corbet 1974; Nisbet and Gurney 1974; Jou et al. 1984; Nettleton 1988). At each position, the mean values of the particle number density n, the energy density per unit volume ρu, the momentum density $\rho \boldsymbol{v}$, the heat flux $\boldsymbol{q}$, and the components of the pressure tensor $\mathbf{P}$ are supposed to be known. Since the equilibrium pressure p is fixed by u and n, the independent knowledge of $\mathbf{P}$ is a constraint on the viscous part $\mathbf{P}^v$ of the pressure tensor.

We now use the information theory to derive an expression for the non-equilibrium distribution function and the non-equilibrium entropy. We assume a one-particle distribution function f, which is satisfactory for particles moving independently because they do not interact except through instantaneous collisions.

The constraints (6.2a) on the distribution function f can be written as

$$n(r) = \int f(\boldsymbol{r}, \boldsymbol{C})\mathrm{d}\boldsymbol{C}, \tag{6.18}$$

$$\rho \boldsymbol{v}(\boldsymbol{r}) = \int mc f(\boldsymbol{r}, \boldsymbol{C})\mathrm{d}\boldsymbol{C}, \tag{6.19}$$

$$\rho u(\boldsymbol{r}) = \frac{3}{2} n k_B T(\boldsymbol{r}) = \int \frac{1}{2} m C^2 f(\boldsymbol{r}, \boldsymbol{C})\mathrm{d}\boldsymbol{C}, \tag{6.20}$$

$$\mathbf{P}^v(\boldsymbol{r}) = \int m\boldsymbol{C}\boldsymbol{C} f(\boldsymbol{r}, \boldsymbol{C})\mathrm{d}\boldsymbol{C} - pU, \tag{6.21}$$

$$\boldsymbol{q}(\boldsymbol{r}) = \int \frac{1}{2} m C^2 \boldsymbol{C} f(\boldsymbol{r}, \boldsymbol{C})\mathrm{d}\boldsymbol{C}, \tag{6.22}$$

with $\boldsymbol{C}$ the peculiar molecular velocity. Since $\mathrm{Tr}\mathbf{P}^v = 0$ in (6.21), it is inferred that the viscous pressure is zero.

In the previous section it was shown that the distribution function $f(\boldsymbol{r}, \boldsymbol{C})$ maximizing the entropy

$$\rho s(\boldsymbol{r}) = -k_\mathrm{B} \int f(\boldsymbol{r}, \boldsymbol{C}) \ln f(\boldsymbol{r}, \boldsymbol{C})\mathrm{d}\boldsymbol{C}, \tag{6.23}$$

subject to conditions (6.18–6.22) has the form

$$f = \exp\left[-\alpha - \beta \frac{1}{2} m C^2 - \boldsymbol{\lambda}_{\boldsymbol{v}} \cdot \boldsymbol{C} - \boldsymbol{\lambda}_{\mathbf{P}^v} : (m\boldsymbol{C}\boldsymbol{C} - pU) - \boldsymbol{\lambda}_{\boldsymbol{q}} \cdot \frac{1}{2} m C^2 \boldsymbol{C}\right], \tag{6.24}$$

where $\exp(-\alpha)$ designates the one-particle partition function z and the Lagrange multiplier $\boldsymbol{\lambda}_v$ has been introduced to ensure the constraint on the value of the relative velocity. The next step is to identify the coefficients α, β, $\boldsymbol{\lambda}_v$, $\boldsymbol{\lambda}_{\mathbf{Pv}}$, and $\boldsymbol{\lambda}_{\boldsymbol{q}}$. We assume that the coefficients $\boldsymbol{\lambda}_v$ $\boldsymbol{\lambda}_{\mathbf{Pv}}$ and $\boldsymbol{\lambda}_{\boldsymbol{q}}$ are small for small values of $\mathbf{P}^v$ and $\boldsymbol{q}$, an ansatz to be confirmed a posteriori. Expanding the exponential in (6.24) up to the first order in these terms results in

$$f(\boldsymbol{r},\boldsymbol{C}) = \exp\left[-\alpha - \beta\frac{1}{2}mC^2\right]\left[1 - \boldsymbol{\lambda}_v \cdot \boldsymbol{C} - \boldsymbol{\lambda}_{\mathbf{P}^v} : (m\boldsymbol{C}\boldsymbol{C} - pU) - \boldsymbol{\lambda}_q \cdot \frac{1}{2}C^2\boldsymbol{C}\right]. \tag{6.25}$$

After substitution of (6.25) in (6.18–6.22), one obtains, up to first order in the fluxes,

$$\exp[-\alpha] = n\left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2}, \quad \beta = \frac{1}{k_{\mathrm{B}}T}, \tag{6.26}$$

$$\boldsymbol{\lambda}_v = \frac{m}{pk_{\mathrm{B}}T}\boldsymbol{q},\ \boldsymbol{\lambda}_{\mathbf{P}^v} = -\frac{1}{2pk_{\mathrm{B}}T}\mathbf{P}^v,\ \boldsymbol{\lambda}_q = -\frac{2m}{5pk_{\mathrm{B}}^2T^2}\boldsymbol{q}. \tag{6.27}$$

Bearing these results in mind, (6.25) becomes

$$f(\boldsymbol{r},\boldsymbol{c}) = n\left(\frac{m}{2k_{\mathrm{B}}T}\right)^{3/2}\exp\left(-\frac{mC^2}{2k_{\mathrm{B}}T}\right)\left[1 + \frac{1}{2pk_{\mathrm{B}}T}\, m\boldsymbol{C}\boldsymbol{C} : \mathbf{P}^v \right.$$
$$\left. + \frac{2m}{5pk_{\mathrm{B}}^2T^2}\left(\frac{1}{2}mC^2 - \frac{5}{2}k_{\mathrm{B}}T\right)\boldsymbol{C}\cdot\boldsymbol{q}\right]. \tag{6.28}$$

This is nothing but the expression of the distribution function (4.36) derived within the thirteen-moment approximation, discussed in Chap. 4. The philosophy behind both formalisms is however very different. In Grad's approach, the distribution function is expanded in terms of Hermite polynomials, in such a way that higher-order terms would contain higher-order Hermite polynomials. In information theory, one takes into account the constraints on the system and limits the expansion of the exponential just to the first order. A higher-order expansion would clearly differ from the corresponding one in Grad's theory. Nevertheless, at the present order of approximation, the expressions for the entropy derived from the information theory and Grad's formalism are identical.

The results (6.14), together with the computation of the Lagrange multipliers carried out in (6.27) yield expressions for η and λ which are equivalent to those obtained in the kinetic theory. The macroscopic Gibbs equation thus appears to be a useful complement to non-equilibrium information theory.

An analysis similar to the one presented here, but focused on the diffusion flux between two discontinuous systems, has been carried out by Ghosh et al. (2006), as a basis of experimental analyses of the distribution of the fluctuations of this flux in microfluidic systems, mentioned in Chap. 5.

6.3 Ideal Gas Under Shear Flow: Non-linear Analysis

The simplest example allowing for a non-linear analysis is the problem of a classical ideal gas under shear (thermal effects are not present) (Bidar et al. 1997; Jou et al. 2001) with the constraints (6.18–6.22). For the distribution function which maximizes the entropy, the technique of Lagrange multipliers results in the following expression

$$f = z^{-1} \exp\left[-\frac{1}{2} \left(\sum_i \beta m C_i^2 + \sum_i \sum_j \lambda_{ij} m C_i C_j \right) \right], \tag{6.29}$$

where β and $\lambda_{ij} (\equiv \lambda_{P_{ij}^v})$ the Lagrange multipliers corresponding to the constraints on the energy and on the components of the viscous pressure tensor and z is the one-particle partition function. Explicit integration of the partition function z gives (see the mathematical identity (6.78))

$$z = \frac{(2\pi)^{3/2}}{m^{3/2} |\mathbf{M}|^{1/2}} \frac{V}{N}, \tag{6.30}$$

where $|\mathbf{M}|$ is the determinant of the matrix

$$M = \begin{pmatrix} \beta + 2\lambda_{11} & \lambda_{12} & \lambda_{13} \\ \lambda_{12} & \beta + 2\lambda_{22} & \lambda_{23} \\ \lambda_{13} & \lambda_{23} & \beta + 2\lambda_{33} \end{pmatrix}. \tag{6.31}$$

The Lagrange multipliers are obtained from the constraints, which may be written as

$$\rho u = -\frac{\partial \ln z}{\partial \beta}, \quad P_{ij}^v = -\frac{\partial \ln z}{\partial \lambda_{ij}}. \tag{6.32}$$

If one rewrites (6.29) in the compact form

$$f = z^{-1} \exp\left[-\frac{1}{2} \mathbf{M} : m\boldsymbol{C}\boldsymbol{C} \right], \tag{6.33}$$

and introduces this result in (6.23), it immediately follows that the expression for the entropy is given by

$$S = n k_{\mathrm{B}} \ln z + \frac{1}{2} k_{\mathrm{B}} \mathbf{M} : \mathbf{P}. \tag{6.34}$$

Furthermore, taking into account that

$$\mathbf{P} = \int m\boldsymbol{C}\boldsymbol{C} f \,\mathrm{d}\boldsymbol{C} = n\mathbf{M}^{-1},$$

and introducing $U = n\langle \frac{1}{2}mC^2\rangle$, one may write

$$\frac{1}{2}\mathbf{M} : \mathbf{P} = \beta U + \frac{1}{2}\mathrm{Tr}\left[\mathbf{U} - \beta \mathbf{P} n^{-1}\right], \tag{6.35}$$

which reduces to the equilibrium expression when $\mathbf{P} = n\beta^{-1}\mathbf{U}$. By taking into account (6.30), (6.35) and expressing $\mathbf{M}$ in terms of $\mathbf{P}$, the entropy (6.34) can be written as follows

$$\begin{aligned} S = &\ \text{const} + Nk_\mathrm{B} \ln V - \frac{3}{2}Nk_\mathrm{B} \ln \beta + \beta U \\ &+ \frac{1}{2}Nk_\mathrm{B}\{\ln[\det(\mathbf{U} + \mathbf{P}^v \beta n^{-1})] - \mathrm{Tr}(\mathbf{P}^v \beta n^{-1})\}, \end{aligned} \tag{6.36}$$

where $\mathbf{P} = n\beta^{-1}\mathbf{U} + \mathbf{P}^v$. In equilibrium, one has $\beta = 1/(k_\mathrm{B}T)$ and $\mathbf{P}^v = 0$, so that the expression for P reduces to $\mathbf{P} = nk_\mathrm{B}\, T U$, as expected. Note that (6.36) is non-linear in $\mathbf{P}^v$, and goes beyond the quadratic non-equilibrium approximation.

It is easy to express the Lagrange multipliers $\boldsymbol{\lambda}$ in terms of $\mathbf{P}^v$. Indeed, since $\mathbf{M} = \beta\mathbf{U} + \lambda$ and on the other hand $\mathbf{M} = n\mathbf{P}^{-1} = n(n\beta^{-1}\mathbf{U} + \mathbf{P}^v)^{-1}$, it follows that

$$\boldsymbol{\lambda} = \beta(\mathbf{U} + \beta n^{-1}\mathbf{P}^v)^{-1} - \beta\mathbf{U}. \tag{6.37}$$

The term within the brackets in the right-hand side of (6.37) may be expanded into a series of $\mathbf{P}^v$, and limiting this to the first term, one has

$$\boldsymbol{\lambda} \approx \beta^2 n^{-1}\mathbf{P}^v \approx -\frac{1}{nk_\mathrm{B}^2T^2}\mathbf{P}^v. \tag{6.38}$$

Introducing this result into the expression (6.11) for the Gibbs equation, written per unit mass, it is found that

$$\mathrm{d}s = k_\mathrm{B}\beta \mathrm{d}u + \frac{1}{2}k_\mathrm{B}\boldsymbol{\lambda} : \mathrm{d}\mathbf{P}^v = T^{-1}\mathrm{d}u - \frac{\tau v}{2\eta T}\mathbf{P}^v : \mathrm{d}\mathbf{P}^v. \tag{6.39}$$

From the well-known kinetic theory result $\eta = nk_\mathrm{B}T\tau$, one observes that (6.39) coincides with the macroscopic expression (3.11) except for the terms in $\mathrm{d}v$ and in $\mathrm{d}\boldsymbol{q}$ and $\mathrm{d}p^v$. This is because we have taken as variables the internal energy u and the viscous pressure $\mathbf{P}^v$ but not the volume neither the other fluxes. However, the term in $\mathrm{d}v$ can be directly obtained from the differential of (6.36), which yields $\pi/\theta = nk_\mathrm{B} = p/T$, as noted in (3.27).

When the system is submitted to a fixed shear viscous pressure P_{12}^v, corresponding to a plane Couette flow, the non-vanishing Lagrange multipliers are β and λ_{12}, and one has

$$z = \frac{(2\pi)^{3/2}}{m^{3/2}}\frac{V}{N}\left(\beta^3 - \beta\lambda_{12}^2\right)^{-1/2}. \tag{6.40}$$

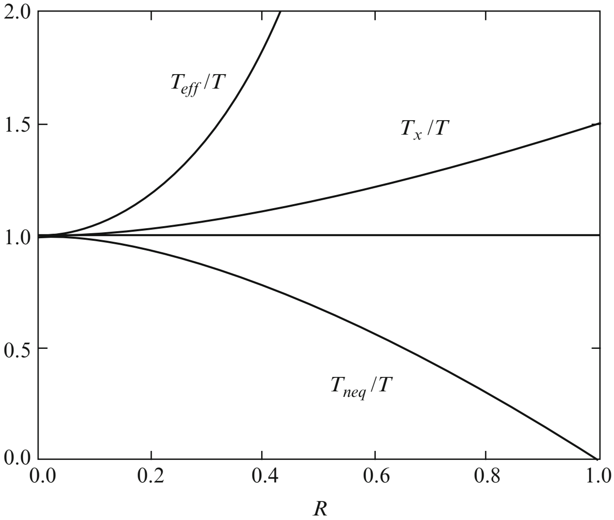


Fig. 6.2 Several temperatures in an ideal gas under Couette flow are plotted as functions of the dimensionless ratio $R = VP_{12}^v/U$. The temperatures shown are: local-equilibrium temperature T (horizontal axis), thermodynamic non-equilibrium temperature $T_{\text{neq}}(\equiv 1/k_B\beta)$; the kinetic temperature in the x and y axes $T_x = T_y$, and in the z axis, which coincides with T_{neq}; and the fluctuation–dissipation effective temperature T_{eff} (reprinted with permission from Criado-Sancho et al. (2006) Phys Lett A 350:339)

The Lagrange multipliers may be obtained in terms of u and P_{12}^v as

$$\beta = \frac{1-y}{2[R^2+(1-y)]}\frac{N}{U}, \quad \lambda_{12} = \frac{3R^2+2(1-y)}{2R[R^2+(1-y)]}\frac{N}{U}, \tag{6.41}$$

with $R = VP_{12}^v/U$ and $y = (1+3R^2)^{1/2}$. Note that near equilibrium, i.e. when λ_{12} tends to zero, we see that $\beta = \frac{3}{2}N/U$ and $\lambda_{12} = -\beta^2(V/N)P_{12}^v$. Thus, when $P_{12}^v = 0$, one recovers from (6.33) the standard Maxwell–Boltzmann distribution function with $\beta = (k_B T)^{-1}$. Instead, out of equilibrium an interesting situation appears in which several definitions of temperature yield different results (Casas-Vázquez and Jou 2003).

In Fig. 6.2 there are plotted the Lagrange multiplier β, corresponding to the reciprocal of the thermodynamic temperature; the kinetic temperature in the x and y axes (directions 1 and 2); the local-equilibrium temperature T, related to the total kinetic energy, and an effective temperature defined through a non-equilibrium fluctuation–dissipation theorem relating the viscosity the fluctuations of the viscous pressure. This illustrates the diversity of forms of the temperature out of equilibrium (Criado-Sancho et al. 2006).

The entropy has now the form of a non-linear non-quadratic expression in the fluxes, namely

$$S = S_{\text{eq}} + \frac{1}{2} N k_B \ln \frac{27R^2[R^2 - (y-1)]^2}{2(y-1)^3}, \tag{6.42}$$

where S_{eq} is the equilibrium entropy.

6.4 Ideal Gas Submitted to a Heat Flux: Non-linear Analysis

Consider an ideal non-relativistic gas at rest under fixed values of energy and heat flux. The distribution function, according to the maximum-entropy formalism, is given by (Domínguez and Jou 1995)

$$f = Z^{-1} \exp\left[-\beta \frac{1}{2} m C^2 - \boldsymbol{\gamma} \cdot \left(\frac{1}{2} m C^2 - \frac{5}{2}\beta^{-1}\right) \boldsymbol{C}\right], \tag{6.43}$$

where the factor $5/(2\beta)$ guarantees that the mean speed is zero. This distribution diverges for high values of the molecular speed, because the operator for the second term in the exponent is odd in the velocity; to avoid this divergence, let us expand (6.43) up to second order in $\boldsymbol{\gamma}$ so that

$$\begin{aligned} f = Z^{-1} \exp\left[-\beta \frac{1}{2} m C^2\right] & \left[1 - \boldsymbol{\gamma} \cdot \left(\frac{1}{2} m C^2 - \frac{5}{2}\beta^{-1}\right) \boldsymbol{C}\right. \\ & \left. + \frac{1}{2} (\boldsymbol{\gamma} \cdot \boldsymbol{C})^2 \left(\frac{1}{2} m C^2 - \frac{5}{2}\beta^{-1}\right)^2\right]. \end{aligned} \tag{6.44}$$

Grad's results are recovered if one truncates the expansion at the first-order in $\boldsymbol{\gamma}$. By keeping up to the second-order terms in $\boldsymbol{\gamma}$, one finds for β and $\boldsymbol{\gamma}$ the following expressions

$$\beta = (k_{\text{B}} T)^{-1} \left[1 + \frac{2}{5} \frac{m}{p^2 k_{\text{B}} T} \boldsymbol{q} \cdot \boldsymbol{q}\right], \tag{6.45a}$$

$$\boldsymbol{\gamma} = -\frac{2}{5} \frac{m}{p k_B^2 T^2} \boldsymbol{q}. \tag{6.45b}$$

The expression for $\boldsymbol{\gamma}$ coincides with that obtained from Grad's expansion. This is not surprising because (6.43) and (4.36) agree up to the first order. It is worth stressing that the Lagrange multiplier β is different from $(k_{\text{B}} T)^{-1}$ and that it depends on the heat flux. In Grad's approach, where second-order terms in $\boldsymbol{q}$ are omitted, one has $\beta = (k_{\text{B}} T)^{-1}$. This is the reason why the question of the difference between absolute non-equilibrium temperature and local-equilibrium temperature does not appear in kinetic theory, where the latter is always used by definition.

Note furthermore that (6.44) yields different values for the averages of v_x^2, v_y^2, and v_z^2. If the heat flux has the direction of the y axis, as in example (3.25), it is found that

$$\left\langle \frac{1}{2}mv_x^2 \right\rangle = \left\langle \frac{1}{2}mv_z^2 \right\rangle < \frac{1}{2}k_{\mathrm{B}}T, \left\langle \frac{1}{2}mv_y^2 \right\rangle > \frac{1}{2}k_{\mathrm{B}}T, \tag{6.46}$$

as derived from a different basis in Sect. 3.4.

6.5 Relativistic Ideal Gas Under an Energy Flow

As a further illustration, consider a relativistic ideal gas in a non-equilibrium steady state, with prescribed internal energy U and integrated energy flux $V\boldsymbol{q}$, where V is the volume and $\boldsymbol{q}$ the energy flux (Ferrer and Jou 1995). The distribution function maximizing the entropy reads

$$f = Z^{-1} \exp\left[-\beta \sum\nolimits_i p_i c - \boldsymbol{\gamma} \cdot \sum\nolimits_i p_i c\mathbf{c}\right], \tag{6.47}$$

where $p_i c$ is the microscopic expression for the energy of the ith particle and $p_i c\boldsymbol{c}$ is the particle contribution to the energy flow (all particles are supposed to move at the speed of light c). According to (6.6), the partition function is defined as

$$Z = \frac{V^N}{N!h^{3N}} \int \mathrm{d}\boldsymbol{p}_1 \ldots \int \mathrm{d}\boldsymbol{p}_N \exp\left[-\beta \sum\nolimits_i p_i c - \boldsymbol{\gamma} \cdot \sum\nolimits_i p_i c\boldsymbol{c}\right], \tag{6.48}$$

where the factor V^N comes out from integration over the positions of the particles. In contrast with the classical gas studied in Sect. 6.4, the distribution function (6.47) does not diverge because the dependence of the energy flux in terms of the momentum is of first order, instead of third order as for the classical gas. This allows to obtain an explicit expression for the partition function without introducing any truncation of the exponential. The explicit result for (6.48) is

$$Z = \frac{1}{N!} \left(\frac{8\pi V}{\beta^3 c^3 h^3} \right)^N \left(1 - \frac{c^2 \gamma^2}{\beta^2} \right)^{-2N}. \tag{6.49}$$

We now determine the Lagrange multipliers β and γ in terms of U and $V\boldsymbol{q}$. We obtain from the conditions on the mean energy and the mean flux, respectively,

$$U = \frac{3N}{\beta} + \frac{4N}{\beta} \frac{c^2\gamma^2}{\beta^2 - c^2\gamma^2}, \tag{6.50}$$

$$V\boldsymbol{q} = -\frac{4Nc^2\boldsymbol{\gamma}}{\beta^2 - c^2\gamma^2}. \tag{6.51}$$

Note that (6.49)–(6.51) diverge for $\gamma = \pm\beta/c$, which sets a maximum value for γ, a feature which will be commented below. Inversion of (6.50) and (6.51) yields for $\beta(U, V\boldsymbol{q}, N)$ and $\boldsymbol{\gamma}(U, V\boldsymbol{q}, N)$

$$\beta = \frac{3N}{U}\frac{1}{y-1}, \tag{6.52}$$

and

$$\gamma = \frac{3N}{Vq^2}\frac{y-2}{y-1}\boldsymbol{q}, \tag{6.53}$$

where y stands for

$$y = \left[4 - 3\left(\frac{Vq}{cU}\right)^2\right]^{1/2}. \tag{6.54}$$

It follows from (6.50–6.51) that for $V\boldsymbol{q} = 0$ one has $\boldsymbol{\gamma} = 0$ and $\beta = (k_\mathrm{B}T)^{-1}$; in addition, (6.49) reduces to the usual equilibrium expression for the partition function. In general, $V\boldsymbol{q} \neq 0$, $\beta \neq (k_\mathrm{B}T)^{-1}$, and the non-equilibrium temperature θ, is given by $\theta = T(y-1)$. Furthermore, it is seen that β and γ diverge for $y = 1$, i.e. when $V\boldsymbol{q}$ tends to Uc. This domain of validity of $V\boldsymbol{q}$ is easy to interpret, because Uc is the maximum energy flow which may be expected: it corresponds to the energy U carried at the maximum possible speed, which is precisely c.

Recalling that the entropy is given by $S = k_\mathrm{B}\,(\ln Z + \beta U + \boldsymbol{\gamma} \cdot V\boldsymbol{q})$ and taking account of (6.49) and (6.53), it is found that

$$S = S_\mathrm{eq} + Nk_\mathrm{B} \ln\left[\frac{1}{16}(y-1)(y+2)^2\right], \tag{6.55}$$

which shows that the entropy may depend on the energy flux $V\boldsymbol{q}$ in a non-quadratic way.

It is easy to obtain from (6.47) the corresponding expression for the pressure tensor, which has the general form

$$\mathbf{P} = \pi\mathbf{U} + b\boldsymbol{q}\boldsymbol{q}, \tag{6.56}$$

where the non-equilibrium pressure π is defined by $\pi/\theta = (\partial S/\partial V)_{V\boldsymbol{q},U.N}$ and b is given by the condition that $\mathrm{Tr}\mathbf{P} = 3\pi + bq^2 = 3p$, with p the local-equilibrium pressure. Note that it is the integrated energy flux $V\boldsymbol{q}$ rather than the flux $\boldsymbol{q}$ which is kept constant during differentiation. By differentiating the entropy with respect to V, one obtains for π

$$\pi = nk_\mathrm{B}\theta = \frac{1}{3}\frac{U}{V}(y-1), \tag{6.57a}$$

and consequently

$$b = -\frac{1}{q^2}(y-2). \tag{6.57b}$$

Inserting these two expressions into (6.56) leads to

$$\mathbf{P} = \frac{1}{3}\frac{U}{V}\left[(y-1)\mathbf{U} - \frac{1}{q^2}(y-2)\boldsymbol{q}\boldsymbol{q}\right]. \tag{6.58}$$

Observe that for $y = 2$, the pressure tensor reduces to $P = \frac{1}{3}(U/V)U = pU$ which is the equilibrium pressure tensor. The term in $\boldsymbol{qq}$ becomes dominant when the energy flux approaches $\boldsymbol{c}U$ (i.e. $y \to 1$) and plays an important role in radiation hydrodynamics, where the pressure tensor is written as (Mihalas and Mihalas 1985)

$$\mathbf{P} = \frac{U}{V}\left(\frac{1-\chi}{2}\mathbf{U} + \frac{3\chi - 1}{2}\frac{\boldsymbol{qq}}{q^2}\right), \tag{6.59}$$

χ being the so-called Eddington factor. By comparison of (6.58) and (6.59), one has

$$\chi = \frac{5-2y}{3}. \tag{6.60}$$

This expression for the Eddington factor has also been obtained by Anile et al. (1991) on arguments based on a rational formulation of EIT, and by requirements of Lorentz invariance (see Problem 17.2) (Levermore 1996; Domínguez-Cascante and Faraudo 1996).

Let us briefly comment about the behaviour of the entropy when the energy flux approaches its maximum value. According to (6.55), the entropy is diverging instead of vanishing, as a result of using classical rather than quantum statistics. If one wishes to study electromagnetic radiation, the relevant statistics is that of Bose–Einstein and one should maximize the corresponding expression for the entropy, namely

$$S = -k_{\mathrm{B}}\left(h^{3N}N!\right)^{-1}\int [f\ln f - (1+f)\ln(1+f)]\mathrm{d}\Gamma. \tag{6.61}$$

This yields for the distribution function

$$f = [\exp(\beta pc + \boldsymbol{\gamma}\cdot pc\mathbf{c}) - 1]^{-1}. \tag{6.62}$$

Here, we do not consider a fixed number of particles because we are dealing with photons whose particle number is not fixed. The calculations of β and γ are rather cumbersome (Larecki 1993) and the final results are

$$\beta = \frac{1}{2k_{\mathrm{B}}}\left(\frac{aV}{U}\right)^{1/4}\frac{(y+2)^{1/2}}{(y-1)^{3/4}}, \tag{6.63}$$

and

$$\boldsymbol{\gamma} = -\frac{3}{4}\left(\frac{a}{V}\right)^{1/4}\frac{V\boldsymbol{q}}{c^2U^2}\frac{1}{(y+2)^{1/2}(y-1)^{3/4}}. \tag{6.64}$$

Here, a is the radiation constant appearing in the well known expression $U = aT^4V$ for the internal energy of radiation at equilibrium. Now expression (6.61) for the entropy becomes

$$\frac{S}{V} = \frac{2}{3} a^{1/4} \left(\frac{U}{V} \right)^{3/4} (y-1)^{1/4} (y+2)^{1/2}, \tag{6.65}$$

which tends to the expected value $S/V = \frac{4}{3} a T^3$ at equilibrium ($V\boldsymbol{q} = 0$) and which vanishes for $V^2 q^2 \to c^2 U^2$.

6.6 Heat Flow in a Linear Harmonic Chain

Harmonic chains are ideal systems which shed an original light on thermodynamics. Heat flow in harmonic chains coupled at each end to heat reservoirs at different temperatures has been studied in Spohn and Lebowitz (1977), Miller and Larson (1979) and many others. In a harmonic chain, the phonon mean free path is infinite, so that the energy flux along it is not proportional to the temperature gradient but to the temperature difference between the reservoirs located at its ends.

To avoid complications associated with the boundary conditions, Miller and Larson (1979) eliminate the boundaries by considering that chain ends are linked together to form a ring. In this case, the system turns out to be a 'superconductor' of thermal energy, because of its infinite heat conductivity: a heat flux lasts indefinitely, without appealing to boundary reservoirs to sustain it. Such a chain ring is characterized by the constraints

$$\langle \mathcal{H} \rangle = U, \quad \langle \mathcal{J} \rangle = Q, \tag{6.66}$$

where $\mathcal{H}$ is the Hamiltonian of the system, $\mathcal{J}$ the heat flux operator, U the mean (internal) energy of the chain, and Q the mean heat flux along the ring.

The system consists of a linear chain of N particles, each of mass m. Each particle is connected to its nearest neighbours by Hookean springs with stiffness κ. The Nth particle is connected by a spring to the first particle, so that the chain forms a closed ring. One may choose a system of dimensionless quantities where the mass is expressed in terms of m, time in units of $(m/\kappa)^{1/2}$, and energy in units of $h(2\pi)^{-1}(\kappa/m)^{1/2}$. Let q_α be the displacement from equilibrium for each particle $\alpha(\alpha = 1, \ldots, N)$ and p_α its conjugate momentum.

The Hamiltonian $\mathcal{H}(q_1, p_1, \ldots, q_N, p_N)$ is given by

$$\mathcal{H} = \frac{1}{2} \sum_\alpha p_\alpha^2 + \frac{1}{2} \sum_\alpha (q_{\alpha+1} - q_\alpha)^2. \tag{6.67}$$

The microscopic operator $\mathcal{J}(q_1, p_1, \ldots, q_N, p_N)$ for the heat flux is

$$\mathcal{J} = -\frac{1}{2} N \sum_\alpha (q_{\alpha+1} p_\alpha - q_\alpha p_{\alpha+1}). \tag{6.68}$$

To obtain this form for $\mathcal{J}$ consider that the system is mentally divided into a right sub-system and a left subsystem. We may identify all the particles with labels $\alpha > \gamma$ where γ is fixed) as the right subsystem, and those with labels $\alpha \leq \gamma$ as the left subsystem. The two subsystems interact via a single coupling spring. Half of the potential energy of the coupling spring is attributed to each subsystem. Let $\mathcal{J}_\alpha$ be the net rate of increase of the energy of the subsystem characterized by $\alpha > \gamma$. It is given by the rate of work performed on it by the coupling spring, $-(q_{\gamma+1}-q_\gamma)p_{\gamma+1}$, plus half the rate of increase of the potential energy of the coupling spring, $\frac{1}{2}(q_{\gamma+1}-q_\gamma)(p_{\gamma+1}-p_\gamma)$. This yields

$$\mathcal{J}_\alpha = -\frac{1}{2}(q_{\alpha+1}-q_\alpha)(p_{\alpha+1}+p_\alpha). \tag{6.69}$$

Taking the average of (6.69) over all pairs gives back (6.68), because of the cancellations due to the fact that the sums are modulo N. From Hamilton's equations of motion, it is also checked that $\mathcal{J}$ is a constant of the motion.

Now we transform $\mathcal{H}$ and $\mathcal{J}$ in terms of normal coordinates η_α and canonical momenta $\xi_\alpha = \mathrm{d}\eta_\alpha/\mathrm{d}t$, which reduce the potential energy to a canonical quadratic form. The transformation matrix A relating $\boldsymbol{q}$ and $\boldsymbol{\eta}$, defined by $\boldsymbol{\eta} = \mathrm{A}\cdot\boldsymbol{q}$, is given by Goldstein (1975)

$$A_{\alpha\gamma} = N^{-1/2}[\sin(2\pi\alpha\gamma/N) + \cos(2\pi\alpha\gamma/N)]. \tag{6.70}$$

In terms of the normal coordinates, the Hamiltonian of the system becomes

$$\mathcal{H}(\eta,\xi) = \frac{1}{2}\sum_\alpha (\xi_\alpha^2 + \omega_\alpha^2\eta_\alpha^2), \tag{6.71}$$

where ω_α, the angular frequency of the α-th mode, is given by $\omega_\alpha = 2\sin(\pi\alpha/N)$. Taking into account that matrix A given by (6.70) is orthogonal and symmetric ($\mathrm{A} = \mathrm{A}^{-1}$), the heat flux operator (6.68) reads as

$$\mathcal{J} = -(1/N)\sum_\mu \sin(2\pi\mu/N)\left[\eta_\mu\xi_{N-\mu} - \eta_{N-\mu}\xi_\mu\right], \tag{6.72}$$

with $M = \frac{1}{2}N$ if N is even and $M = \frac{1}{2}(N-1)$ if N is odd. We have also used the result $\omega_\mu = \omega_{N-\mu}$, which follows from the definition of ω_α.

The dimension of the phase space of the system that we are studying is $2N$, but by assuming that the centre of mass of the system remains fixed, the dimension is reduced to $2(N-1)$. The next problem is to find the reduced probability distribution function f maximizing the entropy

$$S = -k_\mathrm{B}(h^{N-1})^{-1}\int f\ln f\,\mathrm{d}\Gamma_{N-1}, \tag{6.73}$$

subject to the constraints (6.66). Here $\mathrm{d}\Gamma_{N-1} = \mathrm{d}\eta_1\mathrm{d}\xi_1 \cdots \mathrm{d}\eta_{N-1}\mathrm{d}\xi_{N-1}$. Note that the factor $N!$ in (6.1) does not appear in (6.73) because the particles, being kept in a given order, are no longer indistinguishable.

The result for f is, as shown in Sect. 6.1,

$$f = Z^{-1}\exp(-\beta\mathcal{H} - \gamma\mathcal{J}), \tag{6.74}$$

where β and γ are the respective Lagrange multipliers and Z is the partition function

$$Z = (h^{N-1})^{-1}\int \exp(-\beta\mathcal{H} - \gamma\mathcal{J})\mathrm{d}\Gamma_{N-1}. \tag{6.75}$$

To obtain the partition function, note that both $\mathcal{J}$ and $\mathcal{H}$ can be expressed as a sum over pairs μ and $N-\mu$ of normal coordinates sharing the same characteristic frequency ω_μ, i.e. $\mathcal{J} = \sum_\mu \mathcal{J}_\mu$ and $\mathcal{H} = \sum_\mu \mathcal{H}_\mu$, with

$$\mathcal{H}_\mu = \frac{1}{2}\left[\xi_\mu^2 + \xi_{N-\mu}^2 + \omega_\mu^2\left(\eta_\mu^2 + \eta_{N-\mu}^2\right)\right], \tag{6.76a}$$

$$\mathcal{J}_\mu = N^{-1}\sin(2\pi\mu/N)(\eta_\mu\xi_{N-\mu} - \eta_{N-\mu}\xi_\mu). \tag{6.76b}$$

Consequently, the partition function can be expressed as a product $Z = \prod\limits_\mu z_\mu$ with

$$z_\mu = h^{-2}\int \mathrm{d}\eta_\mu\mathrm{d}\eta_{N-\mu}\mathrm{d}\xi_\mu\mathrm{d}\xi_{N-\mu}\exp(-\beta\mathcal{H}_\mu - \gamma\mathcal{J}_\mu). \tag{6.77}$$

To calculate these integrals one may employ the general result

$$\int \mathrm{d}\boldsymbol{r}\exp\left(\boldsymbol{R}\cdot\boldsymbol{r} - \frac{1}{2}\boldsymbol{r}\cdot\mathbf{M}\cdot\boldsymbol{r}\right) = (2\pi)^{n/2}\left(|\mathrm{M}|\right)^{-1/2}\exp\left(\frac{1}{2}\boldsymbol{R}\cdot\mathrm{M}^{-1}\cdot\boldsymbol{R}\right), \tag{6.78}$$

where $\boldsymbol{r}$ and $\boldsymbol{R}$ are n-dimensional vectors and M is a positive-definite square matrix. To evaluate z_μ, $\boldsymbol{r}$ is considered to be the four-dimensional vector with components $(\eta_\mu, \eta_{N-\mu}, \xi_\mu, \xi_{N-\mu})$, $\boldsymbol{R}$ the null vector 0, and M the matrix M_μ, given by

$$\mathrm{M}_\mu = \beta\omega_\mu\begin{pmatrix} \omega_\mu & 0 & 0 & -y_\mu \\ 0 & \omega_\mu & y_\mu & 0 \\ 0 & y_\mu & \omega_\mu^{-1} & 0 \\ -y_\mu & 0 & 0 & \omega_\mu^{-1} \end{pmatrix}, \tag{6.79}$$

where $y_\mu = y\cos(\pi\mu/N)$ and $y = \gamma(N\beta)^{-1}$. It turns out that $z_\mu = |\mathrm{M}_\mu|^{-1/2}$, so that

$$z_\mu = \beta^{-2}\omega_\mu^{-2}\left(1 - y_\mu^2\right)^{-1}. \tag{6.80}$$

The total partition function may be calculated in the thermodynamic limit by noting that $\ln Z = \sum_\mu \ln z_\mu$ may be converted into an integral in the limit of large N since $|\omega_{\mu-1} - \omega_\mu|$ becomes arbitrarily small. One finds asymptotically that

$$\begin{aligned}\ln Z = \int_0^M \ln z_\mu \mathrm{d}\mu &= -(N/\pi)\int_0^{\pi/2} \mathrm{d}\phi\, [2\ln(2\beta) + 2\ln(\sin\phi) \\ &\quad + \ln(1 - y^2\cos^2\phi)] \\ &= -N \ln\left\{\frac{1}{2}\beta\left[1 + (1-y^2)^{1/2}\right]\right\}. \end{aligned} \tag{6.81}$$

The final result for Z can be written as

$$Z = \left\{\frac{1}{2}\beta\left[1 + (1-y^2)^{1/2}\right]\right\}^N. \tag{6.82}$$

The Lagrange multipliers β and γ may be found in terms of U and Q through the constraints (6.66), which in analogy to (6.7) are expressed by

$$U = \langle\mathcal{H}\rangle = -\frac{\partial \ln Z}{\partial\beta},\ Q = \langle\mathcal{J}\rangle = -\frac{\partial \ln Z}{\partial\gamma}, \tag{6.83}$$

When (6.84) is introduced into (6.83), one obtains for β and y

$$\beta = \frac{1 + x^2}{\varepsilon(1 - x^2)},\ y = -\frac{2x}{1 - x^2}, \tag{6.84}$$

with $\varepsilon = U/N$ and $x = Q/\varepsilon$. In terms of these quantities, (6.82) becomes

$$Z = [\varepsilon(1 - x^2)]^N. \tag{6.85}$$

For $x = 0$ one recovers the usual equilibrium results, whereas for $x^2 \to 1$ both β and y diverge. Thus, the presence of a critical heat flux $Q = \varepsilon$ is outlined from the above considerations.

The entropy and the generalised Lagrange multiplier β deserve special comments. According to (6.73) and (6.74), the entropy may be written as

$$S = k_\mathrm{B}(\beta U + \gamma Q + \ln Z). \tag{6.86}$$

In the thermodynamic limit when N tends to infinity, the entropy per particle turns out to be, in view of the explicit form (6.82) of Z,

$$s = \lim_{N\to\infty}\frac{S}{N} = k_\mathrm{B}\left[1 + \ln\varepsilon + \ln(1 - x^2)\right] = s_\mathrm{eq} + k_\mathrm{B}\ln(1 - x^2). \tag{6.87}$$

As expected, the presence of the heat flux modifies the value of s. For small values of the heat flux, (6.87) reduces to

$$s(\varepsilon, Q) = s_{\text{eq}}(\varepsilon) - \frac{k_{\text{B}}}{\varepsilon^2} Q^2. \tag{6.88}$$

The dependence of this expression on the heat flux Q provides a further corroboration of the basic assertions of extended irreversible thermodynamics, stating that the entropy is a function of the heat flux out of equilibrium, and allows one to explore higher-order terms in the heat flux.

The Lagrange multiplier β can be interpreted in terms of a generalised absolute temperature θ defined as $\theta = (k_{\text{B}}\beta)^{-1}$; from (6.84) one has

$$\theta^{-1} = T^{-1}\left(\frac{1+x^2}{1-x^2}\right) = T^{-1}\left(1 + \frac{2x^2}{1-x^2}\right) \tag{6.89}$$

indicating that the generalised temperature θ differs from the usual local-equilibrium temperature T ($\equiv \varepsilon/k_{\text{B}}$) by terms at least of the order x^2 or Q. The same result can be obtained from (6.87) and the definition $\theta^{-1} = (\partial s/\partial \varepsilon)_Q$.

The entropy (6.87) diverges when $x \to 1$, i.e. when the absolute temperature $\theta = (k_{\text{B}}\beta)^{-1}$ tends to zero (in this limit the heat flux tends to the maximum value). This is so because of the use of classical statistics rather than quantum statistics. Indeed, when the non-equilibrium temperature θ becomes lower than the Einstein temperature of the lattice, it is necessary to resort to Bose–Einstein's rather than classical statistics (Camacho and Jou 1995); therefore the results obtained by Miller and Larson are no longer valid for a heat flux larger than a given value. Consider a harmonic chain with a linearized dispersion relation $\omega = c|\boldsymbol{k}|$, c being the phonon speed and $|\boldsymbol{k}|$ the magnitude of the wavevector. A quantum analysis of the system under the constraint of a fixed energy density and fixed energy flux $\boldsymbol{q}$ yields for the distribution function maximizing the entropy

$$f(k; \beta, \gamma) = \left[\exp(\beta\hbar c^2|\boldsymbol{k}| + \gamma\hbar c^2|\boldsymbol{k}|) - 1\right]^{-1}, \tag{6.90}$$

where β and γ are the Lagrange multipliers and $\hbar = h/(2\pi)$.

The entropy behaviour in the quantum limit when $\varepsilon_D(\beta \pm \boldsymbol{\gamma}\cdot\boldsymbol{c}) \gg 1$ (with ε_D the Debye energy $\varepsilon_D = \hbar c\pi/l$) is

$$s = \frac{k_{\text{B}}}{2}\left(\frac{\pi}{6\hbar}\right)^{1/2}\left[(\varepsilon c + q)^{1/2} + (\varepsilon c - q)^{1/2}\right]. \tag{6.91}$$

The Lagrange multipliers β and γ are given by

$$\begin{aligned}\beta &= \frac{1}{2}\left(\frac{\pi}{6\hbar}\right)^{1/2}\left[\frac{1}{(\varepsilon c + q)^{1/2}} + \frac{1}{(\varepsilon c - q)^{1/2}}\right]\\ &= \frac{1}{2k_{\text{B}}T}\left[\frac{1}{(1+x)^{1/2}} + \frac{1}{(1-x)^{1/2}}\right],\end{aligned} \tag{6.92}$$

$$\gamma = \frac{1}{2c}\left(\frac{\pi}{6\hbar}\right)^{1/2}\left[\frac{1}{(\varepsilon c + q)^{1/2}} - \frac{1}{(\varepsilon c - q)^{1/2}}\right]$$
$$= \frac{1}{2ck_{\mathrm{B}}T}\left[\frac{1}{(1+x)^{1/2}} - \frac{1}{(1-x)^{1/2}}\right], \tag{6.93}$$

where $T(\varepsilon) \equiv (6\hbar c\varepsilon/k_{\mathrm{B}}^2\pi)^{1/2}$ is the local-equilibrium temperature and $x = q/\varepsilon c$. At equilibrium $q = 0$ and consequently $\gamma = 0$, $\beta = (k_{\mathrm{B}}T)^{-1}$ and (6.90) becomes the equilibrium Bose–Einstein distribution function. The relation between T and ε follows from the quantum equation of state at low T, namely

$$\varepsilon = \frac{k_{\mathrm{B}}^2\pi^2}{3hc}T^2. \tag{6.94}$$

Note that the results (6.84) are not recovered in the classical limit because, in the present problem, the linearized dispersion $\omega = c|\boldsymbol{k}|$ has been used instead of the exact dispersion relation.

It is interesting to note that the expression for the specific heat at constant heat flux defined as $c_q = (\partial\varepsilon/\partial\theta)_q$ is

$$c_q = \frac{4\varepsilon^{3/2}}{k_{\mathrm{B}}^2\theta^2}\left(\frac{6\hbar c}{\pi}\right)^{1/2}\frac{(1-x^2)^{3/2}}{(1+x)^{3/2}+(1-x)^{3/2}}. \tag{6.95}$$

Note that c_q vanishes in the limit $x \to 1$, i.e. when the non-equilibrium absolute temperature θ tends to zero, and this corresponds to a third-law-like behaviour (Camacho and Jou 1995). This provides a generalization of the third law to non-equilibrium steady states: indeed, in equilibrium, θ coincides with the equilibrium temperature so that the vanishing of θ means the vanishing of T; however, in non-equilibrium, even at a non-zero value of T, θ may approach zero at sufficiently high values of the heat flux. A similar quantum behaviour at high values of the energy flux was also found by Fröhlich who analysed Bose–Einstein condensation of phonons in non-linear systems at high values of the energy flux (Fröhlich and Kremer 1983).

6.7 Information Theory and Non-equilibrium Fluctuations

Fluctuations around non-equilibrium steady states combine dynamical and statistical non-equilibrium contributions (Tremblay et al. 1981; Tremblay 1984; Ortiz de Zarate and Senger 2006). Here, we focus our attention on the statistical aspects. Information theory is particularly useful for studying the fluctuations of the variables around the non-equilibrium steady state. With this objective in mind, let us express the second moments of the macroscopic values of the observables $A_i(\Gamma_N)$ around their average values; it is straightforward to check after differentiation of (6.7) that

$$\langle (A_i(\Gamma_N) - \langle A_i \rangle)(A_j(\Gamma_N) - \langle A_j \rangle) \rangle = \frac{\partial^2 \ln Z}{\partial \boldsymbol{\lambda}_i \partial \boldsymbol{\lambda}_j}. \tag{6.96}$$

Expression (6.96) may be written in terms of the second derivatives of the generalised entropy by taking into account the mathematical relation

$$\sum_k \frac{\partial \langle A_i \rangle}{\partial \boldsymbol{\lambda}_k} \frac{\partial \boldsymbol{\lambda}_k}{\partial \langle A_j \rangle} = \delta_{ij}. \tag{6.97}$$

Using (6.7) and (6.11), (6.97) may be alternatively expressed as

$$-\frac{1}{k_{\mathrm{B}}} \sum_l \frac{\partial^2 \ln Z}{\partial \boldsymbol{\lambda}_i \partial \boldsymbol{\lambda}_l} \frac{\partial^2 S}{\partial \langle A_l \rangle \partial \langle A_j \rangle} = \delta_{ij}, \tag{6.98}$$

from which it follows that $\partial^2 \ln Z / \partial \boldsymbol{\lambda}_i \partial \boldsymbol{\lambda}_l$ is related to the inverse of the derivative $\partial^2 S / \partial \langle A_l \rangle \partial \langle A_j \rangle$; accordingly, the second moments of fluctuations may be written as

$$\langle (A_i(\mu') - \langle \boldsymbol{A}_i \rangle)(A_j(\mu') - \langle A_j \rangle) \rangle = \frac{1}{k_{\mathrm{B}}} \left[\left(\frac{\partial^2 S}{\partial \langle A \rangle \partial \langle A \rangle} \right)^{-1} \right]_{ij}. \tag{6.99}$$

This shows that the maximum-entropy formalism relates the second moments of the fluctuations of thermodynamic quantities in a non-equilibrium steady state to the second order derivatives of a generalised entropy. Formally, this is the same situation as in equilibrium; there is, however, an important difference, because the entropy function is no longer the classical one but contains as supplementary variables the fluxes acting as constraints on the system.

In the usual approaches of non-equilibrium hydrodynamic fluctuations (Tremblay et al. 1981; Tremblay 1984), it is assumed that the hydrodynamic noise, owing to fast fluctuations of $\boldsymbol{q}$ and $\mathbf{P}^v$, keeps its local-equilibrium form, as determined from the local temperature, pressure, and velocity. The intuitive argument in support of this assumption is that these fluctuations are so fast that they do not have enough time to be influenced by the non-equilibrium conditions of the system. However, if the time of decay of the fluctuations of the fluxes is not negligibly small, the noise may ‘know’ that the system is out of equilibrium and may undergo some changes.

Of course, such modifications of the noise are minute for frequencies much lower than the inverse of the relaxation times of the fluxes, as in light scattering in liquids. However, they could be perceptible at frequencies comparable to the inverse of the relaxation times, as observed in light scattering in gases or neutron scattering in liquids.

To obtain an expression for the probability of fluctuations, we define a generalised specific free energy g as

$$g = -k_{\mathrm{B}} \theta \ln Z = -\theta s + \sum_i \boldsymbol{\lambda}_i \cdot \langle A_i \rangle, \tag{6.100}$$

where $\boldsymbol{\lambda}_i$ are the Lagrange multipliers. In analogy with (6.9), the probability of fluctuations at constant $\boldsymbol{\lambda}_i$ is given by

$$W \approx \exp\left(-\frac{1}{k_{\mathrm{B}}\theta}\Delta g\right), \tag{6.101}$$

where Δg is the change in g related to the fluctuations. It is now possible to calculate the second moments of the fluctuations in non-equilibrium steady states by using the identifications (6.14) of the Lagrange multipliers $\boldsymbol{\lambda}_i$ appearing in Eq. (6.13).

As an illustration, we examine the fluctuations in a gas under a temperature gradient; viscous effects are omitted. The respective Lagrange multipliers for the energy and the heat flux in the steady state are $\beta = (k_{\mathrm{B}}\theta)^{-1}$ and $\boldsymbol{\lambda}_{\boldsymbol{q}} = \tau_1 V(k_{\mathrm{B}}T^2)^{-1}\nabla T$. We recall further that the Lagrange multiplier related to the volume is $\lambda_v = \pi(k_{\mathrm{B}}\theta)^{-1}$, where π is the generalised pressure defined by (2.42b). Thus the generalised free energy (6.100) takes the form

$$g = -\theta s + u + \pi v + \frac{\tau_1 v\theta}{T^2}\nabla T \cdot \boldsymbol{q}. \tag{6.102}$$

The first differential of g at constant values of the multipliers is

$$\delta g = -\theta\delta s + \delta u + \pi\delta v + \frac{\tau_1 v\theta}{T^2}\nabla T \cdot \delta\boldsymbol{q}, \tag{6.103}$$

or, taking into account the dependence of s with respect to u, v, and $\boldsymbol{q}$,

$$\delta g = -\theta\left(\theta^{-1}\delta u + \pi\theta^{-1}\delta v - \frac{\tau_1 v\theta}{\lambda T^2}\boldsymbol{q}\cdot\delta\boldsymbol{q}\right) + \delta u + \pi\delta v + \frac{\tau_1 v\theta}{T^2}\nabla T \cdot \delta\boldsymbol{q}. \tag{6.104}$$

It is immediately seen that this expression vanishes in the steady state where $\boldsymbol{q} = -\lambda\,\nabla T$. The second differential of g is simply $\delta^2 g = -\theta\delta^2 s$, because the last three terms of (6.102) are linear in u, v, and $\boldsymbol{q}$, and consequently (6.101) becomes an Einstein–Boltzmann relation in which s is the generalised entropy. From earlier results (see (2.29)) it follows that

$$s = s_{\mathrm{eq}} - \frac{1}{2}\alpha_1\boldsymbol{q}\cdot\boldsymbol{q}, \tag{6.105}$$

with $\alpha_1 = \tau_1 v(\lambda T^2)^{-1}$, while its second differential is

$$\begin{aligned}\delta^2 s = {}& (\theta^{-1})_u(\delta u)^2 + 2(\theta^{-1})_v\delta u\delta v + (\theta^{-1}\pi)_v(\delta v)^2 - \alpha_1\delta\boldsymbol{q}\cdot\delta\boldsymbol{q}\\ &+2\lambda(\nabla T)\alpha_{1v}\cdot\delta v\delta\boldsymbol{q} + 2\lambda(\nabla T)\alpha_{1u}\cdot\delta u\delta\boldsymbol{q}.\end{aligned} \tag{6.106}$$

When this result is inserted into (6.5), one obtains an explicit expression for the probability of the fluctuations δu, δv, and $\delta\boldsymbol{q}$. Up to second order in $\boldsymbol{q}_0 = -\lambda\nabla T$ it is found that the second moments are given by

$$\langle \delta \boldsymbol{q} \delta \boldsymbol{q} \rangle = \frac{k_{\mathrm{B}} \lambda T^2}{\tau_1 v} \left[1 + \frac{c_v T^2}{\alpha_1} \left(\frac{\partial \alpha_1}{\partial u} \right)^2 q_0^2 \right], \tag{6.107a}$$

$$\langle \delta u \delta \boldsymbol{q} \rangle = -\frac{k_{\mathrm{B}} \lambda T^2}{\tau_1 v \Delta} \boldsymbol{q}_0 \left[\left(T^{-1}\right)_v \alpha_{1v} - \left(T^{-1} p\right)_v \alpha_{1u} \right], \tag{6.107b}$$

$$\langle \delta v \delta \boldsymbol{q} \rangle = -\frac{k_{\mathrm{B}} \lambda T^2}{\tau_1 v \Delta} \boldsymbol{q}_0 \left[\left(T^{-1}\right)_v \alpha_{1u} - \left(T^{-1}\right)_u \alpha_{1v} \right], \tag{6.107c}$$

where the subscripts u and v mean the respective partial derivatives and Δ stands for

$$\Delta = \left(T^{-1}\right)_u \left(T^{-1} p\right)_v - \left(T^{-1}\right)_v^2 . \tag{6.108}$$

Two points are worth mentioning: (1) The correlations $\langle \delta u \delta \boldsymbol{q} \rangle$ and $\langle \delta v \delta \boldsymbol{q} \rangle$, which vanish at equilibrium because of the opposite time-reversal symmetry of the corresponding quantities, differ from zero out of equilibrium: this is a manifestation of the breaking of the time-reversal symmetry out of equilibrium; (2) non-equilibrium corrections of order q_0^2 appear in the second moments of the heat flux fluctuations and, as a consequence, in the hydrodynamic noise.

We can write (6.107) explicitly for a monatomic ideal gas. One has $(T^{-1}p)_v = -p(Tv)^{-1}$, $(T^{-1})_v = 0$, $(T^{-1})_u = -(c_v T^2)^{-1}$ with $c_v = \frac{3}{2} k_{\mathrm{B}}/m$. Furthermore, in (6.33) we have found that $\alpha_1 = \frac{2}{5}(k_{\mathrm{B}}^2 T^3 n^2)^{-1}$, and consequently that $\alpha_{1u} = \frac{4}{5} m (k_{\mathrm{B}}^3 T^4 n^2)^{-1}$ and $\alpha_{1v} = \frac{4}{5} m (k_{\mathrm{B}}^2 T^3 n)^{-1}$. The final expressions are thus

$$\langle \delta \boldsymbol{q} \delta \boldsymbol{q} \rangle = \frac{k_{\mathrm{B}} \lambda T^2}{\tau_1 v} \left[1 + \frac{25}{8} \pi \ell^2 (\nabla \ln T)^2 \right], \tag{6.109a}$$

$$\langle \delta u \delta \boldsymbol{q} \rangle = -2uN^{-1} \lambda \nabla T, \tag{6.109b}$$

$$\langle \delta v \delta \boldsymbol{q} \rangle = -2vN^{-1} \lambda \nabla T, \tag{6.109c}$$

where ℓ is the mean free path given by $(8k_{\mathrm{B}}T/\pi m)^{1/2}\tau_1$. These results are of the same order, but not are exactly equal to the non-equilibrium corrections which may be found from the kinetic theory of gases (Tremblay et al. 1981; Tremblay 1984; Schmitz 1988). This is not surprising because of the various approximations which have been introduced.

The above procedure, which relates a generalised thermodynamic potential to non-equilibrium fluctuations, differs from the procedure followed by some authors (Jähnig and Richter, 1976; Keizer 1987) that construct non-equilibrium thermodynamic potentials by starting from knowledge of the non-equilibrium fluctuations, as obtained from suitable dynamical equations, and using then the Einstein relation (6.5) as a definition of the potential. In contrast, we start from a thermodynamic potential and study its consequences for non-equilibrium fluctuations.

The explicit examples studied in Sects. 6.3–6.6 also exhibit the dependence on the fluxes. For instance, the second moments of the fluctuations of the energy and of the heat flux around their mean values in the harmonic chain ring studied in Sect. 6.6 are given by

$$\langle(\mathcal{H}-U)(\mathcal{H}-U)\rangle = \frac{\partial^2 \ln Z}{\partial\beta^2} = N\varepsilon^2\frac{1+x^2}{1-x^2}, \tag{6.110a}$$

$$\langle(\mathcal{J}-Q)(\mathcal{J}-Q)\rangle = \frac{\partial^2 \ln Z}{\partial\gamma^2} = \frac{\varepsilon^2}{2N}\frac{1+4x^2-x^4}{1-x^2}, \tag{6.110b}$$

$$\langle(\mathcal{H}-U)(\mathcal{J}-Q)\rangle = \frac{\partial^2 \ln Z}{\partial\beta\partial\gamma} = -2N\varepsilon^2\frac{x}{1-x^2}. \tag{6.110c}$$

The heat flux influences the second moments of fluctuations, which diverge for a critical value of the heat flux $Q = \varepsilon$. The second moments of the fluctuations of energy and heat flux vanish at equilibrium, because these quantities are of different time-reversal parity. However, the presence of a non-vanishing mean heat flux ($x \neq 0$) leads to a non-vanishing covariance, as predicted by the above macroscopic results.

6.8 Problems

6.1. The thermal conductivity of a dielectric solid is $\lambda = \frac{1}{3}\rho c_v c_0^2 \tau_1$, with c_0 the phonon speed, τ_1 the relaxation time due to resistive phonon collisions, c_v the heat capacity per unit mass, and ρ the mass density. In the Debye model c_v is proportional to T^3 at low temperatures. Starting from (6.107a), determine the second-order non-equilibrium corrections to the second moments of the fluctuations of the heat flux.

6.2. Find the non-equilibrium partition function for the distribution (6.44) for an ideal gas under a heat flux.

6.3. (a) Using the expressions (6.99) for the fluctuations and (6.40) for the entropy, obtain the second moments of the fluctuations of U and P_{12} in terms of β and λ_{12} for a classical gas in Couette shear flow studied in Sect. 6.3.

(b) Using (6.33) and (6.41) find the kinetic temperatures along the three spatial directions to this system (Criado-Sancho et al. 2006).

(c) Assuming, for the sake of simplicity, that τ and T do not depend on P_{12}^v, but that η may depend on it, find $\mu(P_{12}^v)$ from the extension of the Green-Kubo formula

$$\eta(P_{12}) \equiv \frac{\tau}{k_B T V}\,\langle \delta P_{12}^v \delta P_{12}^v \rangle_{\text{neq}},$$

$\langle\cdots\rangle_{\text{neq}}$ being the second moments out of equilibrium.

6.4. Using relation (6.99) obtain the second moments of the fluctuations of the energy and the energy flux in the relativistic gas studied in Sect. 6.5.

6.5. Using the identification for the Lagrange multiplier for the heat flux $\lambda_{\boldsymbol{q}} = -\tau \nabla \theta^{-1}$ and the expression (6.99) for the second moments of the fluctuations, show that

$$-\frac{\partial \boldsymbol{q}}{\partial \nabla \theta} = \frac{\tau V}{k_{\mathrm{B}} \theta^2} \langle \delta \boldsymbol{q} \delta \boldsymbol{q} \rangle_{\mathrm{neq}},$$

where $\langle \cdots \rangle_{\mathrm{neq}}$ stands for the average at non-equilibrium steady states. This expression generalises the fluctuation–dissipation expression (5.19) for non-equilibrium steady states and allows one to compute non-linear thermal conductivities for transport laws of the form $\boldsymbol{q} = -\lambda(\nabla\theta)\nabla\theta$ for an application of this equation to a radiative gas see Jou Zakari (1995)).

6.6. (a) Show that the expressions for the Lagrange multipliers β and $\boldsymbol{\gamma}$ in (6.63) and (6.64) for non-equilibrium radiation in the presence of a radiative heat flux $\boldsymbol{q}$ may also be obtained from $k_{\mathrm{B}}\beta = \theta^{-1} = (\partial S/\partial U)_{V,\boldsymbol{J},N}$ and $k_{\mathrm{B}}\boldsymbol{\gamma} = (\partial S/\partial \boldsymbol{J})_{U,V,N}$ with S given by (6.65). (b) Estimate the ratio $\theta \,/\, T$ for $Vq \,/\, cU = 1\,/\,2$ and $Vq \,/\, cU = 9\,/\,10$.

6.7. It has been proposed in the literature (see Crisanti and Ritort 2003 for a wide review on this topic) to define an effective non-equilibrium temperature T_{eff} by extending the Green-Kubo relation (or analogous fluctuation–dissipation expressions) out of equilibrium. For viscous Couette flow in the presence of a shear viscous pressure P_{12}^{v}, such an effective temperature may be defined as

$$k_{\mathrm{B}} T_{\mathrm{eff}} \equiv \frac{\tau}{\eta} \langle \delta P_{12}^{v} \delta P_{12}^{v} \rangle_{\mathrm{neq}}$$

where $\langle \cdots \rangle_{\mathrm{neq}}$ stands for the second moments out of equilibrium. Using for τ/η the equilibrium value, obtain T_{eff} as a function of the dimensionless non-equilibrium ratio $R \equiv VP_{12}^{v}/U$ (Criado-Sancho et al. 2006).

6.8. Using (6.62)–(6.64) for non-equilibrium electromagnetic radiation in the presence of a radiative heat flux $\boldsymbol{q}$, and $p = h\,/\,\lambda$, with λ the photon wavelength, find how the Wien law giving the wavelength $\lambda_{\max}$ corresponding to maximum emission of a black body at absolute temperature T, namely $\lambda_{\max} = 2.898\,\mathrm{mm}\cdot\mathrm{K}/T$ is modified for non-vanishing values of $Vq \,/\, cU$ (see J. Fort, Physica A **243** (1997) 275, J Fort et al., Phys. Lett. A **236** (1997) 193).

Chapter 7
Linear Response Theory

In Chap. 5 we discussed the microscopic foundations of extended irreversible thermodynamics (EIT) through the fluctuation theory by focusing the attention on the main features of the second moments of the fluctuations. The present chapter deals with more general methods of non-equilibrium statistical mechanics, excerpting in particular the dynamical aspects of fluctuations. First, we start from the Liouville equation and introduce the projection operator technique to relate the memory functions to the time correlation functions of the fluctuations of the fluxes.

This result plays a central role in modern non-equilibrium statistical mechanics and it is also of special interest in EIT, because it emphasizes the role played by the evolution of the fluctuations of the thermodynamic fluxes in specifying the memory functions. The corresponding expressions, though compact and elegant, are merely formal, and they are overwhelmingly difficult to be exploited. To obtain practical results, one must construct models and EIT may be very useful as a thermodynamic tool to propose admissible models for the phenomenological evolution equations of the corresponding fluxes.

The method of projection operators is useful, since it provides a general and explicit method for obtaining the evolution equations of the basic variables. Classically, the set of variables consists of the conserved slow variables (energy, linear momentum, mass) and some order parameters characterizing second-order phase transitions. Here we present a generalisation by adding the dissipative fluxes to the basic set of variables. The projection operator technique is especially helpful when the fluxes become 'slow' variables because their relaxation times become sufficiently long.

7.1 Projection Operator Methods

In this section, we briefly introduce the main concepts and ingredients of the linear response theory (McQuarrie 1976; Résibois and De Leener 1977; Berne 1977; Grabert 1981). Its main objective is to provide a microscopic expression for the memory function relating a flux $\boldsymbol{J}(t)$ at a given time t to its respective conjugate force $\boldsymbol{X}(t')$ at previous times t':

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_7,

$$\boldsymbol{J}(t) = \int_0^\infty \mathbf{K}(t-t') \cdot \boldsymbol{X}(t')\mathrm{d}t'; \tag{7.1}$$

$\mathbf{K}(t-t')$ is the so-called memory function. Note that integration of the relaxational evolution equation of the Maxwell–Cattaneo form, namely,

$$\tau \frac{\partial \boldsymbol{J}}{\partial t} = -(\boldsymbol{J} - \boldsymbol{L} \cdot \boldsymbol{X}) \tag{7.2}$$

with $\mathbf{L}$ the corresponding phenomenological transport coefficient, yields, for a zero initial flux,

$$\boldsymbol{J}(t) = \int_0^\infty \frac{\mathbf{L}}{\tau} \exp[-(t-t')/\tau] \cdot \boldsymbol{X}(t')\mathrm{d}t'. \tag{7.3}$$

By comparing (7.3) and (7.1), one may identify the memory function as

$$\mathbf{K}(t-t') = \frac{\boldsymbol{L}}{\tau} \exp\left(-\frac{t-t'}{\tau}\right), \tag{7.4}$$

indicating that in the linearized version of EIT, the memory function decays exponentially. In Chap. 4 we have justified equations of the form (7.2), and even more general equations, by starting from the Boltzmann equation. However, the latter is valid for semidilute gases, when binary collisions are the dominant relaxation mechanism. Modern statistical mechanics has tried to formulate more general versions of transport theory, without these restrictions on the density. This is achieved by considering N-particle distribution functions instead of the more restrictive one-particle distribution function, and by using the Liouville equation for the description of its evolution.

In contrast to kinetic theory, we work now in the phase space of the whole system instead than in the configuration space of a single particle and we start from the fundamental Liouville equation

$$\frac{\partial f_N}{\partial t} = -\mathrm{i}\mathcal{L}_N f_N, \tag{7.5}$$

where f_N is the N-particle distribution function describing a system of N point particles of mass m and $\mathcal{L}_N$ is the Liouville operator, defined as

$$\mathrm{i}\mathcal{L}_N = \sum_{i=1}^{N} \left(\frac{\partial \mathcal{H}_N}{\partial \boldsymbol{p}_i} \cdot \frac{\partial}{\partial \boldsymbol{r}_i} - \frac{\partial \mathcal{H}_N}{\partial \boldsymbol{r}_i} \cdot \frac{\partial}{\partial \boldsymbol{p}_i} \right) = \{\mathcal{H}_N, \ldots\}, \tag{7.6}$$

with $\boldsymbol{r}_i$ and $\boldsymbol{p}_i$ the position and momentum of the ith particle, and $\mathcal{H}_N$ the Hamiltonian of the system; the braces $\{,\}$ stand for the Poisson bracket. Liouville equation is essentially a reformulation of the Hamilton equations of motion

$$\dot{\boldsymbol{r}}_i = \frac{\partial \mathcal{H}_N}{\partial \boldsymbol{p}_i}, \quad \dot{\boldsymbol{p}}_i = -\frac{\partial \mathcal{H}_N}{\partial \boldsymbol{r}_i}. \tag{7.7}$$

Consider the set of all dynamical properties A, B, C, ... of the system and define a scalar product as

$$(A, B) = \int \mathrm{d}\Gamma_N f_{N\mathrm{eq}} AB. \tag{7.8}$$

At this point, it should be realized that, unlike situations near equilibrium, linear response theory is faced with important problems when the system is driven far from equilibrium. For instance, to study the evolution of perturbations around a non-equilibrium steady state, it could be asked whether the non-equilibrium steady state distribution function should not be preferred in the definition (7.8 instead of the N-particle equilibrium distribution function $f_{N\mathrm{eq}}$.

It is easy to show that the Liouvillian operator $\mathcal{L}_N$ is a linear Hermitian operator $\mathcal{L}_N^{\dagger} = \mathcal{L}_N$) in the Liouville space defined by the set of all dynamical variables and a metric given by the scalar product (7.8. Indeed, integrating by parts and assuming that $f_{N\mathrm{eq}}$ tends sufficiently fast to zero at the boundaries of integration it can be written

$$(\mathcal{L}_N A, B^*)^* = (\mathcal{L}_N B, A^*) \tag{7.9}$$

and consequently

$$\exp[\mathrm{i}\mathcal{L}_N t]A, B^*)^* = \exp[-\mathrm{i}\mathcal{L}_N t]B, A^*), \tag{7.10}$$

where the asterisk denotes the complex conjugate.

One defines a projection operator $\mathcal{P}$ that projects an arbitrary observable B onto a given set of observables A by

$$\mathcal{P}B = (B, A^*)(A, A^*)^{-1}A. \tag{7.11}$$

Note that A can also be considered to be a set of several observables (e.g. mass, linear momentum, energy and so on) instead of a single one, in which case A is a column vector whose components are the set of observables. The idea beyond this projection is to concentrate the attention on the directly observable variables of the set A rather than dispersing the attention on the whole set (in principle infinite) of variables. Therefore, beyond its apparently formal aspect, the idea behind the projection operators has a very physical and intuitive motivation.

The quantity

$$\mathcal{Q} = 1 - \mathcal{P} \tag{7.12}$$

is also a projection operator which projects onto a subspace orthogonal to A. Since by definition of $\mathcal{Q}$, one has $\mathrm{i}\mathcal{L}_N = \mathrm{i}(\mathcal{Q} + \mathcal{P})\mathcal{L}_N$, and

$$e^{A+B} = e^A + \int_0^1 e^{(A+B)(1-\lambda)} B e^{A\lambda} \mathrm{d}\lambda \tag{7.13}$$

(recall that A and B are matrices which in general do not commute), it follows that

$$\exp[\mathrm{i}\mathcal{L}_N t] = \exp[\mathrm{i}\mathcal{Q}\mathcal{L}_N t] + \int_0^t \mathrm{d}t' \exp[\mathrm{i}\mathcal{L}_N (t - t')]\mathrm{i}\mathcal{P}\mathcal{L}_N \exp[\mathrm{i}\mathcal{Q}\mathcal{L}_N t']. \tag{7.14}$$

So far with general considerations; our aim is to obtain evolution equations for the physically relevant variables $A(\Gamma)$ which depend on the phase-space coordinates. When the particles follow the trajectories dictated by the Hamilton equations of motion, the evolution of $A(\Gamma)$ is governed by

$$\frac{\mathrm{d}A(\Gamma)}{\mathrm{d}t} = \sum_{i=1}^{N} \left(\frac{\partial \mathcal{H}_N}{\partial \boldsymbol{p}_i} \cdot \frac{\partial A}{\partial \boldsymbol{r}_i} - \frac{\partial \mathcal{H}_N}{\partial \boldsymbol{r}_i} \cdot \frac{\partial A}{\partial \boldsymbol{p}_i} \right) = \mathrm{i}\mathcal{L}_N A. \tag{7.15}$$

Note that $\mathrm{d}A/\mathrm{d}t$ is not necessarily contained in the subspace of the selected variables A. Integration of (7.15) yields

$$A(t) = \exp[\mathrm{i}\mathcal{L}_N t]A(0) \tag{7.16}$$

and differentiation with respect to time gives

$$\frac{\mathrm{d}A(\Gamma)}{\mathrm{d}t} = \exp[\mathrm{i}\mathcal{L}_N t]\mathrm{i}\mathcal{L}_N A(0) = \exp[\mathrm{i}\mathcal{L}_N t](\mathcal{P} + \mathcal{Q})\mathrm{i}\mathcal{L}_N A(0). \tag{7.17}$$

The insertion of the operator $\mathcal{P} + \mathcal{Q}$ does not alter the result, because it is the identity operator. From the definition (7.11) of $\mathcal{P}$ it follows that

$$\exp[\mathrm{i}\mathcal{L}_N t]\mathcal{P}\mathrm{i}\mathcal{L}_N A(0) = (\mathrm{i}\mathcal{L}_N A A^*)(A, A^*)^{-1} \exp[\mathrm{i}\mathcal{L}_N t]A = \mathrm{i}\Omega A(t), \tag{7.18}$$

where A stands for $A(0)$ and the operator Ω for

$$\mathrm{i}\Omega = (\mathrm{i}\mathcal{L}_N A, A^*)(A, A^*)^{-1}. \tag{7.19}$$

The quantity Ω has the dimensions of the reciprocal of time and gives the frequency at which A rotates in the subspace A, in the absence of the orthogonal variables. Introduction of (7.13)and (7.19) into (7.17) yields

$$\begin{aligned}\frac{\mathrm{d}A(t)}{\mathrm{d}t} &= \mathrm{i}\Omega A(t) + exp[\mathrm{i}\mathcal{Q}\mathcal{L}_N t]\mathcal{Q}\mathrm{i}\mathcal{L}_N A(t) \\ &+ \int_0^t \mathrm{d}t' \exp[\mathrm{i}\mathcal{L}_N (t - t')]\mathrm{i}\mathcal{P}\mathcal{L}_N \exp[\mathrm{i}\mathcal{Q}\mathcal{L}_N t']\mathcal{Q}\mathrm{i}\mathcal{L}_N A.\end{aligned} \tag{7.20}$$

To have a more compact expression, set

$$F(t) = \exp[\mathrm{i}\mathcal{Q}\mathcal{L}_N t]\mathcal{Q}\mathrm{i}\mathcal{L}_N A, \tag{7.21}$$

which is called the random force and may also be written as

$$F(t) = \mathcal{Q}\exp[\mathrm{i}\mathcal{Q}\mathcal{L}_N t]\mathcal{Q}\mathrm{i}\mathcal{L}_N A = \mathcal{Q}F(t). \tag{7.22}$$

This means that $F(t)$ is orthogonal to A, which is expressed by

$$(F(t), A^*) = 0, \tag{7.23}$$

indicating that there is no correlation between A and the random force, an important conclusion to be exploited below.

The term $\mathrm{i}\mathcal{P}\mathcal{L}_N F(t)$ appearing in the last integral of (7.20) can be written as

$$\mathrm{i}\mathcal{P}\mathcal{L}_N F(t) = \mathrm{i}\mathcal{P}\mathcal{L}_N \mathcal{Q}F(t) = (\mathrm{i}\mathcal{L}_N \mathcal{Q}F(t), A^*)(A, A^*)^{-1}A. \tag{7.24}$$

Since $\mathcal{Q}$ and $\mathcal{L}_N$ are both Hermitian, it follows that

$$(\mathrm{i}\mathcal{L}_N \mathcal{Q}F(t), A^*) = -(F(t), (\mathcal{Q}\mathrm{i}\mathcal{L}_N A)^*) = -(F(t), F^*(0)). \tag{7.25}$$

By defining the memory function $K(t)$ as

$$K(t) = (F(t), F^*(0))(A, A^*)^{-1} \tag{7.26}$$

and combining (7.26), (7.8), and (7.20), one obtains the generalised Langevin (or Mori) equation:

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \mathrm{i}\Omega A(t) - \int_0^t \mathrm{d}t' K(t')A(t-t') + F(t). \tag{7.27}$$

Relation (7.26) between the memory function and the random force is known as the fluctuation–dissipation theorem.

From (7.27) it is easy to derive the time correlation function $C(t)$ for the variables A, an interesting quantity in non-equilibrium statistical mechanics because it is measurable from light- and neutron-scattering experiments, and defined by

$$C(t) = (A(t), A^*(0)). \tag{7.28}$$

Taking the scalar product of (7.27) with A^* and using (7.22), one has

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \mathrm{i}\Omega C(t) - \int_0^t \mathrm{d}t' K(t')C(t-t'). \tag{7.29}$$

If (7.27) for the microscopic operator A is averaged over an initial non-equilibrium distribution function, one obtains for the macroscopic value $\langle A\rangle$

$$\frac{\mathrm{d}\langle A(t)\rangle}{\mathrm{d}t} = \mathrm{i}\boldsymbol{\Omega}\langle A(t)\rangle - \int_0^t \mathrm{d}t' K(t')\langle A(t-t')\rangle + \langle F(t)\rangle, \tag{7.30}$$

where $\langle A(t)\rangle$ and $\langle F(t)\rangle$ denote the respective ensemble averages of $A(t)$ and $F(t)$, with $\langle F(t)\rangle$ explicitly given by

$$\langle F(t)\rangle = \int \mathrm{d}\Gamma\, f_N(\Gamma,0)\exp[\mathrm{i}\mathcal{Q}\mathcal{L}_N t]\mathcal{Q}\mathrm{i}\mathcal{L}_N A(\Gamma). \tag{7.31}$$

Equations (7.29) and (7.30) are at the heart of the theoretical efforts to describe the experiments in generalised hydrodynamics (see Chap. 12) and they deserve some comments. On the one side, there exists no clear-cut criterion for selecting the variables, except that of the relative slowness of their evolution, which becomes problematic at very high frequencies. Expression (7.26) is worth of attention, because it relates the memory function to the correlation of the noise. In fluctuating hydrodynamics, the noise is attributed to the fast fluctuations of the heat flux and the viscous pressure tensor. Thus, in the light of (7.26) and (5.18) we could write for the memory functions generalising thermal conductivity and viscosity, the relations

$$\lambda(t-t') = \frac{V}{k_\mathrm{B}T^2}\langle \delta q_i(t)\delta q_j(t')\rangle \tag{7.32a}$$

$$\eta(t-t') = \frac{V}{k_\mathrm{B}T}\langle \delta P^v_{ij}(t)\delta P^v_{ij}(t')\rangle \tag{7.32b}$$

(in these equations, there is no summation with respect to repeated indices). These memory functions complement the transport equations which, in the spirit of (7.1), read as

$$\boldsymbol{q}(t) = -\int_0^t \lambda(t-t')\nabla T(t')\mathrm{d}t'. \tag{7.33a}$$

$$\mathbf{P}^v(t) = -\int_0^t 2\eta(t-t')\mathbf{V}(t')\mathrm{d}t'. \tag{7.33b}$$

When the relaxation times of the fluctuations of the fluxes are very short, in such a way that the memory functions are non-negligible only for very small values of $t-t'$ the bounds of the integrals may be extended to infinity and the thermodynamic forces may be taken out of the integral with the value corresponding to $t = t'$. Doing so, one recovers from (7.32) and (7.33) the Green–Kubo expressions (5.18).

Notwithstanding the elegance and generality of the procedure, the apparent simplicity of Eqs. (7.32–7.33) is misleading because of the complexity of the Liouville operator. This is why some simplifications must be introduced, usually in the form of mathematical models for the memory functions, to be able to deal with practical problems. Extended irreversible thermodynamics is useful as it provides some hints for such modellings. In the next section we illustrate the previous method by deriving evolution equations for the dissipative fluxes when the latter are chosen as independent variables.

7.2 Evolution Equations for Simple Fluids

In their analysis of neutron-scattering experiments in liquids (see Chap. 12), Akcasu and Daniels 1970 go beyond the local-equilibrium description by introducing the heat flux and the viscous pressure tensor among the set of variables and by applying the method presented above to obtain the evolution equations for this enlarged set of variables. We present here the main steps of their formalism, which is of special interest in the context of EIT because it starts from the same selection of basic variables.

The variables in this description are the mass density ρ, the momentum density $\boldsymbol{J} = \rho\boldsymbol{v}$, the energy E, the energy flux $\boldsymbol{Q}$, and the pressure tensor $\mathbf{P}$. In Fourier space, which is suitable to study the response of the system to external solicitations, the microscopic operators of the aforementioned variables for a simple fluid are

$$\rho(\boldsymbol{k}) = m\sum_{\alpha} \exp[i\boldsymbol{k}\cdot\boldsymbol{r}_{\alpha}], \tag{7.34a}$$

$$\boldsymbol{J}(\boldsymbol{k}) = \sum_{\alpha} m\boldsymbol{v}_{\alpha} \exp[i\boldsymbol{k}\cdot\boldsymbol{r}_{\alpha}], \tag{7.34b}$$

$$E(\boldsymbol{k}) = \sum_{\alpha}\left[\frac{1}{2}mv_{\alpha}^{2} + \frac{1}{2}\sum_{\beta}\phi(r_{\alpha\beta})\right]\exp[i\boldsymbol{k}\cdot\boldsymbol{r}_{\alpha}], \tag{7.34c}$$

$$\begin{aligned}\boldsymbol{Q}(\boldsymbol{k}) = {} & \sum_{\alpha}\left[\frac{1}{2}mv_{\alpha}^{2} + \frac{1}{2}\sum_{\beta}\phi(r_{\alpha\beta})\right]\boldsymbol{v}_{\alpha}\exp[i\boldsymbol{k}\cdot\boldsymbol{r}_{\alpha}] \\ & + \frac{1}{4}\sum_{\alpha}(\boldsymbol{v}_{\alpha}+\boldsymbol{v}_{\beta})\cdot\boldsymbol{r}_{\alpha\beta}\boldsymbol{r}_{\alpha\beta}\frac{\phi'(r_{\alpha\beta})}{r_{\alpha\beta}}\frac{1-\exp[-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{\alpha}]}{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{\alpha}}\exp[-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{\alpha}],\end{aligned} \tag{7.34d}$$

$$\begin{aligned}\mathbf{P}(\boldsymbol{k}) = {} & \sum_{\alpha}\left\{m\boldsymbol{v}_{\alpha}\boldsymbol{r}_{\alpha} + \frac{1}{2}\sum_{\beta}\left(\boldsymbol{r}_{\alpha\beta}\boldsymbol{r}_{\alpha\beta}\frac{\phi'(r_{\alpha\beta})}{r_{\alpha\beta}}\frac{1-\exp[-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{\alpha}]}{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{\alpha}}\right)\right\} \\ & \exp[-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{\alpha}],\end{aligned} \tag{7.34e}$$

where $\boldsymbol{r}_{\alpha\beta} = \boldsymbol{r}_{\alpha} - \boldsymbol{r}_{\beta}$ is the relative position of particles α and β, $\phi(r_{\alpha\beta})$ denotes the interaction potential between the particles and $\phi' = \mathrm{d}\phi/\mathrm{d}r_{\alpha\beta}$; the last terms in $E(\boldsymbol{k})$, $\boldsymbol{Q}(\boldsymbol{k})$ and $P(\boldsymbol{k})$ take into account the contributions of the intermolecular potential, as it was already done in Sect. 4.5 for the viscous pressure. Expressions (7.34) are useful for calculating the transport coefficients, but here we are more interested in the general form of the evolution equations rather than in computing these coefficients.

Instead of $E(\boldsymbol{k})$, $\boldsymbol{Q}(\boldsymbol{k})$, and $\mathbf{P}(\boldsymbol{k})$, it is convenient to introduce the quantities

$$\mathcal{E}(\boldsymbol{k}) = E(\boldsymbol{k}) - \frac{(E(\boldsymbol{k}), \rho^*(\boldsymbol{k}))}{(\rho(\boldsymbol{k}), \rho^*(\boldsymbol{k}))}\rho(\boldsymbol{k}), \tag{7.35a}$$

$$\mathbf{P}^v(\boldsymbol{k}) = \mathbf{P}(\boldsymbol{k}) - \frac{(\mathbf{P}(\boldsymbol{k}), \rho^*(\boldsymbol{k}))}{(\rho(\boldsymbol{k}), \rho^*(\boldsymbol{k}))}\rho(\boldsymbol{k}) - \frac{(\mathbf{P}(\boldsymbol{k}), \mathcal{E}^*(\boldsymbol{k}))}{(\rho(\boldsymbol{k}), \mathcal{E}^*(\boldsymbol{k}))}\mathcal{E}(\boldsymbol{k}), \tag{7.35b}$$

$$\boldsymbol{q}(\boldsymbol{k}) = \boldsymbol{Q}(\boldsymbol{k}) - \frac{(\boldsymbol{Q}(\boldsymbol{k}), \boldsymbol{J}^*(\boldsymbol{k}))}{(\boldsymbol{J}(\boldsymbol{k}), \boldsymbol{J}^*(\boldsymbol{k}))}\boldsymbol{J}(\boldsymbol{k}). \tag{7.35c}$$

The variable $\mathcal{E}(\boldsymbol{k})$ may be identified as $\mathcal{E}(\boldsymbol{k} = \rho c_v(\boldsymbol{k})T(\boldsymbol{k})$, with $T(\boldsymbol{k})$ the absolute temperature and $c_v(\boldsymbol{k})$ the specific heat at constant volume. The variables $P^v(\boldsymbol{k})$ and $\boldsymbol{q}(\boldsymbol{k})$ correspond, of course, to the viscous pressure and to the heat flux; indeed in (7.35c) the convective energy current is subtracted from the total energy current, and in (7.35b) the equilibrium pressure (a function of T and ρ) is subtracted from the total pressure tensor.

Let us now establish the evolution equations for the 14 components of the state vector, namely

$$\boldsymbol{A} = \{\rho, \mathcal{E}, P_{11}^v, P_{22}^v, P_{33}^v, P_{13}^v, P_{23}^v, P_{12}^v, J_1, J_2, J_3, q_1, q_2, q_3\}. \tag{7.36}$$

The first eight variables are even, whereas the last six are odd functions of the velocity. Hence, the state vector (7.36) may be decomposed into even and odd parts:

$$ee\boldsymbol{A} = \mathrm{col}\{\boldsymbol{A}^e, 0\} + \mathrm{col}\{0, \boldsymbol{A}^o\}. \tag{7.37}$$

As a consequence, the static correlation matrix $\phi = (\boldsymbol{A}, \boldsymbol{A}^\dagger)$, with $\boldsymbol{A}^\dagger$ the transposed of $\boldsymbol{A}$, splits into two disjoint submatrices

$$\phi = \begin{pmatrix} \phi^e & 0 \\ 0 & \phi^o \end{pmatrix}, \tag{7.38}$$

with

$$\phi^e = (\boldsymbol{A}^e, \boldsymbol{A}^{e\dagger}) = \begin{pmatrix} (\rho, \rho^*) & 0 & 0 \\ 0 & (\mathcal{E}, \mathcal{E}^*) & 0 \\ 0 & 0 & (\mathbf{P}^v, \mathbf{P}^{v\dagger}) \end{pmatrix} \tag{7.39}$$

and

$$\phi^o = (\boldsymbol{A}^o, \boldsymbol{A}^{o\dagger}) = \begin{pmatrix} (\boldsymbol{J}, \boldsymbol{J}^\dagger) & 0 \\ 0 & (\boldsymbol{q}, \boldsymbol{q}^\dagger) \end{pmatrix}. \tag{7.40}$$

The block diagonality of ϕ^e and ϕ^o is a consequence of the choice of the state variables in (7.36).

The frequency matrix $\mathrm{i}\Omega = (\boldsymbol{A}, \boldsymbol{A}^\dagger)\phi^{-1}$ defined by (7.19) is here

$$\mathrm{i}\Omega = \begin{pmatrix} 0 & (\boldsymbol{A}^e, \boldsymbol{A}^{o\dagger})(\phi^o)^{-1} \\ (\boldsymbol{A}^e, \boldsymbol{A}^{e\dagger})(\phi^e)^{-1} & 0 \end{pmatrix}. \tag{7.41}$$

The usual conservation laws of mass, momentum and energy read

$$\frac{\partial \rho}{\partial t} = \mathrm{i}\mathbf{k} \cdot \boldsymbol{J}, \tag{7.42a}$$

$$\frac{\partial \boldsymbol{J}}{\partial t} = \mathrm{i}\boldsymbol{k} \cdot \mathbf{P}, \tag{7.42b}$$

$$\frac{\partial E}{\partial t} = \mathrm{i}\boldsymbol{k} \cdot \boldsymbol{Q}. \tag{7.42c}$$

It follows that the random noise $\boldsymbol{F} = \mathcal{Q}\mathrm{i}\mathcal{L}_N \boldsymbol{A}$ has only nine non-zero components, corresponding to the dissipative fluxes

$$\boldsymbol{F} = \{0, 0, F^v_{11}, F^v_{22}, F^v_{33}, F^v_{13}, F^v_{23}, F^v_{12}, 0, 0, 0, q_1, q_2, q_3\}. \tag{7.43}$$

Accordingly, the memory function matrix $\mathbf{K}(t) = (\boldsymbol{F}(t), \boldsymbol{F}^*(0))$ is of the form

$$\mathbf{K}(t) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \boldsymbol{\phi}^{vv}(t) & 0 & \boldsymbol{\phi}^{vq}(t) \\ 0 & 0 & 0 & 0 \\ 0 & \boldsymbol{\phi}^{qv}(t) & 0 & \boldsymbol{\phi}^{qq}(t) \end{pmatrix}, \tag{7.44}$$

where $\boldsymbol{\phi}^{vv}$ and $\boldsymbol{\phi}^{qq}$ are 6×6 and 3×3 square matrices, while $\boldsymbol{\phi}^{vq}$ and $\boldsymbol{\phi}^{qv}$ are 3×6 and 6×3 rectangular matrices respectively.

Introducing (7.38), (7.43), and (7.44) into (7.29) results in the following evolution equations of $\mathbf{P}^v$ and $\boldsymbol{q}$:

$$\begin{aligned} \dot{\mathbf{P}}^v(t) - (\dot{\mathbf{P}}^v, \boldsymbol{q}^\dagger)(\boldsymbol{q}, \boldsymbol{q}^\dagger)^{-1}\boldsymbol{q}(t) + \int_0^t \mathrm{d}t' \boldsymbol{\phi}^{vq}(t-t') \cdot \boldsymbol{q}(t') \\ - (\dot{P}^v, \boldsymbol{J}^\dagger)(\boldsymbol{J}, \boldsymbol{J}^\dagger)^{-1}\boldsymbol{J}(t) + \int_0^t \mathrm{d}t' \boldsymbol{\phi}^{vv}(t-t') : \mathbf{P}^v(t') = \mathbf{F}^v(t), \end{aligned} \tag{7.45}$$

and

$$\begin{aligned} \dot{\boldsymbol{q}}(t) - (\dot{\boldsymbol{q}}, \mathcal{E}^*)(\mathcal{E}, \mathcal{E}^*)^{-1}\mathcal{E}(t) + \int_0^t \mathrm{d}t' \phi^{qq}(t-t') \cdot \boldsymbol{q}(t') \\ - (\dot{\boldsymbol{q}}, \mathbf{P}^{v\dagger}) \cdot (\mathbf{P}^v, \mathbf{P}^{v\dagger})^{-1}\mathbf{P}^v(t) + \int_0^t \mathrm{d}t' \boldsymbol{\phi}^{qv}(t-t') : \mathbf{P}^v(t') = \boldsymbol{F}^q(t). \end{aligned} \tag{7.46}$$

These equations are exceedingly complicated, and therefore the following simplifications are usually introduced:

$$\int_0^t \mathrm{d}t' \boldsymbol{\phi}^{vv}(t-t') : \mathbf{P}^v(t') = \mathbf{W}^v(k) \cdot \mathbf{P}^v(t), \tag{7.47}$$

$$\int_0^t \mathrm{d}t' \boldsymbol{\phi}^{qq}(t-t') \cdot \boldsymbol{q}(t') = \mathbf{W}^q(k) \cdot \boldsymbol{q}(t), \tag{7.48}$$

with

$$\mathbf{W}^v(k) = \int_0^\infty \mathrm{d}t\,\boldsymbol{\phi}^{vv}(t), \quad \mathbf{W}^q(k) = \int_0^\infty \mathrm{d}t\,\boldsymbol{\phi}^{qq}(t). \tag{7.49}$$

In generalised hydrodynamics, the cross terms in $\boldsymbol{\phi}^{vq}$ and $\boldsymbol{\phi}^{qv}$ are usually neglected. Defining the quantities $\boldsymbol{\Sigma}$, $\boldsymbol{\Lambda}$, $\mathbf{A}$, and $\mathbf{B}$ (which are fourth-rank tensors at the exception of $\boldsymbol{\Lambda}$ which is of second-rank) by

$$\beta V^{-1}(\dot{\mathbf{P}}^v, \boldsymbol{J}_k) = \mathrm{i}\boldsymbol{k} \cdot \boldsymbol{\Sigma}, \tag{7.50a}$$

$$(\dot{\boldsymbol{q}}, \mathcal{E}^*)(\mathcal{E}, \mathcal{E}^*)^{-1} = \mathrm{i}\boldsymbol{k} \cdot \boldsymbol{\Lambda}, \tag{7.50b}$$

$$(\dot{\mathbf{P}}^v, \boldsymbol{q}^\dagger)(\boldsymbol{q}, \boldsymbol{q}^\dagger) = \mathrm{i}\boldsymbol{k} \cdot \boldsymbol{\Sigma}, \tag{7.50c}$$

$$(\dot{\boldsymbol{q}}, \mathbf{P}^{v\dagger})(\mathbf{P}^v, \mathbf{P}^{v\dagger})^{-1} = \mathrm{i}\boldsymbol{k} \cdot \mathbf{B}, \tag{7.50d}$$

one obtains from (7.45) and (7.46) the simplified expressions:

$$\dot{\mathbf{P}}^v - \boldsymbol{\Sigma} \cdot \boldsymbol{\varepsilon} + \mathbf{W}^v \cdot \mathbf{P}^v - \mathbf{A} \cdot \mathrm{i}\boldsymbol{k}\boldsymbol{q} = \boldsymbol{F}^v(t) \tag{7.51}$$

and

$$\dot{\boldsymbol{q}} - \mathrm{i}\boldsymbol{k} \cdot \boldsymbol{\Lambda} + \mathbf{W}^q \cdot \boldsymbol{q} - \mathbf{B} \cdot \mathrm{i}\boldsymbol{k}\mathbf{P}^v = \boldsymbol{F}^q(t), \tag{7.52}$$

where $\boldsymbol{\varepsilon}(\boldsymbol{k})$ is the rate of deformation tensor, i.e.

$$\boldsymbol{\varepsilon} = \frac{\mathrm{i}}{2\rho}(k\boldsymbol{J} + \boldsymbol{J}k). \tag{7.53}$$

Relations (7.51) and (7.52) have the same form as the linear macroscopic equations for the heat flux and the viscous pressure tensor proposed in (2.70–2.72), $\boldsymbol{\Lambda}$ being the thermal diffusivity tensor and $\mathbf{W}^v$ and $\mathbf{W}^q$ frequency matrices. In some aspects (7.51–7.52) are less general than (2.70–2.72), because the coupling between the viscous pressure tensor and the heat flux, which was however present in (7.45–7.46), has been neglected. The contribution of the projection operator formalism is that it yields expressions for the coefficients in terms of correlations between the variables.

It is worth emphasizing that when the space of the relevant dynamical variables is enlarged to include dissipative fluxes, the projection operator method predicts some results derived within macroscopic extended irreversible thermodynamics. Nevertheless, in the microscopic formalism no attention is paid to the thermodynamic implications. By taking thermodynamics into account, EIT may provide a useful complement to the analysis of the evolution equations, whose final form must nevertheless be phenomenologically modelled if it is wanted to study actual problems.

7.3 Continued-Fraction Expansions

In Sect. 4.6 we saw that when higher-order fluxes are introduced into the description one is led to a hierarchy of equations which yields, in Fourier space, a continued-fraction expansion of the transport coefficients. In this section we point out that similar results may also be obtained from a microscopic perspective within the framework of the projection-operator techniques, when the noise appearing in evolution equations of the form (7.27) is taken as a new variable for which an evolution equation must be formulated (Mori 1965). This point of view has some analogy with EIT, when the fluctuations of the dissipative fluxes, which are considered as a noise in classical fluctuating hydrodynamics, are incorporated as additional variables in the theory.

When the noise in the evolution equation of the variable of order $n-1$ is selected as an additional variable, one obtains a hierarchy of equations of the form

$$\frac{\mathrm{d}F_n}{\mathrm{d}t} = \mathrm{i}\Omega_n F_n(t) - \int_0^t K_n(t')F_n(t-t')\mathrm{d}t' + F_{n+1}(t). \tag{7.54}$$

Indeed, the evolution equation for F_0 is

$$\frac{\mathrm{d}F_0}{\mathrm{d}t} = \mathrm{i}\Omega_0 F_0(t) - \int_0^t K_0(t')F_0(t-t')\mathrm{d}t' + F_1(t), \tag{7.55}$$

with (see for instance (7.19) and (7.26))

$$\Omega_0 = \langle \dot{F}_0 F_0^* \rangle \langle F_0 F_0^* \rangle^{-1}, \quad K_0 = \langle F_1(t) F_1^* \rangle \langle F_0 F_0^* \rangle^{-1}. \tag{7.56}$$

The time correlation function of F_0 is defined as

$$C(t) \equiv \langle F_0(t) F_0^* \rangle \langle F_0 F_0^* \rangle^{-1}. \tag{7.57}$$

After multiplying (7.55) by F_0^* and taking into account that $\langle F_1(t) F_0^* \rangle = 0$, one is led to

$$\frac{\mathrm{d}C(t)}{\mathrm{d}t} = \mathrm{i}\Omega_0 C(t) - \int_0^t K_0(t')C(t-t')\mathrm{d}t', \tag{7.58}$$

the Laplace transform of which is

$$C(s) = \frac{C(0)}{s - \mathrm{i}\Omega_0 + K_0(s)}. \tag{7.59}$$

To calculate $K_0(s)$ we use the property that $K_0(t)$ is the time correlation function of F_1 and that F_1 satisfies an equation of the form

$$\frac{\mathrm{d}F_1(t)}{\mathrm{d}t} = \mathrm{i}\Omega_1 F_1(t) - \int_0^t K_1(t')F_1(t-t')\mathrm{d}t' + F_2(t), \tag{7.60}$$

with

$$\boldsymbol{\Omega}_1 = \langle \dot{F}_1 F_1^* \rangle \langle F_1 F_1^* \rangle \quad \text{and} \quad K_1(t) = \langle F_2(t) F_2^* \rangle \langle F_1 F_1^* \rangle^{-1}. \tag{7.61}$$

Multiplying (7.60) by F_1^* and averaging, one finds, after that $\langle F_2(t) F_1^* \rangle = 0$ is taken into account,

$$\frac{\mathrm{d}K_0(t)}{\mathrm{d}t} = \mathrm{i}\Omega_1 K_0(t) - \int_0^t K_1(t') F_1(t-t')\mathrm{d}t'. \tag{7.62}$$

The Laplace transform of (7.62) is

$$K_0(s) = \frac{K_0(0)}{s - \mathrm{i}\Omega_1 + K_1(s)}, \tag{7.63}$$

and introduction of this result into (7.59) yields

$$C(s) = \frac{C(0)}{s - \mathrm{i}\Omega_0 + \dfrac{K_0(0)}{s - \mathrm{i}\Omega_1 + K_1(s)}} \cdot \tag{7.64}$$

This procedure may continue indefinitely because $K_n(t)$ is proportional to $\langle F_{n+1}(t)\, F_{n+1}^* \rangle$, and all the F_n obey evolution equations of the same form, so that the Laplace transform of the correlation function for F_0 may be written as a continued fraction in s of the form

$$C(s) = \frac{C(0)}{s - \mathrm{i}\boldsymbol{\Omega}_0 + \dfrac{K_0(0)}{s - \mathrm{i}\boldsymbol{\Omega}_1 + \dfrac{K_1(1)}{s - \mathrm{i}\boldsymbol{\Omega}_2 + \cdots}}}, \tag{7.65}$$

with

$$\begin{aligned} K_{n-1}(0) &= \langle F_n(0) F_n^*(0) \rangle \langle F_{n-1}(0) F_{n-1}^*(0) \rangle^{-1}, \\ \mathrm{i}\boldsymbol{\Omega}_n &= \langle \dot{F}_n(0) F_n^*(0) \rangle \langle F_n(0) F_n^*(0) \rangle^{-1}. \end{aligned}$$

This result is comparable to (4.103) for the continued-fraction expansion of the transport coefficients by recalling that, according to (7.32), the memory function generalising the transport coefficients is given by the time correlation function of the fluctuations of the dissipative fluxes. Other microscopic justifications of continued-fraction expansions may be found in the non-equilibrium statistical operator method (Madureira et al. 1998). Such a continued fraction was, however, obtained by assuming that the only couplings between variables of different orders are those with the variables of the immediately higher and lower orders, i.e. that the time derivative of variable of order r is related only to the variables of orders $r-1$, r and $r+1$.

In general situations, more general couplings are occurring, and the form of the hierarchy of evolution equations becomes much more intricate.

7.4 Problems

7.1. Assume that the relaxation time τ of the distribution function depends on the peculiar molecular velocity C according to $\tau(C) \sim C^a$, where a is a constant. The respective relaxation times for $\boldsymbol{q}$ and $\mathbf{P}^v$ are then given by

$$\tau_1^{-1} = \langle (\mathrm{d}\hat{q}_x/\mathrm{d}t)\hat{q}_x \rangle (\hat{q}_x \hat{q}_x)^{-1}$$

and

$$\tau_2^{-1} = \langle (\mathrm{d}\hat{P}^v_{xy}/\mathrm{d}t)\hat{P}^v_{xy} \rangle (\hat{P}^v_{xy}\hat{P}^v_{xy})^{-1},$$

with $\hat{q}_x$ and $\hat{P}^v_{xy}$ the microscopic operators for q_x and P^v_{xy} and $\langle (\mathrm{d}\hat{q}_x/\mathrm{d}t)\hat{q}_x \rangle = \langle \tau(C)\hat{q}_x(C) \rangle$ and $\langle (\mathrm{d}\hat{P}^v_{xy}/\mathrm{d}t)\hat{P}^v_{xy} \rangle = \langle \tau(C)\hat{P}^v_{xy}(C)\hat{P}^v_{xy}(C) \rangle$. Find τ_1/τ_2 in terms of a and calculate this ratio for $a = 0$ and $a = -1$.

7.2. In general, the non-equilibrium entropy for an ideal monatomic gas should be expanded in terms of all the moments of the velocity distribution function rather than in terms of just the first thirteen moments. To estimate the relaxation times of the higher-order moments, introduce the quantities

$$M^{(n)} = \int C^n f(C) \mathrm{d}\boldsymbol{c}$$

and compute the corresponding relaxation times according to the expression

$$\tau_n^{-1} = \langle (\mathrm{d}M^{(n)}/\mathrm{d}t) M^{(n)} \rangle \langle M^{(n)} M^{(n)} \rangle^{-1} = \langle \tau^{-1}(C) C^n C^n \rangle \langle C^n C^n \rangle^{-1}.$$

Determine τ_n for $\tau(C) \sim C^a$, with $a = 0$, $a = -1$, and $a = +1$.

7.3. Let the Laplace transform $C(s)$ of an autocorrelation function be given by $C(s) = [s + K(s)]^{-1}$, with $K(s)$ the Laplace transform of the corresponding memory function. Assume that $K(s)$ may be expanded as a continued fraction of the form $K(s) = K_0/s + K(s) = K_0/s + K_1/s + K_2/s + K_3 \cdots$ Show that the first and second approximations, defined by cutting the expansion at K_1 or at K_2 respectively, lead to the following memory functions:

$$K(t) = K_0 \exp[-K_1 t],$$

and

$$K(t) = K_0 \exp(-bt) a^{-1} (a \cos at + b \sin at),$$

with $b = -\frac{1}{2}K_2$ and $a^2 = K_1 - \frac{1}{4}K_2^2$.

7.4. An alternative derivation of (7.14) starts from the Laplace transform of $G(t) \equiv e^{\mathrm{i}Lt}$, namely, $\tilde{G}(s) = 1/(s - \mathrm{i}L)$. Since $\mathrm{i}L = \mathrm{i}(Q + P)L$, it follows that

$$\tilde{G}(s) = \frac{1}{s - \mathrm{i}(Q + P)L}.$$

By using the identity

$$\frac{1}{A} - \frac{1}{B} = \frac{1}{A}(B - A)\frac{1}{B}$$

check that

$$\tilde{G}(s) = \frac{1}{s - \mathrm{i}QL} + \frac{1}{s - \mathrm{i}L}\mathrm{i}PL\frac{1}{s - \mathrm{i}QL}$$

and, by Laplace transforms, show (7.14).

7.5. (a) Let $P_r(t)$ be the probability that a system is in the state r at time t. Assume that the time evolution of $P_r(t)$ is given by the master equation

$$\mathrm{d}P_r/\mathrm{d}t = \sum_s [W_{rs}P_s(t) - W_{sr}P_r(t)],$$

with W_{rs} the transition probability from state s to state r per unit time. For isolated systems, $W_{rs} = W_{sr}$. Show that the master equation satisfies an H-theorem, i.e. define $H = \sum_r P_r \ln P_r$ and show that $\mathrm{d}H/\mathrm{d}t \leq 0$. (b) Consider a very simple situation with only two states, corresponding to particles travelling to the right (state 1) or to the left (state 2). Thus, $W_{11} = W_{22} = \mathcal{T}$ (the transmission coefficient) and $W_{12} = W_{21} = \mathcal{R}$ (the reflection coefficient). Assume that $P_1 + P_2 = n$, with n the total concentration of particles, and that all the particles are moving at speed v. Show that the entropy corresponding to a non-equilibrium steady state with n particles per unit volume and a non-vanishing flux of particles j is

$$S = -\frac{1}{2}k_{\mathrm{B}}\left(n + \frac{j}{v}\right)\ln\left(n + \frac{j}{v}\right) - \frac{1}{2}k_{\mathrm{B}}\left(n - \frac{j}{v}\right)\ln\left(n - \frac{j}{v}\right).$$

This expression shows clearly the highly non-linear character of the dependence of the entropy on the flux.

Chapter 8
Computer Simulations

Computer simulations have become an important tool in statistical mechanics, since they allow the study of systems in conditions hardly accessible to experimental observations. Furthermore, they are useful to assert, at least in some situations, the very foundations of macroscopic formalisms. In particular, in equilibrium, computer simulations have been especially fruitful in the analysis of the equations of state and phase transitions of systems composed of interacting particles; out of equilibrium, they are very helpful in the calculation of transport coefficients and in the formulation of non-equilibrium thermodynamics beyond the local-equilibrium approximation. However, out of local equilibrium several conceptual problems arise which are not present in equilibrium, as, for instance, the definition of temperature or pressure and their relation with measurements.

The interpretation of the results provided by computer simulations relies on assumptions such as the meaning of temperature (which is usually identified as the kinetic temperature) and the kind of average to be performed to obtain truly significant macroscopic results. As a consequence, a detailed comparison of the results of simulations with experimental observations may shed a critical view on these crucial and subtle matters. Most attention has been focused on the calculation of transport coefficients out of equilibrium in the linear regime, and more recently the non-linear regime has been the subject of active research. In particular, non-equilibrium equations of state and non-linear transport equations have been extensively studied by Evans and collaborators (Evans and Morriss 1990); in this chapter we will pay special attention to their contributions and emphasize the aspects which are most closely related to extended irreversible thermodynamics.

8.1 Computer Simulations of Non-equilibrium Steady States

Let us consider a set of particles described by a Lennard–Jones interaction potential in a non-equilibrium steady state characterized by a constant shear rate $\dot{\gamma}$. Systems under a stationary and homogeneous shear rate are one of the most thoroughly investigated situations in non-equilibrium molecular dynamics. Indeed, it is considerably easier to simulate systems in a velocity gradient than systems in

D. Jou et al., *Extended Irreversible Thermodynamics*,

DOI 10.1007/978-90-481-3074-0_8,

a temperature gradient (Hafskjold and Kjelstrup 1995). Dissipation due to viscous pressure produces heat which must be removed to keep the system in a steady state; for this reason, several thermostating procedures have been proposed to maintain the temperature constant. In this section we outline the basic equations used in the molecular analysis and comment briefly on the thermostating problem.

According to Evans and colalaborators (1990), the microscopic equations describing the motion of the molecules under the action of a velocity gradient $\nabla \boldsymbol{v}$ are given by

$$\dot{\boldsymbol{r}}_i = \frac{\boldsymbol{p}_i}{m} + (\nabla \boldsymbol{v})^T \cdot \boldsymbol{r}_i, \tag{8.1a}$$

$$\dot{\boldsymbol{p}}_i = \boldsymbol{F}_i - (\nabla \boldsymbol{v})^T \cdot \boldsymbol{p}_i - \alpha \boldsymbol{p}_i, \tag{8.1b}$$

where $\boldsymbol{F}_i$ is the force acting on the molecule i of mass m_i, and $\alpha \boldsymbol{p}_i$ (with $\boldsymbol{p}_i$ the momentum of the molecule i) is a Gaussian thermostat which removes energy from the system so as to keep the temperature constant. This is achieved by imposing that (see Problem 8.2)

$$\alpha = -\frac{V \mathrm{P}^v : (\nabla \boldsymbol{v})}{\sum\limits_i (p_i^2/m_i)}, \tag{8.2}$$

where V is the total volume. This description is not fully realistic, as it implies that heat is removed at the same point as where dissipation is produced, whereas in real situations heat is eliminated across the boundaries of the system. Furthermore, the Gaussian thermostat produces sharply defined kinetic energy and only potential energy is distributed canonically. A better choice for the thermostat is the so-called Nosé–Hoover thermostat (Hoover 1999), which yields results in agreement with the canonical ensemble, not only for the potential but also for the kinetic energy. Since the rate of viscous heating is quadratic in the shear rate, both thermostats will obviously lead to the same results in the linear regime. Several debates about the best choice of a thermostat have arisen in relation to some ordering transitions in dense fluids (Loose and Hess 1989).

One of the main objectives of non-equilibrium molecular dynamics is to obtain the transport coefficients of fluids with a higher precision than the usual fluctuation–dissipation techniques based on Green–Kubo expressions (see Chap. 6. Furthermore, numerical simulations are also relevant for checking ideas on non-equilibrium temperature and pressure and on fluctuations in non-equilibrium states (Baranyai and Evans 1989; Daivis 2008). In their earlier calculations of 1980, Hanley and Evans (1982) did not calculate the entropy and defined simply the temperature in terms of the average kinetic energy of the particles; however, later, Evans (1989) computed the entropy and the corresponding temperature for an isoenergetic planar Couette flow at low densities. The large mean free paths in this low-density regime require very long runs to achieve an accuracy comparable to that for dense fluids; as a matter of fact, the results were achieved after 15 million time-step calculation runs. Table 8.1, which shows some of Evans' results, makes evident the difference between the kinetic (local-equilibrium) temperature T and the (non-equilibrium)

Table 8.1 Values of the dimensionless quantities p_1 and u_1 of (8.3) obtained at $\dot{\gamma} = 1$ (a density of 0.844 and a temperature of 0.722 correspond to the triple point of the fluid) (Evans 1989)

Temperature	Density	p_1^*	u_1^*
0.72	0.84	2.81	0.58
1.00	0.84	2.20	0.49
1.00	0.73	0.72	0.15
1.75	0.84	1.31	0.31
1.75	0.73	0.44	0.14

thermodynamic temperature θ defined as the derivative of the energy with respect to the entropy. It is to be noticed that $\theta < T$, in agreement with the results of EIT (see Sect. 3.2).

8.2 Non-equilibrium Equations of State

Non-equilibrium equations of state for the pressure and the internal energy of fluids under shear have been computed by Hanley and Evans (1982). These authors have carried out their calculations for a system of 108 particles with an interaction potential of the form $\phi(r) = 4\varepsilon(\sigma/r)^{12}$ (r is the distance between particles, ε and σ the strength and range of the potential) at fixed values of density and temperature, under a constant shear rate $\dot{\gamma}$. The first result deserving special attention is the shear-rate dependence of the pressure $p(T, V, \dot{\gamma})$ and the internal energy per particle $u(T, V, \dot{\gamma})$

$$p(T, V, \dot{\gamma}) = p_0(T, V) + p_1(T, V)\dot{\gamma}^{3/2}, \tag{8.3a}$$

$$u(T, V, \dot{\gamma}) = u_0(T, V) + u_1(T, V)\dot{\gamma}^{3/2}. \tag{8.3b}$$

In Table 8.1 are shown some numerical values for $p_1(T, V)$ and $u_1(T, V)$. Pressure, energy, shear rate, and temperature are expressed in dimensionless form in terms of the parameters ε and σ. The relations between the dimensional and dimensionless quantities are

$$p = p^*(\varepsilon/\sigma^3), \quad u = u^*\varepsilon, \quad \dot{\gamma} = \dot{\gamma}^*(\varepsilon/m\sigma^2)^{1/2}, \quad T = T^*\,(\varepsilon/k_\mathrm{B})\,,$$

where the symbols with asterisks denote dimensionless quantities. The problem is that when these quantities are scaled with the parameters of atomic fluids, the typical shear rates used in non-equilibrium molecular dynamics are much higher than those found in current experiments (Problem 8.3). The results are more satisfactory with colloidal suspensions, which may be modelled by the same two-particle interaction potential, but with a relaxation time of the order of milliseconds, much longer than the relaxation times of atomic fluids, of the order of picoseconds. Correspondingly, for a given value of the dimensionless shear rate (which is given by the product of the actual shear rate times the relaxation time) the actual shear rate corresponding to a colloidal suspension is one millionth of the shear rate corresponding to an atomic fluid.

The main difference between (8.3a and b) and the results of EIT is the non-analytic dependence of p and u on $\dot{\gamma}^{3/2}$, whereas EIT predicts a dependence on $\dot{\gamma}^2$. However, the contradiction is only apparent: computer simulations have been performed at high values of $\dot{\gamma}$ in order to make easily visible the effects of shear; in contrast, in the present description of EIT it is supposed that $\dot{\gamma}$ remains small. The transition from a $\dot{\gamma}^2$ to a $\dot{\gamma}^{3/2}$ behaviour has been studied in the context of extended thermodynamics by Nettleton (1987), who introduced the volume fraction of locally dilated spherical regions as a further state variable. At a high shear rate, Nettleton observes a bifurcation in the asymptotic solution with a $\dot{\gamma}^{3/2}$ dependence for p and u and a $\dot{\gamma}^{1/2}$ dependence for the viscosity. In Sect. 8.3 we reexamine this difference in the frame of a more general non-linear version of EIT.

The second point to be emphasized is that p_1 and u_1 in (8.3) satisfy the relation

$$N\left(\frac{\partial u_1}{\partial V}\right)_{T,\dot{\gamma}} = -p_1 + T\left(\frac{\partial p_1}{\partial T}\right)_{V,\dot{\gamma}} . \tag{8.4}$$

Such a relationship was proved analytically for the soft-sphere fluid but not for the Lennard–Jones fluid, in which case the computed expressions for p_1 and u_1 are consistent with (8.4) within an error of about 5%. Relation (8.4) is well known for equilibrium systems, with p and u being the equilibrium pressure and internal energy. What is new and unexpected is that (8.4) is also satisfied by the non-equilibrium contributions of p and u. This led Hanley and Evans to propose a generalised Gibbs relation of the form

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \zeta\,\mathrm{d}\dot{\gamma} \tag{8.5}$$

where $\zeta(T, V, \dot{\gamma})$ is a state function reflecting the shear-rate dependence of the thermodynamical potential. Expression (8.4) is easily derived from (8.5), since

$$\left(\frac{\partial U}{\partial V}\right)_{T,\dot{\gamma}} = -p + T\left(\frac{\partial S}{\partial V}\right)_{T,\dot{\gamma}} . \tag{8.6}$$

Introducing the Maxwell relation $(\partial S/\partial V)_{T,\dot{\gamma}} = (\partial p/\partial T)_{V,\dot{\gamma}}$ into (8.6) and recalling that the internal energy is $U = Nu$, we see that (8.6) is identical to (8.4).

A third point predicted by the numerical results refers to thermodynamic stability. By using the Helmholtz potential

$$\mathrm{d}\Phi = -S\mathrm{d}T - p\mathrm{d}V + \zeta\,\mathrm{d}\dot{\gamma} \tag{8.7}$$

and proceeding in close analogy with classical thermodynamics, one obtains the following stability conditions:

$$C_v(T, V, \dot{\gamma}) \geq 0 \qquad \text{(thermal stability)}, \tag{8.8a}$$

$$-(\partial p/\partial V)_{T,\dot{\gamma}} \geq 0 \qquad \text{(mechanical stability)}, \tag{8.8b}$$

$$(\partial \zeta/\partial \dot{\gamma})_{T,V} \geq 0 \qquad \text{(shear-rate stability)} \tag{8.8c}$$

$$\left(\frac{\partial p}{\partial V}\right)_{T,\dot{\gamma}} \left(\frac{\partial \zeta}{\partial \dot{\gamma}}\right)_{T,V} \geq \left[\left(\frac{\partial p}{\partial \dot{\gamma}}\right)_{T,V}\right]^2 \tag{8.8d}$$

Such stability conditions are generally not satisfied for any value of the shear rate. For instance, one notes that $(\partial u_1/\partial T)_{V,\dot{\gamma}}$ may be negative according to Table 8.1, which means that a fluid may be thermally less stable in the presence of a shear. In view of Table 8.1, $(\partial p/\partial \rho)_{T,\dot{\gamma}}$ is seen to be positive so that, under a shear, mechanical instability is enhanced. The fourth condition in (8.8a–d) is more severe than the second one in the sense that it leads to a value of the critical shear rate lower than the one inferred from the thermal stability condition. Hanley and Evans have interpreted the shear-rate influence on phase transitions as a consequence of the breakdown of solid-like structures of charged suspended colloidal particles when the system is sheared (Ackerson and Clark 1981; Hanley et al. 1983). Clearly, numerical simulations strongly suggest that thermodynamics should be extended beyond its classical description.

Numerical simulations are also useful to test the theoretical ideas on non-equilibrium temperature and non-equilibrium pressure. In their earlier calculations Hanley and Evans (1982) did not evaluate the entropy and defined the temperature in terms of the average kinetic energy of the particles. Later on, Evans computed explicitly the entropy of shear states under shear flow for a system of 32 soft discs interacting through a potential of the form $\phi(r) = \varepsilon(\sigma/r)^{12}$, truncated at $r = 1.5\sigma$. Evans calculated the entropy for an isoenergetic planar Couette flow by using the following expression for the entropy (see Sect. 4.5):

$$\frac{S}{N} = 1 - k_B \ln\left(\frac{n}{2\pi m k_B T}\right) - \frac{1}{2} n k_B \int g(r_{12}) \ln g(r_{12}) \mathrm{d}r_{12} \tag{8.9}$$

with $g(r_{12})$ being the radial distribution function; the entropy was obtained by integrating the relevant distribution functions over the whole simulation volume, by forming histograms for $g(\boldsymbol{r})$ and $f(\boldsymbol{r})$. Table 8.2 shows some of Evans' results, which make evident the difference between the kinetic (local-equilibrium) temperature T and the (non-equilibrium) thermodynamic temperature θ defined as the derivative of the energy with respect to the entropy.

Furthermore, Evans has calculated the non-equilibrium pressure, defined as $\pi = -(\partial U/\partial V)_{\dot{\gamma}}$, and has compared it with the kinetic pressure p obtained from the trace of the pressure tensor. From a microscopic point of view, the non-equilibrium corrections may be attribute to a deformation of the pair-correlation $g(r_{12})$ in the presence of the shear flow. Some of Evans' results are reproduced in Table 8.3.

It is evident from these results that there are significative differences between the values of θ and T and between those of π and p in the presence of shear rates.

Table 8.2 Values for the non-equilibrium entropy, the kinetic temperature T and the thermodynamic temperature θ at energy $u = 2.134$ at different densities and different values of the shear rate $\dot{\gamma}$. All the quantities are expressed in units of the parameters of the molecular potential ε, σ and k_B (Evans and Morriss 1990). The uncertainties in the entropy are ±0.005 and in temperature ±0.04

ρ	$\dot{\gamma}$	s	T	θ
0.100	0.0	5.917	2.175	2.126
0.100	0.5	5.653	2.171	2.048
0.100	1.0	5.392	2.169	1.963
0.075	0.0	6.213		
0.075	0.5	5.852	2.190	2.088
0.075	1.0	5.499	2.188	1.902

Table 8.3 Values of the local-equilibrium pressure p versus the non-equilibrium pressure π at energy $u = 2.134$ and density $\rho = 0.100$ for different values of the shear rate $\dot{\gamma}$ (Evans and Morriss 1990)

$\dot{\gamma}$	p	π
0.0	0.244	0.215
0.5	0.245	0.145
1.0	0.247	0.085

Note, furthermore, that $\theta < T$ and $\pi < p$, as predicted by EIT, according to the arguments presented in Sect. 3.5 Evans (1989) noticed that the numerical data for the thermodynamic pressure π agree with the minimum eigenvalue of the pressure tensor and conjectured that this is a general feature. He argued that, if the entropy is related to the minimum reversible work to accomplish a virtual change, in a non-equilibrium steady state the minimum work, changing the volume by $\mathrm{d}V$, will be that carried out by moving the wall perpendicular to the direction corresponding to the minimum eigenvalue of the pressure tensor. We have found in (3.23) a similar result for a gas submitted to a heat flux, where the pressure becomes lower in the directions perpendicular to the heat vector, and in (3.29a) for fluids under shear flow.

8.3 Dependence of the Free Energy on the Shear Rate: Non-linear Approach

We have already stated that the main difference between the results (8.3) of numerical simulations and those of EIT is that the former predicts a non-analytical dependence of p and E on the shear rate $\dot{\gamma}$ while EIT exhibits a dependence on $\dot{\gamma}^2$. Indeed, it is found from (8.3) that the free energy $\Phi(T, V, \dot{\gamma})$ is

$$\Phi(T, V, \dot{\gamma}) = \Phi_{\mathrm{eq}}(T, V) + \Phi_1(T, V)\dot{\gamma}^{3/2}, \tag{8.10}$$

in contrast with the $\dot{\gamma}^2$ behaviour found in Chap. 2.

A strict comparison with EIT requires a macroscopic theory valid at very high values of the shear rate. Indeed, computer simulations have been performed at high values of $\dot{\gamma}$ in order to emphasize the effects of shear (Problem 8.3 shows the very unrealistic values of the actual shear rate which correspond to the value $\dot{\gamma} = 1$ of the dimensionless shear rate considered in NEMD (Non-Equilibrium Molecular Dynamics) simulations of atomic fluids). In contrast, the quadratic approximation supposes that $\dot{\gamma}$ remains small. Nevertheless, the transition from a $\dot{\gamma}^2$ to a $\dot{\gamma}^{3/2}$ regime may be apprehended qualitatively in a rather simple way in the context of EIT (Bidar 1997). To achieve this goal, let us start from the following expression of the free energy of EIT

$$\Phi(T, V, \dot{\gamma}) = \Phi_{\mathrm{eq}}(T, V) + \frac{1}{2}\tau V \eta \dot{\gamma}^2, \tag{8.11}$$

where we have used $P_{12}^{v} = \eta\dot{\gamma}$ to write $F(T, V, \dot{\gamma})$ instead of $F(T, V, P_{12}^{v})$. In general, the viscosity η will be a function of $\dot{\gamma}$ and will decrease with increasing $\dot{\gamma}$ (a phenomenon known as shear-thinning). Detailed expressions for such a dependence of $\eta(\dot{\gamma})$ may be obtained from kinetic theory, from numerical simulations, and from maximum-entropy arguments. Here, we will use the latter to emphasize the internal unity of the present text. Taking into account expression (6.41) for the Lagrange multiplier λ_{12} conjugated to the viscous pressure component P_{12}^{v} in information theory, as well as the identification

$$\lambda_{12} = -\frac{\tau}{\eta k_{\mathrm{B}} T} P_{12}^{v} = \frac{\tau\dot{\gamma}}{k_{\mathrm{B}} T}, \tag{8.12}$$

one may obtain η as a function of P_{12}^{v} as

$$\eta = -\frac{P_{12}^{v}}{\dot{\gamma}} = -\eta_0 \frac{3R^2\left[R^2 + (1-y)\right]}{2\left[R^2 + \frac{2}{3}(1-y)\right]}, \tag{8.13}$$

where R and y are given by

$$R = P_{12}^{v}(Nu)^{-1}, \ y = (1 + 3R^2)^{1/2}, \tag{8.14}$$

while η_0 is the shear viscosity in the low shear-rate limit. For low values of R, this expression tends to η_0, whereas it tends to 0 when R approaches 1, in such a way that $\eta(\dot{\gamma})\dot{\gamma}$ tends to the finite value Nu (corresponding to $R = 1$). The behaviour of $\eta(\dot{\gamma})$ is given implicitly by (8.13), but it is difficult to invert this relation analytically. Its behaviour can be grossly modelled by Bidar (1997)

$$\eta = \frac{\eta_0}{[1 + (a\tau\dot{\gamma})^n]^{1/n}}, \tag{8.15}$$

where a and n are fitting parameters. It must be noted that (8.15) does not follow from first principles; it is rather a heuristic simplification of (8.13), but it captures the essential features of the asymptotic behaviour of the pressure tensor at high and low values of the shear rate. Accordingly, expression (8.11) for the free energy may be written as

$$\Phi(T, V, \dot{\gamma}) = \Phi_{\text{eq}}(T, V) + \frac{1}{2}\tau V \eta_0 \left[1 + (a\tau\dot{\gamma})^n\right]^{-1/n} \dot{\gamma}^2. \tag{8.16}$$

Note that the asymptotic behaviour of F at low $\dot{\gamma}$ is of the form $\dot{\gamma}^2$, whereas for high values of $\dot{\gamma}$ it behaves like $\dot{\gamma}$; therefore, at the intermediate regime F is expected to depend on $\dot{\gamma}$ as $\dot{\gamma}^{3/2}$. A linear behaviour of F (or S) with $\dot{\gamma}$ is moreover observed in NEMD; when the calculations are extrapolated to regions with small shear rate, which are the most difficult to simulate, the possibility of a crossover to a $\dot{\gamma}^2$ dependence is not excluded by the results of NEMD.

8.4 Shear-Induced Heat Flux and the Zeroth Law

It was stressed that numerical simulations may lead to a non-equilibrium temperature dependent on the shear rate, as in EIT. In this last section, we examine the relation between this temperature and the heat flux, which is of interest in connection with temperature measurements. This was pointed out in our discussion about non-equilibrium temperature in Chap. 3. Here, we will consider it from the perspective of NEMD.

Evans and co-workers have studied the flow of a fluid in a Poiseuille configuration (Todd et al. 1995a,b; Todd and Evans 1995) and in a non-homogeneous shear flow produced by a sinusoidal transverse force (Baranyai et al. 1992). The purpose was to study the conditions of thermal 'equilibrium' between non-equilibrium steady states characterized by different shear rates, in mutual thermal and mechanical contact. One interesting result is the occurrence of a heat flow between different 'subsystems' even when they are at the same kinetic (i.e. local-equilibrium) temperature. This reinforces the arguments presented in Chap. 3, in which it was claimed that the heat flux is related to the gradient of the temperature θ rather than to the gradient of the local-equilibrium temperature T. Here, instead of a heat flux, the non-equilibrium parameter is the shear rate. The results of Evans et al. (1995) confirm that layers with identical kinetic temperatures may have shear-rate dependent thermodynamic temperatures, since they exchange heat.

However, as commented in Chap. 3 and in Sect. 8.2, such thermodynamic temperature should decrease with increasing shear rates. In contrast, Evans et al. (1995) obtained a heat flux in the opposite sense, i.e. from the layers with higher shear rate to those with lower shear rate. To describe this result in a macroscopic way, they assumed an ad hoc constitutive equation for the heat flux of the form

$$\boldsymbol{q} = -\lambda \nabla T - \xi \left[(\nabla \boldsymbol{v}) : (\nabla \boldsymbol{v})^T \right], \tag{8.17}$$

where ξ is a coupling coefficient which describes the 'isothermal' generation of heat flux due to a velocity gradient between parallel plates located at $y = 0$ and $y = d$. For a planar Poiseuille flow with constant viscosity η, the solution for the velocity profile is

$$v_x(y) = -\frac{1}{2\eta} \frac{\mathrm{d}p}{\mathrm{d}x} (y - d) y, \tag{8.18}$$

and the leading-order terms in the heat equation are

$$\rho c_v \frac{\mathrm{d}T}{\mathrm{d}t} = \lambda \nabla^2 T + \xi \nabla^2 \dot{\gamma}^2 + \eta \dot{\gamma}^2, \tag{8.19}$$

where $\dot{\gamma} \equiv \partial v_x / \partial y$ as usual. The temperature profile in a steady state now has the form

$$T(y) = -\frac{\xi}{4\lambda\eta^2} \left(\frac{\mathrm{d}p}{\mathrm{d}x} \right)^2 (d - 2y)^2 - \frac{1}{192\lambda\eta} \left(\frac{\mathrm{d}p}{\mathrm{d}x} \right)^2 (d - 2y)^4 + \text{constant}. \tag{8.20}$$

The effect of the coupling in the first term will dominate when $d - 2y < \sqrt{48\xi/\eta}$ and will change the shape of the temperature profile from quartic to parabolic in the central region of the flow.

Although the modelling (8.17) fits the results of the non-equilibrium molecular dynamics simulations, it is an ad hoc assumption and does not clarify the role of the non-equilibrium temperature. In contrast, an equation analogous to (8.17) may be obtained in the framework of EIT. We may start from the evolution equation (2.69) for the heat flux, namely

$$\tau \dot{\boldsymbol{q}} + \boldsymbol{q} = -\lambda \nabla \theta - \frac{a\lambda}{n k_\mathrm{B}} \nabla \cdot \mathbf{P}^v, \tag{8.21}$$

with a being a numerical constant. Furthermore, recall that in Sect. 3.3 we wrote the pressure tensor as

$$\mathbf{P} = \pi \mathbf{U} + \mathbf{P}^v = n k_\mathrm{B} \theta \mathbf{U} + \mathbf{P}^v. \tag{8.22}$$

For a plane shear flow, this tensor is given the form

$$\mathbf{P} = \begin{pmatrix} n k_\mathrm{B}\theta & 0 & 0 \\ 0 & n k_\mathrm{B}\theta & 0 \\ 0 & 0 & n k_\mathrm{B}\theta \end{pmatrix} + \begin{pmatrix} b\dot{\gamma}^2 & -\eta\dot{\gamma} & 0 \\ -\eta\dot{\gamma} & b\dot{\gamma}^2 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{8.23}$$

up to the second order in the shear rate. The value of the coefficient b is given by the condition that $\mathrm{Tr}\mathbf{P} = 3p = 3 n k_\mathrm{B} T$, identically. This implies that

$$3 n k_\mathrm{B} \theta + 2 b \dot{\gamma}^2 = 3 n k_\mathrm{B} T,$$

and therefore

$$b\dot{\gamma}^2 = \frac{3}{2} n k_B (T - \theta). \tag{8.24}$$

The expression (8.23) for **P** may be introduced into (8.21) and it follows that, in a steady state, the component of the heat flux in the y direction (perpendicular to the flow) is

$$q_y = -\lambda \frac{\partial \theta}{\partial y} - \frac{a\lambda}{n k_B} \frac{\partial}{\partial y}(b\dot{\gamma}^2). \tag{8.25}$$

This equation shows a coupling between the heat flux and the gradient of the shear rate; however, in contrast to (8.17), it exhibits explicitly the role of θ. Moreover, (8.25) does not exclude the possibility that the heat flows in the direction of $\nabla\theta$. To see that, let us eliminate b between (9.24) and (9.25) so that

$$q_y = -\lambda \frac{\partial \theta}{\partial y} - \frac{3}{2} a\lambda \frac{\partial}{\partial y}(T - \theta) = \left(\frac{3a}{2} - 1\right) \lambda \frac{\partial \theta}{\partial y}, \tag{8.26}$$

where in the second equality we have assumed that T is homogeneous. It follows that for $3a > 2$, the coupling between $\mathbf{P}^v$ and $\boldsymbol{q}$ in (8.24) justifies that q_y has the same direction as the gradient of θ instead of the opposite direction.

In EIT, the presence of coupling terms comes out in a rather natural way from the general framework. Furthermore, the existence of this coupling shows that the vanishing of the non-equilibrium temperature gradient in (8.21) does not guarantee a zero heat flux. Therefore, the zeroth principle of thermodynamics must be taken with caution in non-equilibrium situations, because of the different possible couplings between the system being analysed and the system being used as a thermometer. This conclusion is not completely surprising; for instance, in classical irreversible thermodynamics, when both heat and matter may flow, it is possible to combine the temperature gradient and concentration gradient in such a way that the net heat exchange vanishes in spite of the existence of a temperature gradient. Here, the heat flux could be made to vanish by a suitable combination of the gradients of θ and $\dot{\gamma}$.

8.5 Problems

8.1 In one of the earliest versions of non-equilibrium molecular dynamics of fluids under shear, the microscopic equations of motion were derived from a so-called DOLLS Hamiltonian (Hoover 1999), defined as

$$\mathcal{H} = \sum_i \frac{\boldsymbol{p}_i \cdot \boldsymbol{p}_i}{2m} + \sum_{i,j} \phi(\boldsymbol{r}_i, \boldsymbol{r}_j) + \sum_i (\nabla \boldsymbol{v}) : \boldsymbol{p}_i \boldsymbol{r}_i,$$

where ϕ is the intermolecular potential and the last term describes the action of the flow. (a) By using the Hamiltonian algorithm, i.e.

$$\dot{\boldsymbol{r}}_i = \frac{\partial \mathcal{H}}{\partial \boldsymbol{p}_i}, \; \boldsymbol{p}_i = -\frac{\partial \mathcal{H}}{\partial \boldsymbol{r}_i},$$

derive the equations of motion from $\mathcal{H}$ and compare them with (8.1). (b) Check that in contrast with the equations derived from the DOLLS Hamiltonian (8.1) (also called the SLLOD equations of motion) (Evans and Morriss 1990) are not derivable from a Hamiltonian.

8.2 In order for the kinetic energy of the system to remain constant one must require that $\sum_i \boldsymbol{p}_i \cdot \dot{\boldsymbol{p}}_i = 0$. (a) Apply this condition to (8.1b) and show that

$$\alpha = \frac{\sum_j \boldsymbol{F}_j \cdot \boldsymbol{p}_j - (\nabla \boldsymbol{v}) : \sum_j \boldsymbol{p}_j \boldsymbol{p}_j}{\sum_i \boldsymbol{p}_i \cdot \boldsymbol{p}_i}.$$

(b) Show that this expression may be rewritten in the form of (8.2).

8.3 In the tables of this chapter, the several quantities (temperature, density, shear rate, etc.) are given in dimensionless form in units of m (mass of the particles) and of the parameters ε and σ describing the strength and range of the intermolecular potential. The values of the dimensionless temperature and number density at the triple point are

$$T^* = \frac{k_\mathrm{B} T}{\varepsilon} = 0.722, \; n^* = n\sigma^3 = 0.844.$$

The triple point of Ar (molecular mass $= 40\,\mathrm{g\,mol^{-1}}$) corresponds to $T_t = 83.8\,\mathrm{K}$ and $p_t = 6.88 \times 10^5\,\mathrm{N\,m^{-2}}$, and the number density corresponding to the liquid phase is $n = 2.6 \times 10^{28}\,\mathrm{m^{-3}}$. (a) Find ε and σ for Ar. (b) Estimate the actual value of the shear rate corresponding to the dimensionless value $\dot{\gamma} = 1$. (c) Evaluate the relaxation time for Ar and compare it with that of a globular polymer with $\sigma = 10^{-4}\,\mathrm{m}$ and molar mass $10^3\,\mathrm{kg} \times \mathrm{mol^{-1}}$ and $T_t = 300\,\mathrm{K}$. Recall that

$$\dot{\gamma} = \gamma^* \left(\frac{\varepsilon}{m\sigma^2}\right)^{1/2}, \; \tau = \left(\frac{m\sigma^2}{\varepsilon}\right)^{1/2}.$$

8.4 To describe fluid systems under shear flow with shear rate $\dot{\gamma}$, the following generalised free energy per unit mass is used

$$f(T, v, \dot{\gamma}) = f_{\mathrm{eq}}(T, v) + \alpha(T, v, \dot{\gamma}),$$

$\alpha(T, v, \dot{\gamma})$ is a function given, for instance, by $\alpha = A v^{-x} T^{-z} \dot{\gamma}^{2(y+1)}$, A is a positive constant and x, y, and z are constant parameters. From the stability conditions

$$\left(\frac{\partial^2 f}{\partial T^2}\right)_{v,\dot{\gamma}} \le 0, \; \left(\frac{\partial^2 f}{\partial v^2}\right)_{T,\dot{\gamma}} \ge 0, \; \left(\frac{\partial^2 f}{\partial \dot{\gamma}^2}\right)_{T,v} \ge 0,$$
$$\left(\frac{\partial^2 f}{\partial v^2}\right)_{T,\dot{\gamma}} \left(\frac{\partial^2 f}{\partial \dot{\gamma}^2}\right)_{T,v} \ge \left(\frac{\partial^2 f}{\partial v \partial \dot{\gamma}}\right)^2,$$

analyse how a shear rate can modify the stability of the system.

Table 8.4 Values of the non-equilibrium entropy s for different values of the internal energy u and of the shear rate $\dot{\gamma}$

u	$s(\dot{\gamma} = 0.0)$	$s(\dot{\gamma} = 0.5)$	$s(\dot{\gamma} = 1.0)$
1.921	5.812	5.539	5.275
2.134	5.917	5.653	5.392
2.346	6.013	5.492	5.747

Table 8.5 Values of the non-equilibrium entropy s for different values of the density ρ and of the shear rate $\dot{\gamma}$

ρ	$s(\dot{\gamma} = 0.0)$	$s(\dot{\gamma} = 0.5)$	$s(\dot{\gamma} = 1.0)$
0.100	5.917	5.653	5.392
0.125	5.686	5.478	5.267
0.075	6.213	5.852	5.499

8.5 The values obtained by Evans (1989) for the internal energy u and the entropy s for density $\rho = 0.100$ in a numerical analysis of a system constituted of 32 soft discs described by a potential $\phi(r) = \varepsilon(\sigma/r)^{12}$, at different values of the shear rate $\dot{\gamma}$, are listed in Table 8.4.

Estimate the mean value of the non-equilibrium temperature θ at different shear rates by using the values of the entropy presented in Table 8.4, and the definition $\theta = (\partial U/\partial S)_{\dot{\gamma}}$, and by approximating the derivative by the corresponding incremental ratio.

8.6 According to Evans (1989), the values for the entropy of the system of 32 soft discs mentioned in the previous problem, at internal energy $u = 2.134$ and for different densities, are given in Table 8.5.

Obtain the thermodynamic pressure at different shear rates by approximating the derivative $\pi\theta^{-1} = (\partial s/\partial v)_{u,\dot{\gamma}}$ by the corresponding incremental ratio.

8.7 In their analysis of the isothermal shear-induced heat flow discussed in Sect. 8.4, Baranyai et al. (1992) proposed for the heat flux the constitutive equation (8.17), namely

$$\boldsymbol{q} = -\lambda\nabla T - \xi\nabla\left[\nabla\boldsymbol{v} : (\nabla\boldsymbol{v})^T\right],$$

with ξ being a coupling coefficient. (a) Show that for a velocity profile of the form $\boldsymbol{v} = (\dot{\gamma}y, 0, 0)$ the energy balance equation takes the form (8.19). (b) Given the classical expression for the entropy production, namely

$$\sigma^s_{\mathrm{CIT}} = \boldsymbol{q}\cdot\nabla T^{-1} - T^{-1}\mathbf{P}^v : (\nabla\boldsymbol{v}),$$

and if the fluid is assumed to be Newtonian, discuss under which conditions expression (8.17) for the heat flux is compatible with positive entropy production.

8.8 The extended Gibbs equation for a viscoelastic fluid in the internal energy representation is

$$\mathrm{d}U = \theta\mathrm{d}S - \pi\mathrm{d}V + \mu\mathrm{d}N + \frac{\tau}{2\eta}\mathbf{P}^v : \mathrm{d}(V\mathbf{P}^v).$$

(a) Show that in a steady state

$$\left(\frac{\partial U}{\partial (V\mathbf{P}^v)}\right)_{S,V,N} = -\tau(\nabla \boldsymbol{v})^s.$$

(b) In equilibrium thermodynamics, the way to change a variable in $U(S, V, N)$ for the corresponding derivative of U with respect to this variable is a Legendre transform. For instance, when S is replaced by $T = (\partial U/\partial S)_{V,N}$, the Legendre transform is

$$\Phi(T, V, N) = U - \frac{\partial U}{\partial S} S = U - TS.$$

Analogously to the equilibrium situation, if one wishes to use $\tau\,(\nabla \boldsymbol{v})^s$ as variable instead of $\mathbf{P}^v$, one should make a Legendre transform as

$$\Phi(\theta, V, N, \tau(\nabla \boldsymbol{v})^s) \equiv U - \frac{\partial U}{\partial S} S - \frac{\partial U}{\partial (V\mathbf{P}^v)} : V\mathbf{P}^v.$$

Compare this expression with that obtained by direct substitution of $\mathbf{P}^v$ with $-2\eta(\nabla \boldsymbol{v})^s$ in the free energy $\Phi = \Phi_{\text{eq}} + \frac{1}{4} J V \mathbf{P}^v : \mathbf{P}^v$.

(c) Compare the form of the chemical potential derived from the Legendre transform $\Phi(\theta, V, N, \tau\,(\nabla \boldsymbol{v})^s)$ and from the direct substitution of $\mathbf{P}^v$ with $-2\eta(\nabla \boldsymbol{v})^s$ in Φ. Note that the non-equilibrium contribution has opposite sign in the two expressions.

8.9 By following the statements of Problem 8.8, discuss the Legendre transform from $V\boldsymbol{q}$ to its conjugate in the generalised Gibbs equation, namely $-\tau\nabla T^{-1}$, with τ being the relaxation time of the heat flux in the Maxwell–Cattaneo equation.

Part III
Selected Applications

Chapter 9
Hyperbolic Heat Transport in Rigid Conductors

There exists an impressive amount of literature on heat conduction and hyperbolic equations. It is not our purpose to examine this topic exhaustively, but to stress the more significant and illustrative aspects in connection with extended irreversible thermodynamics (EIT). Two main motivations underlie such a vast literature. One of them, of a theoretical nature, refers to the so-called 'paradox' of propagation of thermal signals with infinite speed. The second, more closely related to experimental observations, deals with the propagation of second sound, ballistic phonon propagation, and phonon hydrodynamics in solids at low temperatures, where heat transport departs dramatically from the usual parabolic description.

In the classical theory of heat transport, thermal signals obey a parabolic equation. In the linear approximation, this implies that the influence of such a signal is felt instantaneously throughout the whole system, or, otherwise stated, that the thermal signal propagates at infinite velocity. One of the first motivations for EIT was precisely to remove the paradox of infinite speed of propagation.

A macroscopic theory with finite speed of propagation finds its roots in the kinetic theory and in experiments. From an experimental point of view, the search for generalising the Fourier equation was launched in the 1960s by the discovery of second sound and ballistic phonon propagation in some dielectric crystals at low temperature. This observation stimulated also the development of microscopic models of heat conduction supporting the generalised macroscopic transport equations. Such analyses are of interest in solid-state physics because they provide useful and relevant information on phonon scattering processes. However, most works on heat propagation are concerned with the dynamical consequences of the transport equations, without paying much attention to their thermodynamic implications. In Chap. 2 we have already emphasized the need to deal consistently with both dynamical and thermodynamical aspects. In Chap. 10 we complete the analysis of heat transport by focussing our attention on nanosystems, because of their technological applications and their conceptual challenges.

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_9, © Springer Science+Business Media LLC 2010

9.1 Linear Wave Propagation: Second Sound and Telegrapher Equation

The thermodynamical analysis of hyperbolic heat transport (described by the Maxwell–Cattaneo's equation) has been carried out in Sect. 2.1. Here we explore the physical consequences of the presence of relaxational terms in the transport equation (2.4) when the relaxation time τ and the heat conductivity λ are constant. For simplicity, we consider a rigid solid or an incompressible perfect fluid at rest, which, according to the hypotheses of EIT, is locally characterized by the specific internal energy u per unit mass and the heat flux vector $\boldsymbol{q}$. The energy balance equation reduces in this case to

$$\rho\frac{\partial u}{\partial t} = -\nabla\cdot\boldsymbol{q}, \tag{9.1}$$

where no energy supply has been considered. The evolution equation for $\boldsymbol{q}$ is assumed to be the Eq. (2.4),

$$\tau\frac{\partial \boldsymbol{q}}{\partial t} = -(\boldsymbol{q} + \lambda\nabla\theta). \tag{9.2}$$

Consider infinitesimally small thermal disturbances around an equilibrium reference state with vanishing velocity. In this case, θ and T are identical up to second-order corrections and $\partial u/\partial t$ is given by $\partial u/\partial t = c_v\partial T/\partial t$, with c_v the heat capacity per unit mass at constant volume. The evolution equations of T and $\boldsymbol{q}$ are therefore given by:

$$\rho c_v\frac{\partial T}{\partial t} = -\nabla\cdot\boldsymbol{q}, \tag{9.3}$$

and

$$\tau\frac{\partial \boldsymbol{q}}{\partial t} = -\left(\boldsymbol{q} + \lambda\nabla T\right). \tag{9.4}$$

Introduction of (9.4) into (9.3), results in a hyperbolic equation of the telegrapher type, namely,

$$\tau\frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} - \chi\nabla^2 T = 0, \tag{9.5}$$

with $\chi = \lambda/\rho c_v$ being the thermal diffusivity. General properties of the telegrapher equation have been extensively studied. By assuming plane thermal waves of the form

$$T = T'\exp\left[\mathrm{i}\left(\omega t - kx\right)\right], \tag{9.6}$$

where ω is the (real) frequency, k the (complex) wave number, and T' the amplitude, the dispersion relation obtained by substituting (9.6) into (9.5) reads

$$-\tau\omega^2 + \mathrm{i}\omega + \chi k^2 = 0. \tag{9.7}$$

It follows that the phase velocity v_p and the attenuation distance α are given by

$$v_p = \frac{\omega}{\operatorname{Re} k} = \frac{\sqrt{2\chi\omega}}{\sqrt{\tau\omega + \sqrt{1+\tau^2\omega^2}}} \tag{9.8a}$$

and

$$\alpha = -\frac{1}{\operatorname{Im} k} = \frac{2\chi}{v_p}. \tag{9.8b}$$

At low frequencies ($\tau\omega \ll 1$), it is found that $v_p = (2\chi\omega)^{1/2}$ and $\alpha = (2\chi/\omega)^{1/2}$, which are the results predicted by the classical theory based on Fourier's law. In the high-frequency limit ($\tau\omega \gg 1$), the first-order term derivative $\partial T/\partial t$ in (9.5) is small compared with the two other terms and (9.5) becomes a wave equation whose solutions are known in the literature as second sound. The quantities v_p and α tend to the limiting values $v_{p\,\infty}$ and α_∞ which are given by

$$v_{p\,\infty} \equiv U = \sqrt{\chi/\tau}\,,\ \alpha_\infty = 2\sqrt{\chi\tau}, \tag{9.9}$$

where $v_{p\infty}$ can be identified with the speed of propagation of thermal pulses as shown in the next section. The velocity U is usually called the velocity of second sound. It is interesting to note that within the limit $\tau = 0$, which corresponds to the Fourier law, one has $v_{p\infty} = \infty$ and $\alpha_\infty = 0$. Note that when τ and λ diverge but τ/λ remains finite, as in the case of superfluids and solids at low temperature, (9.5) reduces to a wave equation. According to kinetic theory, it is found that for solids in the Debye approximation $\chi/\tau = c_0^2/3$, with c_0 the phonon velocity. As a consequence, the second sound speed in a solid is

$$U(\text{solid}) = \frac{1}{\sqrt{3}} c_0. \tag{9.10}$$

The problem of propagation of thermal signals was first dealt with by Cattaneo (1948) and Vernotte (1958) (see also Jou et al. 1998; Sieniutycz and Salamon 1992), who based their analysis on kinetic theory arguments and added a relaxation term to the Fourier equation. This point of view has been used in several contexts, such as in the analysis of waves in thermoelastic media, fast explosions, and second sound in solids. The presence of second sound in solids, suggested by Peshkov in 1947 and by Wards and Wilks in 1951, was analysed in terms of the Maxwell–Cattaneo equation by Chester (1963, 1966), who obtained for the second sound the result (9.10). Wide-ranging bibliography can be found in Luikov et al. (1976), Joseph and Preziosi (1989), Ozisik and Tzou (1994) and Tzou (1997). However, all is not well with the Maxwell–Cattaneo equation, which is insufficient in several aspects: it does not describe accurately the broadening of the second-sound signals, it does not incorporate the phenomenon of ballistic phonon propagation (i.e. the propagation of phonons without any collision) nor the dependence of the second sound on temperature, and it does not deal with phonon hydrodynamics. A more general equation is therefore proposed and discussed in Sect. 9.3.

It should also be noticed that the telegrapher equation (9.5) does not conserve the positive character of the solutions, i.e. it may yield negative values for T even when the initial profile for T is positive everywhere. This unpleasant feature may be avoided by imposing not only an initial positive profile for T but also a restriction on the heat flux, namely, that $q \leq \rho u U$ (see Problem 9.8). This condition is one of the requirements of thermodynamic stability obtained in Chap. 3 and will receive a confirmation in the foregoing sections.

It is not necessary to introduce relaxation terms into the heat equation to obtain a finite velocity for the propagation of thermal signals. This feature is also predicted by taking a non-linear diffusion equation with a thermal conductivity depending on the temperature, for instance $\lambda \approx T^n$ with $n > 0$ (Luikov et al. 1976). However, experiments show that, for fluids or metals at intermediate and high temperatures, this dependence is not realistic.

9.2 Transient Heat Conduction: Parabolic Versus Hyperbolic Regimes

Our purpose is to compare parabolic and hyperbolic response of thermal conductors whose boundaries are submitted to imposed temperature fields, heat pulses induced by a laser pulse or an electrical discharge. Combining the energy balance

$$\rho c_v \frac{\partial T}{\partial t} = -\nabla \cdot \boldsymbol{q} + g(\boldsymbol{r}, t), \tag{9.11}$$

where $g(\boldsymbol{r}, t)$ is the volumetric internal energy supply, with Cattaneo equation (9.4) results in

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} - \chi \nabla^2 T = \frac{1}{\rho c_v} \left(g + \tau \frac{\partial g}{\partial t} \right), \tag{9.12}$$

for constant relaxation time τ and thermal coefficients λ and c_v. Equation 9.12 can be solved by several techniques, like Laplace's transformation or Green's function method (see Problem 9.17) and is particularly well suited to describe microscale applications involving small time (sub-picoseconds) and small space scales (smaller than one micron). We have in mind materials characterized by non-homogeneous inner structures, like porous media, sand and processed meat. As it is here wished to discuss a simple analytic solution, we shall consider the problem of heat conduction in a thin film, say a dielectric crystal sandwiched between two metallic plates, in absence of internal energy supply.

9.2.1 Formulation of the Problem in Absence of Internal Source

Consider a one-dimensional slab of thickness L whose initial temperature is T_0. At time $t = 0^+$, the temperature at the boundary $x = 0$ is suddenly increased to

$T = T_1$ while it is maintained at $T = T_0$ at the other extremity $x = L$. Introducing the following dimensionless variables

$$x^* = x/L,\ t^* = t/\tau,\ T^* = (T - T_0)/(T_1 - T_0), \tag{9.13}$$

the boundary and initial conditions take the form

$$x = 0: \quad T^*(0, t^*) = 1,\ x^* = 1: \qquad T^*(1, t^*) = 0, \tag{9.14a}$$

$$t^* = 0: \quad T^*(x^*, 0) = 0,\ \partial T(x^*, 0)/\partial t^* = 0. \tag{9.14b}$$

Making use of the method of separation of variables, it is found that the solution of Eq. (9.12), with $g(\boldsymbol{r}, t) = 0$, is given by

$$\begin{aligned} T^* = 1 - x^* - \frac{1}{2\pi} \exp\left(-\tfrac{1}{2}t^*\right) \sum_{n=1}^{\infty} \frac{1}{n} \sin(n\pi x^*) \\ \times \left[\frac{1 + 2\alpha_n}{\alpha_n} \exp(\alpha_n t^*) + \frac{2\alpha_n - 1}{\alpha_n} \exp(-2\alpha_n t^*) \right], \end{aligned} \tag{9.15}$$

with $\alpha_n = (1 - \frac{1}{3}n^2\pi^2)^{1/2}$.

The heat flux at $x^* = 0$, adimensionalized by $\lambda(T - T_0)/L$, is

$$q^* = \frac{1}{3}[1 - \exp(-t^*)] + 2 \exp\left(-\frac{1}{2}t^*\right) \sum_{n=1}^{\infty} \frac{\alpha_n}{n} \sinh(\alpha_n t^*). \tag{9.16}$$

In the Fourier approximation, i.e. letting $\tau \to 0$ and defining $t^* = t/(L\nu)$, with ν a reference velocity, say the phonon velocity, the solutions (9.15) and (9.16) take the form

$$T^* = 1 - x^* - (2/\pi) \sum_{n=1}^{\infty} \sin(n\pi x^*) \exp\left[-\tfrac{1}{3}(n^2\pi^2 t^*)\right], \tag{9.17}$$

$$q^* = 1 + 2 \sum_{n=1}^{\infty} \exp\left[-\tfrac{1}{3}(n^2\pi^2 t^*)\right]. \tag{9.18}$$

Solution (9.15) and (9.16) are representative of waves damped by heat diffusion and are converging to the Fourier solution for sufficiently long times. Expression (9.17) reflects the property that temperature is instantaneously felt everywhere in the whole slab, moreover, it follows from (9.18) that for $t^* \to 0$, the heat flux q^* tends to infinity.

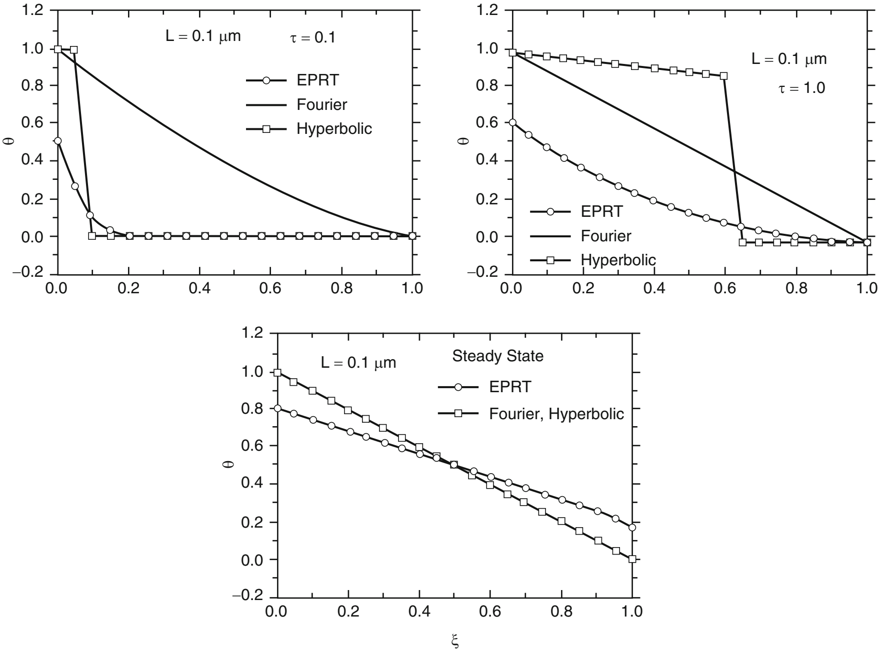


Fig. 9.1 Non-dimensional temperature profiles for Fourier, Cattaneo (hyperbolic) and kinetic (EPRT) evolution laws at three different dimensionless times (reprinted with permission from Joshi AA, Majumdar A (1993) J Appl Phys 74:31)

9.2.2 Results for Diamond Films

The above analysis is applied to the problem of transient heat transport in a thin diamond film, initially at temperature $T_0 = 300\,\mathrm{K}$, when the temperature at the face $x = 0$ is suddenly brought at $T_1 = T_0 + 0.1\,\mathrm{K}$. The results of Fig. 9.1 (Joshi and Majumdar 1993) reproduce the temperature profiles for a layer of thickness $L = 1\,\mu\mathrm{m}$ at the dimensionless times $t^* = 0.1$, 1.0 and ∞ (steady state) obtained from Fourier's law, Cattaneo's law (hyperbolic model), and a kinetic model based on an equation of phonon radiative transfer (EPRT), which is discussed in the next chapter, in Sect. 10.2.

According to Fourier's law, a well-established temperature distribution is observed within the slab at any time, the steady state solution is predicted after time is increased beyond $t^* > 1$. Cattaneo's law gives rise to a temperature wave travelling across the film, the attenuation of the wave is due to diffusion effects which increase with time. The wave moves with a velocity $c_0/\sqrt{3}$ as discussed in Sect. 9.1. When compared to Fourier's equation, it is seen that Cattaneo's predicts a higher value of the temperature, because behind the wave front, a higher amount of energy is trapped into a smaller volume. Of course, at large time values, energy is distributed over a larger volume because of diffusion and the hyperbolic temperature becomes

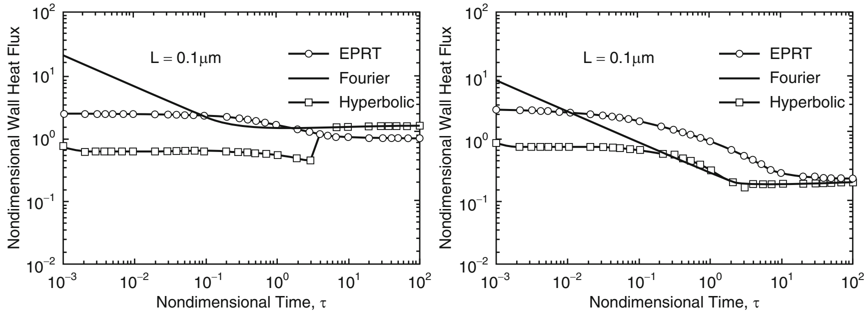


Fig. 9.2 Heat flux evolution at the wall $x^* = 0$ for Fourier, Cattaneo (hyperbolic) and kinetic (EPRT) evolution laws as a function of dimensionless time, for systems of two different lengths (reprinted with permission from Joshi AA, Majumdar A (1993) J Appl Phys 74:31)

closer to Fourier's one. In Fig. 9.2 is reported the variation of the heat flux as a function of time at the face $x^* = 0$.

In virtue of Fourier's law, the wall heat flux decreases rapidly to its steady state value while Cattaneo's law predicts a practically constant value around $t^* = 0$, which decays gradually to the steady state value at $t^* = 3$. Fourier's model overestimates the wall heat flux because the temperature gradient which sets in instantaneously is larger than with Cattaneo's, generating a large value of the heat flux.

In short, it can be said that Fourier's law remains a very useful tool when the relaxation time is sufficiently small to neglect heat flux relaxation. However, when the relaxation time is of the same order as the time scale of the experiment under study, Cattaneo's equation must be preferred, like for instance in materials undergoing very short thermal pulses.

9.2.3 Heating in Presence of Internal Energy Source: Application to Thermal Ignition

General equation (9.12) is of interest in the treatment of combustion problems like thermal ignition in reactive solids. In the present sub-section, we shall determine the role of heat flux relaxation on the ignition time in a rigid body undergoing, for example, a laser pulse for a short time of the order of picoseconds, fast exothermic chemical reactions or internal electric discharges. The selected body may be a granular propellant as frequently used in rocket motors and guns, this kind of propellant constitutes a non-homogeneous medium formed by grains of interactive solids and voids between them. The analysis is also of application in emerging technologies of ceramic production, wherein ignition and solid phase reactions play a central role. Typically, after mixing powdered reactants, like C and Ti, these are compacted to form a porous cylinder one of whose extremities is ignited; after ignition, the reaction propagates through the cylinder and the final result is a porous product TiC. We have shown that Cattaneo's equation leads to higher temperature fields than Fourier's relation, the consequence will be an increase of the reaction rate, as the latter grows exponentially with temperature.

9.2.3.1 The Model

The reactive semi-infinite rigid body is assumed to occupy the one-dimensional space $x > 0$. The initial temperature is T_0; at time 0^+, a constant heat flux q_0 is applied across the bounding surface $x = 0$. The internal volumetric energy source obeys an Arrhenius law of the form

$$g = \rho H \exp(-E/RT), \tag{9.19}$$

in which H designates the constant heat of reaction, E the activation energy, R the universal gas constant, and the mass density ρ is also a constant, as well as τ, λ, and c_v. The non-dimensional Cattaneo and energy laws read as

$$\frac{\partial T^*}{\partial x^*} + \tau^* \frac{\partial q^*}{\partial t^*} + q^* = 0, \tag{9.20}$$

$$\frac{\partial T^*}{\partial t^*} + \frac{\partial q^*}{\partial x^*} - H^* \exp(-E^*/T^*) = 0, \tag{9.21}$$

with

$$x^* = \frac{x q_0}{\lambda T_0},\ t^* = \frac{t q_0^2}{\rho c_v \lambda T_0^2},\ T^* = \frac{T}{T_0},\ q^* = \frac{q}{q_0}, \tag{9.22a}$$

$$\tau^* = \frac{\tau q_0^2}{\rho c_v \lambda T_0^2},\ H^* = \frac{\rho H \lambda T_0}{q_0^2},\ E^* = \frac{E}{R T_0}. \tag{9.22b}$$

The initial and boundary conditions are given by

$$T^*(x^*,0) = 1,\ q^*(x^*,0) = 1,\ q^*(0,t^*) = 1,\ T^*(\infty,t^*) = 1. \tag{9.23}$$

The corresponding Fourier ignition problem is obtained by setting $\tau^* = 0$. The set (9.20–9.23) has been solved numerically with the method of characteristics by Antaki (1998) to which we refer for calculation details. Because of the hyperbolicity property, heat is initially confined in a thin layer adjacent to the bounding surface causing a jump in the temperature surface. According to Antaki (1998), the jump at the surface is $\Delta T^* = (\tau^*)^{1/2}$ and is of course equal to zero for $\tau = 0$.

Ignition occurs when the rate of external heating by the applied heat flux is equal to the rate of internal energy by chemical reactions. For the moment being, it is sufficient to define the ignition time t_i^* by the time characterized by thermal runaway at the surface, i.e. $\partial T^*/\partial t^* \to \infty$ at $x^* = 0$. The calculation of this ignition time implies the determination of the temperature at the surface by solving the set (9.20)–(9.23).

9.2.3.2 Results for Solids Propellants

Typical values for solid propellants (Antaki 1998) are $\lambda = 0.21\,\mathrm{W/mK}$, $c_v = 1.555\,\mathrm{kJ/(kgK)}$, $E = 83.91 \times 10^3\,\mathrm{kJ/kmol}$, $H = 2.62 \times 10^9\,\mathrm{kW/kg}$, $\rho = 1.6 \times 10^3\,\mathrm{kg/m^3}$, $\tau = 6.62\,\mathrm{s}$, $T_0 = 300\,\mathrm{K}$, $q_0 = 41.87\,\mathrm{kW/m^2}$ to which correspond $H^* = 1.5$, $E^* = 33.03$, $\tau^* = 0.25$. Figure 9.3 reproduces the Fourier and Cattaneo surface temperature profiles T_s^* as a function of time t^*. The results have been shown to remain qualitatively the same by selecting other values for H^*, E^* and τ^*.

The quantities $t_{i\mathrm{F}}^*$ and $t_{i\mathrm{C}}^*$ stand for the Fourier and Cattaneo ignition times respectively. The Cattaneo solution exhibits a temperature jump $\Delta T^* = 1.5$ at $x^* = 0$. At short times, the temperature remains small because heat input is weak ($H^* = 0$) at these low temperatures. At longer times, heating is dominated by the exponentially increasing rate of heat release and ends finally with thermal runaway which defines the ignition temperature. One observes a drastic reduction (of the order of 33%) of the ignition time in the hyperbolic case in comparison to the parabolic solution. This diminution is explained by the occurrence of a higher surface temperature that in turn gives rise to higher reaction rates and, in consequence, larger heat release. The reduction of the ignition time is increased with larger values of the relaxation time.

In Fig. 9.4 are drawn the temperature profiles inside the sample for the inert ($H^* = 0$) and reactive ($H^* \neq 0$) Cattaneo (hyperbolic) models at ignition time $t_{\mathrm{iC}}^* = 0.4$ and for the sake of comparison is also represented the corresponding reactive Fourier solution. The higher value of the reactive Cattaneo temperature is

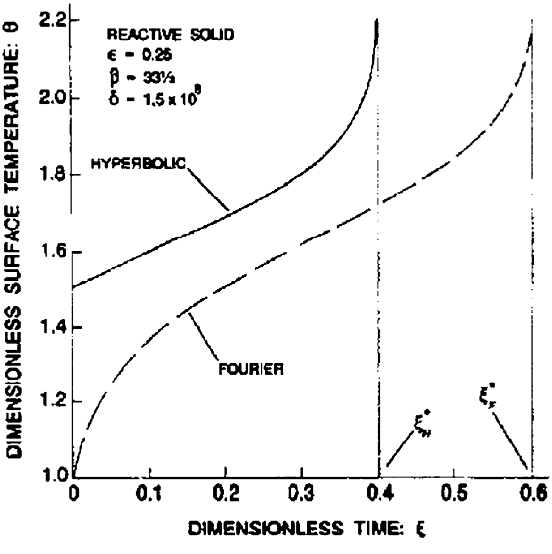


Fig. 9.3 Dimensionless surface temperature T^* as a function of dimensionless time t^* for Fourier's and Cattaneo's (hyperbolic) models (reprinted from Antaki PJ (1998) Comb Flame 112: 329)

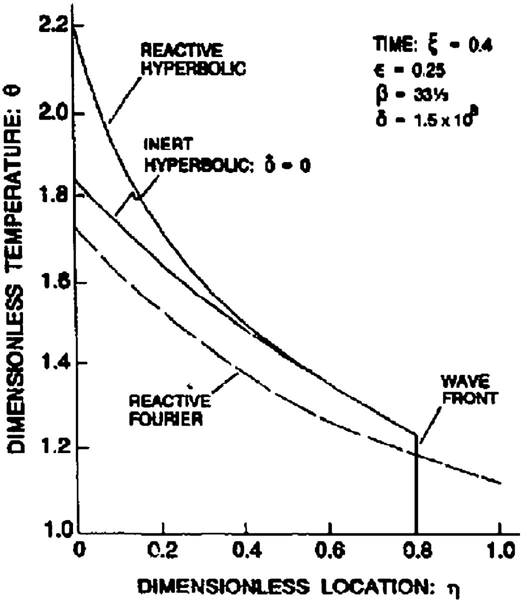


Fig. 9.4 Reactive Fourier's temperature profile versus the corresponding inert and reactive Cattaneo (hyperbolic) solutions at ignition dimensionless time $t_{iC}^{*} = 0.4$ (reprinted with permission from Antaki PJ (1998) Comb Flame 112:329)

explained by the larger amount of heat released by the chemical reaction in absence of reaction. It is worth to note that even the inert Cattaneo temperature is larger than the reactive Fourier solution.

The above results illustrate the property that heat flux relaxation contributes to an important reduction of the ignition time in a process involving solid phase Arrhenius reaction rates. Accounting for heat flux relaxation may also be clarified in better apprehending the processes behind Arrhenius kinetics. In micro-engineering, many phenomena are governed by Arrhenius-like laws. One example is laser annealing of silicon thin films to repair damages undergone during the fabrication of integrated circuits.

9.3 Beyond the Cattaneo Equation

A more sophisticated model than Cattaneo's, including non-local effects, was proposed by Guyer and Krumhansl (1966). These authors base their description on the phonon kinetic theory; accordingly, heat transport is described by momentum and energy exchanges between colliding massless particles called phonons. One distinguishes three mechanisms of transport of phonons: at very low temperature and in nanosystems, phonons travel freely without being scattered, they are referred to as *ballistic* phonons, when the temperature and (or) the dimensions of the sample are increased, collisions occur and a wave-like behaviour is observed. During this process, momentum and energy are conserved and the corresponding collisions are called *normal* or N-collisions characterized by a time scale τ_N. By increasing still more the temperature and (or) the dimensions, resistive R-collisions which conserve energy but not momentum are expected, and their characteristic time is denoted τ_R; these R-collisions which result of collisions with the defects of the lattice and the boundaries are the so-called "Umklamp" phonon–phonon collisions. The wavy nature of heat transport is quickly damped and after a while, heat propagates by diffusion.

- Fourier's law corresponds to high frequency of R- and N-collisions, i.e. $(\tau_R)^{-1} \to \infty$, $(\tau_N)^{-1} \to \infty$.
- Cattaneo's equation is associated with the limiting values $(\tau_R)^{-1} \to 0$ and $(\tau_N)^{-1} \to \infty$, i.e. $\tau_R >> \tau_N$.
- Ballistic phonons are characterized by vanishing frequencies of both normal and resistive collisions, i.e. $(\tau_R)^{-1} \to 0$, $(\tau_N)^{-1} \to 0$.

At low temperature, frequencies of normal and resistive collisions may be comparable and it is not excluded that $\tau_N \geq \tau_R$. In these regimes, it was soon recognized that non-local effects play an important role. Although non-local terms have already been introduced formally in Chap. 2, we shall here explore in more details their physical meaning and consequences on heat transport properties. After recalling the essentials of the Guyer–Krumhansl formalism, we propose a generalised version of heat wave propagation with application to heat transport in dielectric crystals at very low temperature ($0\,\mathrm{K} < T < 20\,\mathrm{K}$).

9.3.1 Guyer–Krumhansl's Model

The main merit of Guyer–Krumhansl's formalism is to emphasize the role of non-local effects in heat transport. It is a linear model originally established on kinetic theory foundations but it can also be derived on strictly thermodynamic bases as shown in the foregoing. The space of state variables is constituted as usually by the temperature T and the heat flux vector $\boldsymbol{q}$, with T obeying the energy conservation law (9.1) and $\boldsymbol{q}$ the following time-evolution equation

$$\frac{\partial \boldsymbol{q}}{\partial t} = -\nabla \cdot \mathbf{Q} + \boldsymbol{\sigma}^q, \tag{9.24}$$

the second-order tensor $\mathbf{Q}$ represents the flux of the heat flux and $\boldsymbol{\sigma}^q$ a vectorial source term, both $\mathbf{Q}$ and $\boldsymbol{\sigma}^q$ will be given by constitutive equations. In the kinetic theory, T is interpreted as the kinetic energy, $\boldsymbol{q}$ is the flux of energy, and $\mathbf{Q}$ is the next higher-order moment. Designating by $f(\boldsymbol{r}, \boldsymbol{C}, t)$ the distribution function and $\boldsymbol{C}$ the relative velocity of phonons with respect to the barycentric velocity, one has in virtue of the results of Chap. 4,

$$\mathbf{Q} = \int \tfrac{1}{2} mfC^2 \boldsymbol{C}\boldsymbol{C}\,\mathrm{d}\boldsymbol{c}, \tag{9.25}$$

indicating that $\mathbf{Q}$ is a symmetric second-order tensor. The constitutive relations of $\mathbf{Q}$ and $\boldsymbol{\sigma}^q$ are assumed to be linear in $\boldsymbol{q}$ and $\nabla \boldsymbol{q}$ and given by

$$\mathbf{Q} = -d\left[(\nabla \boldsymbol{q})^{\mathrm{sym}} + \tfrac{1}{2}(\nabla \cdot \boldsymbol{q})\mathbf{U}\right], \tag{9.26}$$

$$\boldsymbol{\sigma}^q = -\frac{1}{\tau}(\boldsymbol{q} + \lambda \nabla T), \tag{9.27}$$

where the phenomenological coefficient d is constant but τ and λ may be temperature dependent. Substitution of (9.26) and (9.27) into (9.24) leads to

$$\frac{\partial \boldsymbol{q}}{\partial t} + \frac{\boldsymbol{q}}{\tau} + \frac{\lambda}{\tau}\nabla T = \frac{1}{2}d\left(\nabla^2 \boldsymbol{q} + 2\nabla\nabla \cdot \boldsymbol{q}\right). \tag{9.28}$$

Starting from the linearized Boltzmann equation in the Callaway approximation, Guyer and Krumhansl obtain the following evolution equation

$$\frac{\partial \boldsymbol{q}}{\partial t} + \frac{1}{\tau_R}\boldsymbol{q} + \frac{1}{3}\rho c_v c_0^2 \nabla T = \frac{1}{5}c_0^2 \tau_N \left(\nabla^2 \boldsymbol{q} + 2\nabla\nabla \cdot \boldsymbol{q}\right). \tag{9.29}$$

Clearly, expression (9.28) is the same as Guyer–Krumhansl's result (9.29) at the condition to perform the following identifications:

$$\tau = \tau_R, \quad \frac{\lambda}{\tau} = \frac{1}{3}\rho c_v c_0^2, \; d = \frac{2}{5}\tau_N c_0^2. \tag{9.30}$$

The relaxation time of the heat flux is thus identified as the relaxation time of the resistive collisions and the coefficient d, associated to non-locality, is related to the relaxation time of the normal collisions, underlining the interdependence of normal collisions and non-locality. Guyer–Krumhansl's equation is frequently employed to study heat transport in non-metallic solids. It should however be stressed that similarly to Fourier's law, Guyer–Krumhansl's result predicts that signals propagate at infinite velocity because the corresponding temperature equation obtained by eliminating $\boldsymbol{q}$ between (9.29) and the energy balance (9.1) is a parabolic equation. Note finally that in steady states, Guyer–Krumhansl's equation does not reduce to Fourier's.

9.3.2 A Generalised Guyer–Krumhansl's Model

Our objective is twofold: firstly, to generalise Guyer–Krumhansl's equation by upgrading the second-order tensor $\mathbf{Q}$ to the status of independent variable; secondly, to circumvent the problem of infinite velocity of propagation. In the following, the space $\mathcal{V}$ of variables is formed by θ (the non-equilibrium temperature), $\boldsymbol{q}$ (the heat flux vector), $\mathbf{Q}$ (a second-order symmetric tensor $\mathbf{Q} = \overset{0}{\mathbf{Q}} + Q\mathbf{U}$ split into its deviatoric $\overset{0}{\mathbf{Q}}$ and bulk part Q considered as independent variables): $\mathcal{V} = \theta, \boldsymbol{q}, \overset{0}{\mathbf{Q}}, Q$.

For practical reasons and to avoid the introduction of a temperature field depending on the fluxes, we prefer to select θ rather than the internal energy u as independent variable. The evolution equations of the state variables are assumed to be given in the general form (Valenti et al. 1997):

$$\frac{\partial u}{\partial t} = -\nabla \cdot \boldsymbol{q}, \tag{9.31}$$

$$\frac{\partial \boldsymbol{q}}{\partial t} = -b\nabla \cdot \overset{0}{\mathbf{Q}} - d\nabla Q - \frac{1}{\tau_1}\boldsymbol{q} - \frac{\lambda}{\tau_1}\nabla\theta, \tag{9.32}$$

$$\frac{\partial \overset{0}{\mathbf{Q}}}{\partial t} = -\frac{1}{\tau_2}\overset{0}{\mathbf{Q}} - \frac{2\eta}{\tau_2}\overset{0}{(\nabla \boldsymbol{q})}{}^{\text{sym}}, \tag{9.33}$$

$$\frac{\partial Q}{\partial t} = -\frac{1}{\tau_0}Q - \frac{\xi}{\tau_0}\nabla \cdot \boldsymbol{q}. \tag{9.34}$$

where u is measured per unit volume. The coefficients b and d are introduced for the sake of generality, it is only in the case that $b = d = 1$ that $\mathbf{Q}$ can be considered as the flux of the heat flux. To take spatial non-local effects into account, it has been assumed that the evolution equations of $\overset{0}{\mathbf{Q}}$ and Q depend on the gradient and divergence of the heat flux respectively. All the phenomenological coefficients are allowed to depend on the temperature and will be identified in the foregoing. It is checked that by setting $\tau_0 = \tau_2 = 0$ and by eliminating $\overset{0}{\mathbf{Q}}$ and Q between (9.32, 9.33 and 9.34), one finds back Guyer–Krumhansl's relation (see Problem 9.13). When the time variations of $\overset{0}{\mathbf{Q}}$ and Q are negligible, the above two expressions parallel the Newton–Stokes equations with $\boldsymbol{q}$ playing the role of the velocity and $\mathbf{Q}$ that of the mechanical stress tensor, and η and ξ may be viewed as viscosity coefficients. This is characteristic of the hydrodynamic regime of phonon flow which is indeed described by these equations.

The thermodynamics underlying the model (9.32–9.34) is easily derived by following the same procedure as in Sect. 2.4. It is left as an exercise (Problem 9.13) to show that the expressions of the entropy flux and the positive dissipated energy are given respectively by

$$\boldsymbol{J}^s = \frac{1}{\theta}\boldsymbol{q} + \beta\,\overset{0}{\mathbf{Q}}\cdot\boldsymbol{q} + \beta' Q\boldsymbol{q}, \tag{9.35}$$

$$\theta\sigma^s \equiv \frac{1}{\lambda\theta}q^2 - \frac{\beta\theta}{2\eta}\overset{0}{\mathbf{Q}} : \overset{0}{\mathbf{Q}} - \frac{\beta'\theta}{\xi}Q^2 \geq 0. \tag{9.36}$$

The coefficients β and β' are undetermined at this stage of the analysis but, without loss of generality, they can be taken as constants, while the coefficients b and d introduced in the generalised Cattaneo's equation (9.32) are given by

$$b = -\frac{\beta\theta^2\lambda}{\tau_1}, \quad d = -\frac{\beta'\theta^2\lambda}{\tau_2}. \tag{9.37}$$

From the positiveness of (9.36) follows that the next quantities are positive definite:

$$\lambda \geq 0, \quad -\frac{\beta}{\eta} \geq 0, \quad -\frac{\beta'}{\xi} \geq 0. \tag{9.38}$$

Since the temperature is selected as independent variable, it is more convenient to use the Helmholtz free energy $\phi = u - \theta s$ as basic potential in Gibb's relation, which takes the form

$$\mathrm{d}\phi = -s\mathrm{d}\theta + \frac{\tau_1}{\lambda\theta}\boldsymbol{q}\cdot\mathrm{d}\boldsymbol{q} - \frac{\beta\theta\tau_2}{2\eta}\overset{0}{\mathbf{Q}}:\mathrm{d}\overset{0}{\mathbf{Q}} - \frac{\beta'\theta\tau_0}{\xi}Q\cdot\mathrm{d}Q. \tag{9.39}$$

After expanding ϕ in Taylor's series around its (local) equilibrium value ($\boldsymbol{q} = 0$, $\overset{0}{\mathbf{Q}} = 0$, $Q = 0$) one obtains from (9.39) that

$$\phi(\theta, \boldsymbol{q}, \overset{0}{\mathbf{Q}}, Q) = \phi_{\mathrm{eq}}(\theta) + \frac{\tau_1}{2\lambda\theta}q^2 - \frac{\beta\theta\tau_2}{4\eta}\overset{0}{\mathbf{Q}}:\overset{0}{\mathbf{Q}} - \frac{\beta'\theta\tau_0}{2\xi}Q^2. \tag{9.40}$$

Imposing the constraint that ϕ is minimum at local equilibrium and combining with inequalities (9.38), it is concluded that the three relaxation times are positive definite: $\tau_1 \geq 0$, $\tau_2 \geq 0$, $\tau_0 \geq 0$.

In view of future developments, it is interesting to derive the corresponding expressions of the entropy and internal energy per unit volume. It is easily checked (Problem 9.14) that the integrability conditions for (9.39) lead to

$$s = s_{\mathrm{eq}}(\theta) - \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\frac{\tau_1}{\lambda\theta}\right)q^2 + \frac{1}{4}\beta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\frac{\theta\tau_2}{\eta}\right)\overset{0}{\mathbf{Q}}:\overset{0}{\mathbf{Q}} + \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\frac{\theta\tau_0}{\xi}\right)Q^2, \tag{9.41a}$$

$$\begin{aligned} u = u_{\mathrm{eq}}(\theta) &- \frac{1}{2}\theta^2\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\frac{\tau_1}{\lambda\theta^2}\right)q^2 + \frac{1}{4}\beta\theta^2\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\frac{\tau_2}{\eta}\right)\overset{0}{\mathbf{Q}}:\overset{0}{\mathbf{Q}} \\ &+ \frac{1}{2}\beta'\theta^2\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\frac{\tau_0}{\xi}\right)Q^2, \end{aligned} \tag{9.41b}$$

wherein $s_{\mathrm{eq}}(\theta)$ and $u_{\mathrm{eq}}(\theta)$ denote respectively the entropy and energy at (local) equilibrium satisfying the classical relation

$$\theta\frac{\mathrm{d}s_{\mathrm{eq}}}{\mathrm{d}\theta} = \frac{\mathrm{d}u_{\mathrm{eq}}}{\mathrm{d}\theta} = c_{\mathrm{eq}} > 0, \tag{9.42}$$

with c_{eq} the heat capacity at equilibrium. Relations (9.41a and b) are important as they provide explicit expressions of entropy and internal energy outside (local) equilibrium in terms of physically well defined quantities like the relaxation times, heat conductivity and the viscosity coefficients. At this stage of the analysis, we will introduce the simplifying hypotheses that the ratios τ_2/η and τ_0/ζ appearing in the evolution equations (9.33) and (9.34) of $\overset{0}{\mathbf{Q}}$ and Q remain constant. This can be justified on the basis of the property that $\overset{0}{\mathbf{Q}}$ and Q are of higher order than the other state variables, as evidenced by the kinetic definition (9.25). As a consequence, the expression of u will only depend on θ and $\boldsymbol{q}$ and is given by

$$u(\theta, \boldsymbol{q}) = u_{\mathrm{eq}} + a(\theta)q^2 \tag{9.43}$$

with

$$a(\theta) = -\frac{1}{2}\theta^2 \frac{\mathrm{d}}{\mathrm{d}\theta}\left(\frac{\tau_1}{\lambda\theta^2}\right). \tag{9.44}$$

It should be stressed that the internal energy u is only temperature dependent in the case that the ratio $\tau_1/\lambda\theta^2$ is temperature-independent.

Moreover, introduction of higher-order moments raises the problem of the determination of the corresponding initial and boundary conditions. The problem is delicate and has not found a definite solution yet, as commented in Box 9.1

Box 9.1 Boundary Conditions and Higher-Order Moments The occurrence of higher-order variables like the tensors $\mathbf{Q}$ or, more generally, higher-order moments implies the specification of supplementary initial and boundary conditions to guarantee the well-posedness of the problem and the uniqueness of the solution. The problem becomes more acute when more than 13 moments are involved. Indeed, such higher moments do not have a precise physical meaning and are not controllable, so that the question arises how to prescribe these quantities at the initial time and at the boundaries.

The determination of the initial conditions is of no concern in steady situations. In transient problems, it is not so fundamental as it is generally admitted that initially, the system is in thermodynamic equilibrium. A similar attitude is followed in the calculation of shock propagations, where equilibrium is assumed far before and far behind the shock front.

The problem of the boundary conditions is more delicate and controversial. It is not clear how to obtain the values of the higher moments at the boundaries without appealing to new strategies. Several directions can be distinguished. The first one can be classified as a variational approach. It consists in formulating variational principles whose admissible solutions are not only the bulk equations but also some classes of boundary conditions, the so-called natural boundary conditions. Many examples are found in continuum mechanics in relation with finite elements methods (e.g. Lebon 1980; Zienkiewics and Morgan 1983). It should however be noticed that the physical meaning of this kind of boundary conditions is rarely addressed. The second route is based on the formulation of principles more akin to the physics taking place at the boundaries. In that respect, an interesting approach was followed by Struchtrup and Weiss (1998) with their *minimax entropy production principle*. Accordingly, in stationary and one-dimensional situations, the boundary values for the higher moments are identified as the ones that minimize the maximum value of the local entropy production. The motivation underlying this criterion is that the entropy production constitutes a rather natural measure of the distance to equilibrium. By selecting the boundary conditions in such a way, one ensures that the corresponding solutions try to be as close as possible of the equilibrium state in every point. The minimax criterion of Struchtrup and Weiss should not be confused with the principle of minimum global entropy production of Prigogine (1961), who demonstrated that some particular classes of processes described by linear constitutive relations are characterized by a minimum of the global entropy production. Struchtrup and Weiss' formulation has been the subject of severe criticisms because it has only been applied to rather simple one-dimensional heat conduction problems in gases and does not rest on firm physical bases. Indeed there is no sound justification that the system adjusts its boundary values in order to minimize its entropy production. In addition, application of Prigogine's minimum entropy principle is subordinated to the observance of several restrictions which are generally not met in practical applications (e.g. Lebon 1980). It was also shown by Castillo and Hoover (1998), who studied the motion of a heat conducting viscous fluid, that the maximum of the entropy production is the smallest for the unstable solution. Moreover, as pointed out by Liu et al. (2002), the minimax entropy production criterion yields unrealistic results in pure heat conduction problems. Some alternatives were proposed like this by Ruggeri (2000) who uses the difference $\Delta s = s - s_{\mathrm{eq}}$ between the non-equilibrium entropy and its equilibrium value to measure the distance to equilibrium. The undetermined boundary values are conjectured to be these which minimize the maximum of Δs. The arguments supporting Ruggeri's approach are unfortunately subject to criticisms similar to these raised by the entropy production minimax principle. Another modified version of Struchtrup and Weiss' approach was formulated by Grmela et al. (2007) who suggested that the domain of integration of the entropy production should not be the whole bulk but a thin layer close to the boundaries. Their results are comparable to these of Struchtrup and Weiss, the advantage is a simplification of the computational operations. It follows from the above comments that reference to any supplementary principle based on minimax considerations does not appear as the definite solution of the problem. More recently, Struchtrup and Torrilhon (2007) proposed a mixed phenomenological-kinetic analysis based on the linearized Grad's 13-moment equations. It is suggested to determine the boundary values of the higher moments by calculating the entropy production due to collisions of the gas particles with the wall and by requiring that this quantity is positive. It is observed that the expression of the wall entropy generation takes a bilinear form in the fluxes (the higher moments) and conjugated terms playing the role of forces. The boundary conditions are then identified with linear phenomenological flux–forces relations with positive phenomenological coefficients to comply with a positive entropy generation.

Many analyses on the derivation of the most appropriate boundary conditions of higher moments have been formulated in the context of kinetic theories. But the results refer generally to ideal situations, as linearized equations, the BKG relaxation time approximation, steady states, one-dimensional problems and particular gases. Using kinetic methods raise also the question of the difference between the definition of the kinetic and the non-equilibrium temperatures (see Chap.3).

At the present time, a consistent procedure at the phenomenological level is still lacking. Some authors (e.g. Waldmann 1967; Bedeaux et al. 1976; Kjelstrup and Bedeaux 2008) model the boundaries as autonomous thermodynamic systems to which are applied the rules and techniques of classical irreversible thermodynamics to study transport though surfaces and along surfaces. It is interesting to notice that this methodology presents striking similarities with the more recent developments by Struchtrup and Torrilhon (2007) and Grmela et al. (2007) and it represents, in our opinion, a prospective worth to be deepened in the future.

A final alternative is provided by direct numerical simulations but it is generally computer time consuming and is dramatically characterized by the absence of sound and serious physical background leading to non-uniqueness of the solutions. It is true that numerical methods are extraordinary tools at the service of science but they cannot pretend to replace science.

9.3.2.1 Heat Propagation Velocity: Non-linear Acceleration Waves

We now determine the speed of propagation of weak discontinuities in presence of non-local effects on the basis of the model described by relations (9.31–9.34). Consider a smooth surface $\varphi(\boldsymbol{r},t)$ moving through the body: by weak discontinuities, or acceleration waves, are understood that across $\varphi(\boldsymbol{r},t)$, the variables θ, $\boldsymbol{q}$, $\overset{0}{\mathbf{Q}}$ and Q are continuous whereas their gradient and time derivative may suffer jump discontinuities. According to the classical procedure (e.g. Jeffrey and Taniuti 1964), the normal wave speed ν and the unit normal vector $\boldsymbol{n}$ to the wave front are defined by

$$\nu = -\frac{\partial\varphi/\partial t}{|\nabla\varphi|}, \ \boldsymbol{n} = \frac{\nabla\varphi}{|\nabla\varphi|}, \tag{9.45}$$

and the jump of the first derivatives across φ expressed by

$$\delta := (\partial/\partial\varphi)_{\varphi=0^+} - (\partial/\partial\varphi)_{\varphi=0^-}. \tag{9.46}$$

On making the formal substitution $\partial_t \to -\nu\delta$, $\nabla = -\boldsymbol{n}\delta$ in (9.31)–(9.34) and after use of (9.43) and the notation $u_\theta \equiv \partial u/\partial\theta$, one obtains the following homogeneous algebraic set for the discontinuities

$$\nu u_\theta \delta\theta + 2\nu a\boldsymbol{q}\cdot\delta\boldsymbol{q} - \boldsymbol{n}\cdot\delta\boldsymbol{q} = 0, \tag{9.47}$$

$$\nu\tau_1\delta\boldsymbol{q} = -\beta\lambda\theta^2\boldsymbol{n}\cdot\delta\overset{0}{\mathbf{Q}} - \beta'\lambda\theta^2\boldsymbol{n}\delta Q + \lambda\boldsymbol{n}\delta\theta, \tag{9.48}$$

$$\nu\tau_2\delta\overset{0}{\mathbf{Q}} = \eta\left[\boldsymbol{n}\delta\boldsymbol{q} + (\boldsymbol{n}\delta\boldsymbol{q})^T - \tfrac{2}{3}(\boldsymbol{n}\cdot\delta\boldsymbol{q})\mathbf{U}\right], \tag{9.49}$$

$$\nu\tau_3\delta Q = \xi\boldsymbol{n}\cdot\delta\boldsymbol{q}. \tag{9.50}$$

When ν is non-zero, the linear set (9.47)–(9.50) has non-trivial solutions on condition that the following characteristic polynomial is satisfied:

$$P(\nu) := u_\theta\nu^2 + 2\frac{\lambda}{\tau_1}aq_n\nu - \frac{\lambda}{\tau_1}\left(1+\gamma\theta^2u_\theta\right) = 0, \tag{9.51}$$

q_n stands for $\boldsymbol{q}\cdot\boldsymbol{n}$ while γ is a positive constant reflecting the non-local properties:

$$\gamma = -\left(\frac{4}{3}\frac{\beta\eta}{\tau_2} + \frac{\beta'\xi}{\tau_0}\right) > 0, \tag{9.52}$$

by setting $\gamma = 0$, one recovers the results of Coleman and Newman (1988). Equation 9.51 admits real solution if and only if

$$\left(\frac{\lambda}{\tau_1}aq_n\right)^2 + \frac{\lambda}{\tau_1}(1+\gamma\theta^2u_\theta)u_\theta > 0, \tag{9.53}$$

i.e. for $u_\theta > 0$ or, more explicitly, in virtue of (9.43) for u

$$c_{\text{eq}} + \frac{\mathrm{d}a}{\mathrm{d}\theta}q^2 \geq 0. \tag{9.54}$$

In the case $\mathrm{d}a/\mathrm{d}\theta < 0$, there exists an upper bound on q given by

$$q < q_{\text{cr}} = \sqrt{-c_{\text{eq}}(\mathrm{d}a/\mathrm{d}\theta)^{-1}}, \tag{9.55}$$

beyond which hyperbolicity is lost; this result is typical of non-linear hyperbolicity and will be discussed in more details in Sect. 9.3.4. Solutions of the polynomial (9.51) represent the characteristic velocities of propagation and will be denoted as $\nu_+(\theta,\boldsymbol{q})$ and $\nu_-(\theta,\boldsymbol{q})$. When the signals move in a medium at equilibrium for which θ is uniform and equal to T and where in addition $\boldsymbol{q} = \overset{0}{\mathbf{Q}} = Q = 0$, the velocity of propagation is simply given by

$$\nu_{\text{eq}}^2 = \frac{\lambda}{\tau_1c_{\text{eq}}}(1+\gamma T^2c_{\text{eq}}). \tag{9.56}$$

With the identifications established for example in Problem 9.13, it is possible to express (9.56) in terms of the relaxation times τ_R and τ_N of the resistive and normal phonon–phonon collisions. Assuming that τ_0 can be confused with τ_2, it is found that

$$\nu_{\text{eq}}^2 = \frac{\lambda}{c_{\text{eq}}\tau_R} + \frac{3}{5}\frac{\tau_N}{\tau_2}c_0^2. \tag{9.57}$$

In the limit that normal phonon–phonon collisions are of high frequency ($1/\tau_N \to \infty$), the above relation simplifies to $\nu_{\text{eq}}^2 = \lambda/(c_{\text{eq}}\tau_R)$. Combined with the expression of the heat conductivity $\lambda = \frac{1}{3}c_0^2 c_{\text{eq}} \tau_R$, it is found that $v^2 = \frac{1}{3}c_0^2$, which is the regime generally referred to as the second sound. In the ballistic regime characterized by weak frequencies of collisions, $1/\tau_R \to 0, 1/\tau_N \approx 1/\tau_2 \to 0$, (9.57) reduces to $v_{\text{eq}}^2 = \frac{3}{5}c_0^2$. This result is not fully satisfactory as the velocity of ballistic phonons should be equal to the sound velocity c_0. By increasing the number of higher moments up to 30, Dreyer and Struchtrup (1993) were able to recover the correct value c_0. An alternative way (Dedeurwaerdere et al. 1996) is to introduce an infinite number of moments, to define an effective relaxation time in analogy with the continued fraction expansions proposed in Sect. 4.7.

Although most of the experiments on second sound in solids at low temperature have been performed on samples in equilibrium, interesting features arise by studying heat pulses or high frequency thermal waves in non-equilibrium states. For simplicity, consider a one-dimensional propagation for which the real roots of the characteristic polynomial (9.51) are given by

$$v_\pm = -\left(\frac{a\lambda}{u_\theta \tau_1}\right) q \pm \frac{1}{u_\theta}\sqrt{\Delta}, \tag{9.58}$$

where Δ stands for

$$\Delta = \left(\frac{\lambda}{\tau_1} aq\right)^2 + \frac{\lambda u_\theta}{\tau_1}(1 + \gamma\theta^2 u_\theta). \tag{9.59}$$

With the following notation

$$v_c = \sqrt{\lambda/(u_\theta \tau_1)}, \; \phi = v_c aq, \tag{9.60}$$

where the velocity v_c is generally a function of θ and q, not to be confused with v_{eq}, the solutions $v_\pm$ take the form

$$v_+(\theta, q) = v_c\left[-\phi + \sqrt{1 + \phi^2 + \gamma\theta^2 u_\theta}\right], \tag{9.61}$$

$$v_-(\theta, q) = -v_+(\theta, -q) = v_c\left[-\phi - \sqrt{1 + \phi^2 + \gamma\theta^2 u_\theta}\right] \tag{9.62}$$

It is worth noticing that if $q > 0$, $v_+(\theta, +q)$ is the velocity of propagation in the direction of q, while $v_+(\theta, -q)$ is the velocity of propagation in the opposite direction; when $q < 0$, we are faced with the opposite situation. It is a simple matter to check that the difference $\Delta v = v_+(\theta, +q) - v_+(\theta, -q)$ between the velocity of propagation in the direction of the heat flux and the velocity in the opposite direction is

$$\Delta v = -2v_c\phi = -2(\lambda/u_\theta \tau_1)aq. \tag{9.63}$$

It follows that provided $a > 0$, the difference Δv is smaller than zero, indicating that a signal travelling in the direction of the heat flux will move more slowly than in the opposite direction. The property that $a > 0$ has been confirmed experimentally as shown in the next section and by phonon dynamics where it is proved that for a gas in D dimensions, a is proportional to $(D+2)\tau_R/(2\lambda u_\theta \theta^3) > 0$. As far as we are aware, experimental measurements of Δv have not been performed yet. The non-local effects do not only modify the speed of propagation with respect to the value predicted by Cattaneo's equation but they produce a rounding up and a widening of the pulse profile which becomes larger and larger in the course of time.

9.3.2.2 Application to Dielectric Crystals at Low Temperature (<20 K)

Experiments on thermal waves in high-purity crystals at low temperature have been performed by perturbing systems at equilibrium, characterized by a uniform temperature and absence of fluxes. To compare our theoretical results with experimental observations, we need only the simplified mathematical expressions derived in the particular case of equilibrium, i.e. $\theta = \theta_{\text{eq}} \equiv T$ (a uniform quantity), $q_1 = 0$, $Q_{11} = 0$. Nevertheless, these results provide interesting information about the coefficients $a(T)$ and γ of our model. Measurements have been performed on NaF and Bi samples (Jackson et al. 1976; Narayanamurti and Dynes 1972). It is shown by Coleman and Newman (1988) that the measured speed of propagation is well fitted by an empirical law of the form

$$v_{\text{eq}}^{-2} = A + BT^n, \tag{9.64}$$

where A, B and n are constant. For NaF and Bi, the values of A, B and n giving a good fit are, respectively

$$\begin{aligned} A &= 9.09 \times 10^{-12}, \quad B = 2.22 \times 10^{-15}, \quad n = 3.1 \\ A &= 9.07 \times 10^{-11}, \quad B = 7.58 \times 10^{-13}, \quad n = 3.75 \end{aligned}$$

when velocities are measured in centimetres per second and the temperatures in kelvins. The temperature ranges where heat pulse propagations have been observed are $10\,\text{K} < T < 18.5\,\text{K}$ for NaF and $1.4\,\text{K} < T < 4\,\text{K}$ for Bi. An important quantity is the heat capacity, which varies with T according to the Debye law

$$c_{\text{eq}} = \varepsilon T^3, \tag{9.65}$$

the constant ε depends on the nature of the crystal: for NaF, $\varepsilon = 2.3\,\text{J}\,\text{m}^{-3}\,\text{K}^{-4}$ and for Bi, $\varepsilon = 55\,\text{J}\,\text{m}^{-3}\,\text{K}^{-4}$. Our objective is to determine the values of the parameters $a(T)$ and γ for NaF and Bi from the experimental data of A, B, n and ε. After identifying the two expressions (9.56) and (9.64) of v_{eq}, one obtains

$$\frac{\tau_1}{\lambda T^2} = \frac{A + BT^n}{\varepsilon T^5} + \gamma(A + BT^n) \tag{9.66}$$

and from the definition (9.44) of a,

$$a = 5 - \frac{n}{2\varepsilon}BT^{n-4} + \frac{5A}{2\varepsilon}T^4 - \frac{1}{2}n\gamma BT^{n+1}. \tag{9.67}$$

A further differentiation with respect to the temperature yields

$$\frac{\mathrm{d}a}{\mathrm{d}T} = -20A + \frac{(n-5)(n-4)BT^n}{2\varepsilon T^5} - \frac{1}{2}n(n+1)\gamma T^n. \tag{9.68}$$

Since $A,\ B$ and γ are positive with $n < 4$, (9.68) indicates that $\mathrm{d}a/\mathrm{d}T < 0$, i.e. that a is a decreasing function of the temperature. But as it was argued in the preceding section that a is non-negative, there exists a maximum temperature T^* (see Fig. 9.5) beyond which thermal waves will not be observed. This property has received experimental confirmations: for NaF, $T^* = 18.5\,\mathrm{K}$, for Bi, $T^* = 4\,\mathrm{K}$. Substituting these maximum values of T in (9.67) leads to:

$$\gamma = \frac{(5-n)B(T^*)^n + 5A}{n\varepsilon b(T^*)^{n+5}}, \tag{9.69}$$

it is found that $\gamma = 2.7928 \times 10^{-8}$ (for NaF), $\gamma = 2.6157 \times 10^{-6}$ (for Bi). Once the value of γ is known, one may use (9.66) to determine the value of the relaxation time τ since λ is generally a well-known quantity. Relation (9.68) of $\mathrm{d}a/\mathrm{d}t$ is also of interest because it allows to find the critical value of the heat flux beyond which the model is not applicable. From (9.55) and the results (9.68) and (9.65), it is checked that

$$q_{cr} = \frac{\sqrt{2}\varepsilon T^4}{\sqrt{20A + (n-5)(n-4)BT^n + n(n+1)\varepsilon\gamma BT^{n+5}}}. \tag{9.70}$$

The critical values q_{cr} for NaF and Bi are plotted in Fig. 9.6. It is observed that the non-local effects ($\gamma \neq 0$) reduce the values of the critical bound with respect to a local theory ($\gamma = 0$).

9.3.3 Other Examples of Flux Limiters

We have seen that hyperbolicity imposes an upper bound on the heat flux. This property is not exclusive of hyperbolic systems and has also been displayed in other situations. Physically, it is expected that this limit value will be of the order of magnitude of the energy density times the maximum wave propagation speed. A typical example arises, for instance, in radiative heat transfer, where the maximum speed of the photons is the speed of light c, the energy density is aT^4 (with a the black body constant so that the maximum flux is aT^4c (Levermore 1984). Another illustration can be found in plasma physics (Shvart et al. 1981) where the speed of electrons is of the order of $(k_\mathrm{B}T/m)^{1/2}$ and the energy density is proportional to $k_\mathrm{B}T$ so that the maximum heat flux is of the order of $(k_\mathrm{B}^3T^3/m)^{1/2}$. Other examples

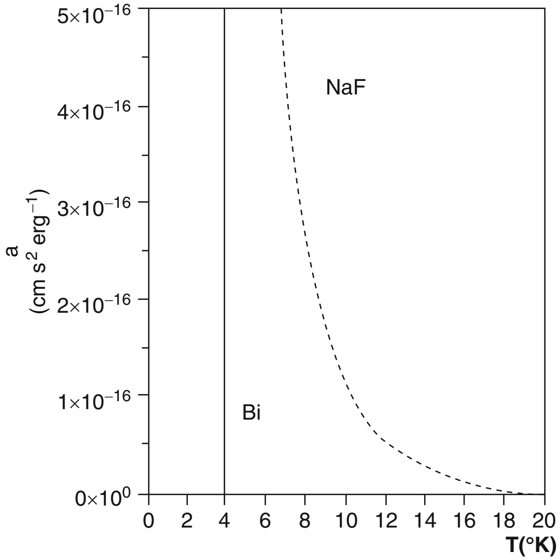


Fig. 9.5 The coefficient $a(T)$ of (9.67) versus temperature for Bi (*solid line*) and NaF (*dotted line*) (reprinted with permission from Valenti et al. A (1997) J Phys C 9:3117)

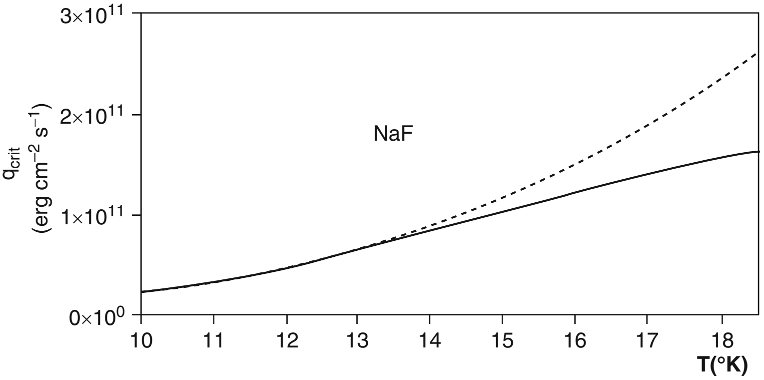


Fig. 9.6 The critical heat flux (9.79) as a function of temperature respectively for NaF and Bi crystals. Solid line: non-local effects ($\gamma \neq 0$). Dotted line: local theory ($\gamma = 0$) (reprinted with permission from Valenti A et al. (1997) J Phys C 9:3117)

of bounded heat fluxes are observed in laser-plasma interactions and in the collapse of stars, where temperature gradients are very important.

Such a saturation effects cannot be explained from the classical Fourier's law, which predicts a unlimited increase of the heat flux with temperature gradient, but may be obtained by introducing an effective thermal conductivity $\lambda(T, \nabla T)$ that depends not only on the temperature but also on the temperature gradient:

$$\boldsymbol{q} = -\lambda(T, \nabla T)\nabla T. \tag{9.71}$$

For instance, a typical dependence giving rise to a bounded heat flux is

$$\boldsymbol{q} = -\frac{\lambda_0(T)}{\sqrt{1 + b(\nabla \ln T)^2}} \nabla T, \tag{9.72}$$

with b a numerical factor. This law reduces to Fourier's law for small temperature gradients and predicts a limiting value at very high temperature gradients.

The form of $\lambda(T, \nabla T)$ has been the subject of many works in radiation hydrodynamics, and several expressions have been proposed. One of the best known is

$$\lambda(T, x^*) = 3\lambda_0(T)(x^*)^{-1}[\coth x^* - (x^*)^{-1}] \tag{9.73}$$

derived by Levermore (1984) from a modified diffusion model for photons, in which $x^* = l'\nabla T/T$, l' being a length of the order of the mean free path, while $\lambda_0(T)$ is the thermal conductivity near equilibrium. For small values of the temperature gradient ∇T ($x^* \to 0$), one has $\lambda \to \lambda_0$, whereas for high values of ∇T, $\lambda \to 3\lambda_0 T l'(\nabla T)^{-1}$, and the corresponding saturation value of the heat flux is given by $q_{\max} = 3\lambda_0 T/l'$. Since $\lambda_0 = \frac{4}{3} a T^3 c^2 \tau$ (see (5.56a)) and taking $l' = 4c\tau$ one finds finally that the maximum allowable value of q is $q_{\max} = aT^4 c$.

The use of flux limiters is necessary for practical purposes in astrophysical problems, but expression (9.73) turns out to be too cumbersome. Therefore several simpler approximations have been proposed such as

$$\lambda = \lambda_0 \frac{6 + 3x^*}{6 + 3x^* + x^{*2}}. \tag{9.74}$$

Extended irreversible thermodynamics has been applied to the analysis of flux limiters in two particular circumstances. On the one side, Anile et al. (1991) have shown that a flux limiter especially interesting in radiation theory is obtained by assuming that there is a reference frame where the observer may see the radiation in equilibrium, because in this case the entropy of the gas in motion coincides with that derived in extended irreversible thermodynamics. A Lorentz transform yields then expressions for both the Eddington factor and the flux limiter. In this case, the flux-limiter $\lambda(x^*)$ has no closed analytic form, but it is given by eliminating β from the relations

$$\lambda = \lambda_0 \frac{3(1 - \beta^2)^2}{(3 + \beta^2)^2}, \quad x^* = \frac{4\beta(3 + \beta^2)}{(1 - \beta^2)^2}, \tag{9.75}$$

where βc is the speed of the Lorentz frame in which the radiation is in equilibrium.

Another analysis carried out by Jou and Zakari (1995) is based on the fluctuation–dissipation expression for the thermal conductivity in non-equilibrium steady states derived in Problem 6.10 and on the maximum entropy description for ultrarelativistic gases presented in Sect. 6.5; the result cannot be expressed in closed form but the numerical values are in good agreement with those given by (9.75).

9.4 Phonon Hydrodynamics

The wording "phonon hydrodynamics" has been introduced because of the similarities with the equations of hydrodynamics. Phonon hydrodynamics is useful to gain information about the physics of phonons motion. As an illustration, we will discuss the problem of the Poiseuille flow of phonons, first detected in solid He^4, as observed in a cylindrical heat conductor of radius R when the mean free paths $\ell_N = c_0\tau_N$ and $\ell_R = c_0\tau_R$ satisfy $\ell_N\ell_R \gg R^2$ and $\ell_N \ll R$. In this case, τ_R is very large and Guyer–Krumhansl's equation (9.29) reduces in a steady state ($\partial\boldsymbol{q}/\partial t = 0$, $\nabla\cdot\boldsymbol{q} = 0$) to

$$\nabla T - \frac{9}{5}\frac{\tau_N}{\rho c_v}\nabla^2\boldsymbol{q} = 0. \tag{9.76}$$

This form is similar to the equation describing Poiseuille flow of Newtonian fluids provided that $\boldsymbol{q}$, ∇T, and $\frac{9}{5}\tau_N/(\rho c_v)$ are regarded as the velocity $\mathbf{v}$, the pressure gradient ∇p, and the viscosity η respectively. In cylindrical coordinates, (9.76) reads, for an imposed temperature gradient, and defining $q(r)$ as the axial component of $\boldsymbol{q}$,

$$\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}q}{\mathrm{d}r}\right) = \frac{5}{3}\frac{\rho c_v}{\tau_N}\nabla T, \tag{9.77}$$

so that

$$q(r) = -\frac{5}{12}\frac{\rho c_v}{\tau_N}(R^2 - r^2)\nabla T, \tag{9.78}$$

and the total heat flux across the cylinder is

$$Q = 2\pi\int_0^R rq(r)\mathrm{d}r = -\frac{5\pi}{24}\frac{\rho c_v}{\tau_N}R^4\nabla T. \tag{9.79}$$

In contrast to the Fourier regime, where the total rate of heat transfer across the cylinder for a given temperature gradient is proportional to R^2, in the Poiseuille phonon flow it is proportional to R^4. This difference allows one to distinguish which of the two regimes is actually satisfied. By defining an apparent thermal conductivity as

$$\lambda_{\mathrm{ap}} = -\frac{Q}{\pi R^2\nabla T}, \tag{9.80}$$

it turns out from (9.79 and (9.30) that

$$\lambda_{\mathrm{ap}} = \frac{5}{24}\frac{\rho c_v}{\tau_N}R^2. \tag{9.81}$$

This result is important as it provides a way to evaluate the normal collision times τ_N, by measuring λ_{ap}, while according to the second of expressions (9.30), the resistive collision time τ_R will be determined by the measurement of the thermal conductivity λ. Furthermore, it predict that the apparent thermal conductivity will tend to zero for small radii, as it is observed in nanowires (see Chap. 10).

9.5 Two-Temperature Models

Up to now, we have considered relaxational effects described by one single temperature. However, many systems consist of several subsystems, each of which being assigned its own temperature. These subsystems are, for instance, the electrons and the lattice in a metal submitted to a short-pulse laser heating, where the electron temperature is much higher than the lattice temperature for a short time. This situation may be described by the following evolution equations for the electron and lattice temperatures T_e and T_l respectively (Tzou 1997):

$$c_e \frac{\partial T_e}{\partial t} = \nabla \cdot (\lambda \nabla T_e) - C(T_e - T_l), \tag{9.82}$$

$$c_l \frac{\partial T_l}{\partial t} = C(T_e - T_l). \tag{9.83}$$

The constant C describes the electron–phonon coupling, which accounts for the energy transfer from the electrons to the lattice, and c_e and c_l are the specific heats of the electrons and lattice per unit volume respectively. When the solution of Eq. (9.83), namely, $T_e = T_l + (c_l/C)(\partial T_l/\partial t)$, is introduced into (9.82), one is led to

$$\nabla^2 T_l + \frac{c_l}{C}\frac{\partial \nabla^2 T_l}{\partial t} = \frac{c_l + c_e}{\lambda}\frac{\partial T_l}{\partial t} + \frac{c_e c_l}{\lambda C}\frac{\partial^2 T_l}{\partial t^2}. \tag{9.84}$$

Such an equation can also be obtained by eliminating $\boldsymbol{q}$ between the energy balance equation and Guyer–Krumhansl equation under the following identifications: $3\tau_N/5 = c_l/C$, $3/\tau_R c^2 = (c_l + c_e)/\lambda$, $3/c^2 = c_e c_l/(\lambda C)$.

It is still interesting to note that an equation of the form of (9.84) may be derived from the following constitutive equation, known as the dual-phase-lag equation (Tzou 1997)

$$\tau_1 \dot{\boldsymbol{q}} + \boldsymbol{q} = -\lambda \left(\nabla T + \tau' \frac{\partial \nabla T}{\partial t} \right), \tag{9.85}$$

which takes into account relaxation effects in both the heat flux and the temperature gradient. However, such a procedure yields a parabolic equation, while by starting with the heat flux and the flux of the heat flux as independent variables one is led to a hyperbolic equation which contains the parabolic equation (9.84) in the limit of a vanishing relaxation time of the flux of the heat flux.

Other systems where a two-temperature description is convenient are, for instance, heterogeneous systems where the liquid and solid phases are at different temperatures; polyatomic gases, wherein one can ascribe different temperatures for translational and internal degrees of freedom; and liquid helium II, where different temperatures may be assigned to the normal and superconductor fluids. These situations, and the derivation of the suitable generalised equations for heat transfer, have been thoroughly reviewed by Tzou (1997) within the framework of the dual-phase-lag formalism.

9.6 Other Applications

We end this chapter by mentioning several situations where the hyperbolic equations of heat transfer have found successful practical applications:

1. *High local heating rate*: An example is the short-pulse laser heating of metals, which is used in the fabrication of microstructures, synthesis of advanced materials, measurement of thin-film properties, and the analysis of structure transformations. The duration of these short laser pulses ranges from nanoseconds to femtoseconds. These heating rates are comparable with the thermalization time required by electrons to exchange energy with the lattice and to the relaxation time needed by electrons to change their state. This problem has been studied extensively by Qiu and Tien 1992. Other examples of high heating rates are high-speed grinding, high-speed friction or fast explosions.
2. *Fast motion of the heating source*: The rate of heating increases with the speed of the moving heat source. The various consequences of this fast motion have been examined extensively by Tzou (1997). The swinging phenomenon of temperature during the transition of the thermal Mach number (speed of the source divided by the speed of thermal waves) from the subsonic to the supersonic ranges, the physical mechanisms of thermal shock formation, and the local heating induced by dynamic crack propagation in the transonic regime are three examples of problems whose effects cannot be depicted by parabolic diffusion equations but which have been satisfactorily accounted for by hyperbolic equations.
3. *Fast moving interfaces*: Fast motions of interfaces, at a speed higher than the diffusion speed, are found in rapid solidification. Such rapid motions produce significant deviations from local equilibrium at the solid–liquid interfaces, leading, for example, to solute trapping and interfacial undercooling below the equilibrium temperature. These phenomena have been investigated by Sobolev (1995) (see Problem 9.12) and by Herlach et al. (2007) (see Chap. 13).

Many other subjects have been explored, both from a theoretical and a practical point of view. For instance, observations of thermal waves are reported in processed meat, applications of the telegrapher equation to IC chips and thermal laser stereo-lithography have been investigated, and general mathematical properties of the telegrapher equations have been studied in the linear and non-linear range,

4. *Superfluids*: The classical theory of superfluid helium II is the two-fluid model proposed by Landau, which regards the system as composed of a normal component with normal viscosity and nonzero entropy and a superfluid component with zero entropy and zero viscosity. The latter component, which is absent above the lambda transition temperature, was originally considered to be composed by the

particles in the condensed Bose–Einstein state, and the normal fluid by the particles in excited states. The expression for the heat flux in this theory has the form $\boldsymbol{q} = -\lambda \nabla T + T s \rho_s (v^{(n)} - v^{(s)})$, with $v^{(n)}$ and $v^{(s)}$ the barycentric velocities of the normal and the superfluid components, s the entropy of the normal fluid and ρ_s the density of the superfluid component. The thermal conductivity is extremely high; the heat flux is not entirely determined by ∇T but its dominant contribution comes from the relative motion of the two components.

The two-fluid model is able to describe many features of liquid helium. However, it is not completely satisfactory because the two components cannot have independent existence and because the superfluid component cannot be strictly interpreted as the Bose–Einstein condensed phase, due to the intense interactions in the liquid. For these reasons, several authors have tried to describe superfluids by adding to the conventional fluid theory a vectorial degree of freedom, to take into account the relative motion of the excitations with respect to the bulk of the fluid. EIT offers a rather natural framework for this kind of description, as it takes the heat flux as an independent variable and, therefore, the dynamics of the relative motion of the excitations may be described by the dynamics of the heat flux. Analyses of the dispersion relation and of the contribution of the heat flux to the pressure tensor, and detailed comparisons of this model with the two-fluid model have been carried out in the literature (Lebon and Jou 1979; Greco and Müller 1983). For a wide bibliography on these topics see Mongiovì (1993) and Mongiovì and Jou (2007) where quantum turbulence in superfluids is also paid much attention.

9.7 Problems

9.1. The thermal conductivity of a dielectric solid is given by $\lambda = \frac{1}{3}\rho c_v c_0^2 \tau_1$, with c_0 being the phonon speed, τ_1 the relaxation time due to resistive phonon collisions, c_v the specific heat per unit mass at constant volume, and ρ the mass density. In the Debye model for d-dimensional systems, c_v is proportional to T^d at low temperatures.
(a) Calculate the speed of the second sound in terms of c_0. (b) Assume that the solid sample is in a non-equilibrium steady state characterized by a heat flux $\boldsymbol{q}$; when the sample is perturbed, heat waves may move either in the sense of $\boldsymbol{q}$ or in the opposite sense. Determine the difference Δv between the speed of thermal waves along and against $\boldsymbol{q}$. (*Hint*: Use (9.61–9.62).)

9.2. Show that for ideal gases the expression (9.10) for the speed of thermal waves may be written as

$$U^2 = \frac{5}{2}\left(\frac{c_p}{c_v} - 1\right)\frac{k_B T}{m}.$$

Compare U with the speed of sound for monatomic and diatomic gases. (*Hint*: Use the results for λ obtained in Chap. 4).

9.3. (a) Show that the entropy production corresponding to the Guyer–Krumhansl equation (9.29) is

$$T\sigma^s = \frac{3}{\tau_R \rho c_v c_0^2}\boldsymbol{q}\cdot\boldsymbol{q} + \frac{3\tau_N}{5\rho c_v}[(\nabla\boldsymbol{q}):(\nabla\boldsymbol{q})^T + 2(\nabla\cdot\boldsymbol{q})(\nabla\cdot\boldsymbol{q})].$$

(b) Show that the stationary heat flux that satisfies the Guyer–Krumhansl equation is that corresponding to the minimum entropy production with the constraint $(\nabla\cdot\boldsymbol{q}) = 0$, i.e. show that the Euler–Lagrange equations that come from

$$\delta\int(T\sigma^s - \gamma\nabla\cdot\boldsymbol{q})\mathrm{d}V = 0$$

with respect to variations of $\boldsymbol{q}$ and γ are the steady-state equations corresponding to $\partial u/\partial t = 0$ and $\partial\boldsymbol{q}/\partial t = 0$ provided one identifies the Lagrange multiplier γ as twice the absolute equilibrium temperature (Lebon Dauby (1990)).

9.4. In the relaxation-time approximation, the solution of the Boltzmann equation for a heat-conducting disk subject to a radial temperature gradient $\mathrm{d}T/\mathrm{d}r$ is

$$f = f_{\text{eq}} - f_{\text{eq}}\frac{\tau}{k_{\text{B}}T}\left(\frac{1}{2}mc^2 - 2k_{\text{B}}T\right)c_r\frac{\mathrm{d}\ln T}{\mathrm{d}r},$$

with τ being the relaxation time and c_r the radial component of the molecular velocity. (a) Show that in a frame rotating counterclockwise with angular velocity ω, the solution of the Boltzmann equation is, up to the first order in ω

$$f = f_{\text{eq}} - f_{\text{eq}}\frac{\tau}{k_{\text{B}}T}\left(\frac{1}{2}mc^2 - 2k_{\text{B}}T\right)(c_r - 2\omega\tau c_\theta)\frac{\mathrm{d}\ln T}{\mathrm{d}r}{}^{,}$$

c_θ being the axial component of the molecular velocity. (b) Find the ratio q_θ/q_r between the axial and radial components of $\boldsymbol{q}$. (See Hoover et al. (1981)).

9.5. Sieniutycz and Berry (1991) have proposed for heat-conducting fluids in convective motion the following Lagrangian:

$$\mathcal{L}(\rho, \rho s, \boldsymbol{v}, \boldsymbol{v}_s) = \tfrac{1}{2}\rho v^2 + \tfrac{1}{2}\rho g s^2 v_s^2 - \rho u(\rho, s),$$

with $\boldsymbol{v}$ being the barycentric velocity, $\boldsymbol{v}_s$ a velocity of entropy diffusion defined as $\boldsymbol{v}_s = J^s(\rho s)^{-1}$, and g a coefficient. (a) Obtain the generalised mechanical momentum $\boldsymbol{J} = \partial\mathcal{L}/\partial\boldsymbol{v}$ and thermal momentum $\boldsymbol{I} = \partial\mathcal{L}/\partial\boldsymbol{v}_s$. (b) Show that the corresponding Hamiltonian per unit volume defined by

$$\mathcal{H}(\rho, \rho s, \boldsymbol{I}, \boldsymbol{J}) = \boldsymbol{v}\cdot\frac{\partial\mathcal{L}}{\partial\boldsymbol{v}} + \boldsymbol{v}_s\cdot\frac{\partial\mathcal{L}}{\partial\boldsymbol{v}_s} - \mathcal{L}$$

can be written as

$$\mathcal{H}(\rho, \rho s, \boldsymbol{I}, \boldsymbol{J}) = \rho u(\rho, \rho s) + \tfrac{1}{2}\rho^{-1}\boldsymbol{J}^2 + \tfrac{1}{2}\rho g^{-1}(\rho s)^{-2}\boldsymbol{I}^2.$$

(c) Compare this expression with the expression of the generalised $\rho u(\rho, s, \boldsymbol{q})$ (for $\boldsymbol{v} = 0$) obtained from the generalized Gibbs equation used in this book and identify g. Show that for a Boltzmann monatomic gas $g = \frac{2}{5}m^2/k_B^2$.

9.6. An energy ε per unit length is suddenly released at the axis of a conducting cylinder. The time evolution of the system is described by the energy balance equation expressed by

$$\rho c_v \frac{\partial T}{\partial t} = -\frac{1}{r}\frac{\partial (rq)}{\partial r},$$

and the Maxwell–Cattaneo equation

$$\frac{\partial q}{\partial t} = -\frac{q}{\tau} - \frac{\lambda}{\tau}\frac{\partial T}{\partial r},$$

with q the radial component of the heat flux. In metals at low temperature λ is a constant whereas $\tau = aT^{-1}$. Write $T(r,t) = at^{-1}f(\xi)$ and $q(r,t) = (\lambda \rho c_v)^{1/2} at^{-3/2} g(\xi)$, with ξ the dimensionless quantity $\xi = r[\lambda t/(\rho c_v)]^{-1/2}$. (a) Show that $g = \frac{1}{2}\xi f$ and that $f(\xi)$ is implicitly given by

$$\xi^2 = 8 + \left(\frac{f-2}{f}\right)^{1/2} \{C - 8\ln[f^{1/2} + (f-2)^{1/2}]\},$$

with C being an integration constant related to ε. (b) Show that at $\xi = 2\sqrt{2}$ there is a discontinuity in the solution, where f drops from $f(\xi = 2\sqrt{2}) = 2$ to $f = 0$ for $\xi > 2\sqrt{2}$. Find the speed of the front (Wilhelm Choi (1975)).

9.7. (a) Show that when the thermal conductivity λ depends on T according to $\lambda = \lambda_0 T^n$, the evolution equation for T in cylindrical coordinates is

$$\frac{\partial T}{\partial t} = a\frac{1}{r}\frac{\partial}{\partial r}\left(T^n r \frac{\partial T}{\partial r}\right),$$

where $a = \lambda_0/(\rho c_v)$. (b) When $t = 0$, an energy ε per unit length is suddenly released along the axis of the cylinder. Assume

$$T(r,t) = [Q/(at)]^{1/(n+1)} f(\xi),$$

with ξ being the non-dimensional combination $\xi = r(aQ^n t)^{-1/[2(m+1)]}$, where $Q = \varepsilon/(\rho c_v)$, and show that for $n > 0$ and ρc_v taken as a constant the solution of the equation for T is

$$f(\xi) = \left(\frac{n(\xi_0^2 - \xi^2)}{4(n+1)} \right)^{1/n} H(\xi_0 - \xi),$$

in which $H(x)$ the Heaviside function. (See Wilhelm Choi (1975)) (c) Find ξ_0 from the initial condition

$$2\pi \int_0^{\xi_0} f(\xi)\xi \mathrm{d}\xi = 1$$

and calculate the position of the front $R(t)$ such that $T = 0$ for $r > R(t)$.

9.8. Assume an unidimensional system with an initial temperature profile given by $T(x,0) = T_0 + \delta T_0 \cos kx$, with T_0 being a uniform value. (a) Obtain the expression for the temperature profile $T(x,t)$ by using the telegrapher equation for T. Note that $T(x,t)$ may reach negative values even though the initial $T(x,0)$ is everywhere positive. (b) Show that, in the high-frequency limit, a sufficient condition for $T(x,t)$ being always positive is that the initial heat flux $q(x,0)$ is smaller everywhere than the critical value $q_{crit} = \rho u(\chi/\tau)^{1/2}$ (Criado-Sancho Llebot (1993)).

9.9. (a) Compare the values of the heat flux obtained from the Fourier law with that obtained from the non-linear expression (9.73) for $x = 0.1$, $x = 1$ and $x = 5$. (b) Show that the maximum difference between (9.73) and (9.75) is of the order of 7% for $x \approx 2.5$.

9.10. (a) Use expression (4.100) to obtain the non-linear thermal conductivity $\lambda(\boldsymbol{q})$. (b) Show that for high values of ∇T, $\boldsymbol{q}$ behaves as $|\boldsymbol{q}| \approx a^{-1} \ln(2\lambda_0 a \nabla T)$, with $a = [\tau_{\mathrm{E}}/(nk_{\mathrm{B}}\lambda_0 T^2)]^{1/2}$ (see Sect. 4.6). Thus, note that (4.100) does not describe a saturation of the heat flux, in spite of the fact that it describes a substantial reduction of the non-linear heat flux as compared with the linear theory.

9.11. In Sect. 9.3 we have studied the consequences of the non-equilibrium temperature on the speed of thermal pulses under a heat flux $\boldsymbol{q}_0$. Assume, instead, that $\theta = T$ is the local-equilibrium temperature and that Guyer–Krumhansl equation (9.29) is used. Show that the speed $\boldsymbol{v}$ of thermal pulses along and against the direction of $\boldsymbol{q}_0$ are

$$\boldsymbol{v}_{\pm} = \boldsymbol{v}_c \left[-\phi \pm \sqrt{1 + \phi^2 + \gamma T^2 (\partial u/\partial T)} \right]$$

with $\phi = v_c a q_0$, $v_c = \sqrt{\lambda/[\tau_1(\partial u/\partial T)]}$, $a = -\frac{1}{2}\partial[\tau_1(\lambda T^2)^{-1}]/\partial T$ and $\gamma = (\lambda T^2)^{-1} \times [\frac{4}{3}\beta'' \tau_2^{-1} + \beta' \tau_0^{-1}]$. Compare this result with (9.61–9.62). (See Valenti et al. (1997))

9.12. A two-temperature model used to describe ultrafast melting and solification in pulse-laser irradiated materials (see e.g. Sobolev (1995)) assumes a fast relaxing mode (related to heat-conducting vibrational modes) and a slow relaxing one (related to structural rearrangements). Their respective temperatures and heat capacities are T_1, C_1 and T_2, C_2. Consider a system composed of a liquid and a solid parts separated by an interface at $x = z$. The equations for T_1

and T_2 for the liquid phase are assumed to be

$$\begin{aligned} C_{1L}\frac{\partial T_1}{\partial t} &= \nabla \cdot (\lambda_L \nabla T_1) - \alpha_L(T_1 - T_2) + W_L \\ C_{2L}\frac{\partial T_2}{\partial t} &= \alpha_L(T_1 - T_2) \end{aligned}$$

with W a heat source term and α a heat transfer coefficient between the fast and the slow modes, and analogously for the solid phase (with S subscript instead of L).

(a) Show that after expressing T_2 in terms of T_1 one obtains

$$\frac{\partial T_1}{\partial t} + \tau\frac{\partial^2 T_1}{\partial t^2} = a\frac{\partial^2 T_1}{\partial x^2} + l^2\frac{\partial^3 T_1}{\partial t \partial x^2} + \frac{W}{C_1 + C_2} + \frac{\tau}{C_1}\frac{\partial W}{\partial t},$$

with $\tau = C_1C_2[\alpha(C_1 + C_2)]^{-1}$, $l^2 = \lambda C_2[\alpha(C_1 + C_2)]^{-1}$ and $a = \lambda(C_1 + C_2)^{-1}$.

(b) Show that in the steady-state regime in the frame moving with the interface, this equation writes as

$$l^2 v\frac{\mathrm{d}^3 T}{\mathrm{d}x^3} + (a - \tau v^2)\frac{\mathrm{d}^2 T}{\mathrm{d}x^2} - v\frac{\mathrm{d}T}{\mathrm{d}x} + \frac{W}{C_1 + C_2} + \frac{\tau v}{C_1}\frac{\mathrm{d}W}{\mathrm{d}x} = 0$$

with $\boldsymbol{v}$ being the velocity of the interface, and find the form of the profile, assuming that $T(x) = \sum_{i=1}^{3} A_i \exp(\mu_i x)$ and $W = 0$. (c) From the matching conditions at the interface and after some cumbersome analyses it may be shown that the interface overheating, defined as $\delta T = T_1(0) - T_2(0)$ is given by (Sobolev (1995))

$$\delta T = T_2(0)[v/(a\mu_1) - 1]$$

where μ_1 is the highest value of the μ_i Show that this tends to 0 for slow interfaces and reaches a maximum for $v \approx (a/\tau)^{1/2}$. This maximum may be rather high if $C_2 \gg C_1$.

9.13. (a) Show that the set (9.32–9.34) reduces to Guyer–Krumhansl's model after setting $\tau_2 = \tau_0 = 0$, substituting θ and $\overset{0}{\mathbf{Q}}$ in (9.32) and making the following identifications $\tau_1 = \tau_R$, $\frac{1}{2}\lambda\beta\eta\theta^2 = -\frac{1}{5}\tau_R\tau_N c_0^2$, $\lambda\beta'\theta^2 = -\frac{1}{3}\tau_R\tau_N c_0^2$. (b) Determine the expressions (9.35), (9.36) and (9.37) of the entropy flux, entropy production and coefficients b and d. Check expression (9.39) of the Gibbs' equation. (c) Repeat the developments by using Liu's multiplier technique (Liu 1972).

9.14. Reconsider the model discussed in Sect. 9.3.2 when $\mathbf{Q}$ represents the flux of the heat flux, i.e. $b = d = 1$ with β and β' constants. Show that the internal energy is then only temperature dependent and that hyperbolicity is guaranteed unconditionally if and only if $c_v > 0$.

9.15. Determine the expressions (9.41a and b) of entropy and internal energy from the integrability conditions of (9.39).

9.16. In Problem 9.14, assume that **Q** is traceless ($Q=0$); eliminate **Q** between the evolution equations.

(a) Show that the resulting evolution equation for the temperature is given by

$$\tau_1\tau_2\frac{\partial^3\theta}{\partial t^3}+(\tau_1+\tau_2)\frac{\partial^2\theta}{\partial t^2}+\frac{\partial\theta}{\partial t}+(l^2+\tau_2\chi)\nabla^2\left(\frac{\partial\theta}{\partial t}\right)=\chi\nabla^2\theta,$$

wherein $l^2=2c_v\eta$, $\chi=\lambda/c_v$.

(b) Establish the dispersion relation between the frequency ω and the wave number k.

(c) Determine the phase velocity in the two particular cases: $l=0,\ \tau_1\neq 0,\ \tau_2=0$; $l\neq 0, \tau_1\neq 0,\ \tau_2=0$.

9.17. *Heat conduction in a rotating rigid conductor.* A rigid cylinder is rotating with at constant angular velocity ω around its vertical axis of symmetry $0z$. The cylinder is hold at the uniform temperature θ_0. Using the transformation law (2.46), Cattaneo's equation takes the form

$$\tau\frac{\partial q}{\partial t}=-(q-\lambda\nabla\theta)+\tau a\boldsymbol{W}\cdot\boldsymbol{q}$$

where **W** is the skew-symmetric part of the velocity gradient tensor satisfying $\mathbf{W}\cdot\boldsymbol{q}=\boldsymbol{\omega}\times\boldsymbol{q}$. Show that in the steady state, the radial q_r and azimuthal q_φ components of $\boldsymbol{q}$ in a reference system rotating with the angular velocity ω are given by

$$q_r=-\frac{\lambda}{\Delta}\frac{\partial\theta}{\partial r},\quad q_\phi=\frac{\lambda}{\Delta}\tau\omega(1-a)\frac{\partial\theta}{\partial r},$$

with $\Delta=1+\tau^2\omega^2(1-a)^2$. It is seen that unless $a=1$, the components of $\boldsymbol{q}$ depend on the angular velocity of the reference frame. The principle of frame indifference (see Chap. 1) imposes therefore $a=1$ to avoid the dependence of $\boldsymbol{q}$ on the reference frame. This result is however in contradiction with the kinetic theory, which predicts that $a=-1$.

9.18. *Second sound under an imposed heat flux.* Consider a non-equilibrium steady state described by Eqs. (9.1) and (9.2) and expression (3.14) of the non-equilibrium temperature. Show that the time-evolution of $\boldsymbol{q}$ is governed by

$$\tau\frac{\partial\boldsymbol{q}}{\partial t}=-\boldsymbol{q}-\lambda\nabla\theta+\frac{1}{2}\nabla\left(\frac{\partial\alpha}{\partial u}q^2\right),$$

with $\alpha=\tau/(\lambda\theta^2)$. Linearizing around the steady value $\boldsymbol{q}_0$, determine the corresponding temperature equation and find the velocities of propagation of the thermal wave respectively in the direction of $\boldsymbol{q}_0$ and in the opposite direction $-\boldsymbol{q}_0$. Compare with (9.61–9.62) and with problem 9.11.

9.19. At initial time t_0, a one-dimensional semi-infinite rigid slab is subject at its face $x_0 = 0$ to a heat pulse $g(x_0, t_0) = g_0\delta(x_0)\delta(t_0)$. Find the temperature distribution as a function of x and t by using Green function technique (Morse and Feshbach 1953).

Hint: the Green function $G(x, t, x_0, t_0)$ satisfies the relation

$$\tau\frac{\partial^2 G}{\partial t^2} + \frac{\partial G}{\partial t} - \chi\nabla^2 G = \delta(x - x_0, t - t_0)$$

with χ designating the heat diffusivity; its Fourier transformation $\hat{G}(k, t)$ verifies the relation

$$\tau\frac{\partial^2 \hat{G}}{\partial t^2} + \frac{\partial \hat{G}}{\partial t} + \chi k^2\hat{G} = \frac{1}{2\pi}\delta(t),$$

Show that the original solution is

$$G(x, t) = \frac{U}{2\chi}\exp[-t/(2\tau)]I_0(\zeta)H(Ut - |x|)$$

wherein $\zeta = \frac{1}{2}\left[(t/\tau)^2 - (x/(U\tau))^2\right]^{1/2}$, U is the second sound velocity, $H(t)$ the Heaviside step function and $I_n(n = 0, 1, \ldots)$ the modified Bessel function of order n. Check that the corresponding temperature distribution is given by

$$\begin{aligned}\theta(x, t) &= \frac{g_0}{4\pi}\exp(-t/2\tau)\left\{2I_0(\zeta)U\tau\delta(Ut - |x|)\right.\\ &\quad\left.+\left[I_0(\zeta) + \frac{1}{\tau\zeta}I_1(\zeta)\right]H(Ut - |x|)\right\}.\end{aligned}$$

Note that for $|x| > Ut$, $\theta = 0$, i.e. the front of the heat perturbation travels with the finite speed $U = (\chi\,/\,\tau)^{1/2}$.

Chapter 10
Heat Transport in Micro- and Nano-systems

The surge of interest in nanosystems and thin films technology has opened new perspectives and developments in the analysis of heat transport. In such small size systems, thermal processes are significantly different from these in macro-systems. As a matter of fact, as long that the ratio between the mean free path of the heat carriers ℓ and the characteristic length L of the system, i.e. the Knudsen number $Kn = \ell/L$, is such that $Kn \ll 1$, the heat carriers collide which each other or with the defects and the corresponding regime is called the *diffusive* or the acoustically thick limit. When $Kn \gg 1$, which is characteristic of small scale systems, heat carriers originated from one boundary will most likely reach the opposite boundary without undergoing collisions, this is the so-called *ballistic* regime or acoustically thin limit. This regime cannot be characterized by an equilibrium state if the walls are at different temperatures and there will be a non-negligible exchange between non-adjacent regions. As a first consequence, heat transport is no longer *diffusive*, i.e. dominated by multiple scattering of the heat carriers inside the sample, but becomes *ballistic*, i.e. dominated by collisions with the boundaries; the second consequence is that the interactions are no longer *local* but governed by strong *non-local* effects.

The usual laws of macroscopic continuum physics must therefore be revisited to take into account the wall and interface effects as well as retardation mechanisms due to the finite relaxation time of the heat carriers. Note that systems whose dimensions are comparable or smaller than the mean free path of the carriers are not necessarily small. For instance, multilayers materials or superlattices constituted by the superposition of thin layers, may exhibit non-classical heat transport when the width of each layer is smaller than the mean free path of the phonons. In ultrafast solidification of undercooled liquids, a transition from a diffusive to a ballistic regime is also observed (Herlach et al. 2007). The behaviour of small systems is also strongly influenced by *non-linear* effects, as a small difference of temperature over a short distance will generate a very high gradient. As a consequence, the transport equations will generally be highly nonlinear. It is was soon recognised that the classical Fourier law breaks down at these small scales, as it is only applicable at large wavelength and large time scale. Cattaneo's law is not more appropriate as it does not capture ballistic transport effects and, more generally, non-local effects. This means that Fourier's and Cattaneo's relations are not valuable candidates for describing heat conduction at the small length scale, as in

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_10,

micro- and nano-devices. Heat conduction processes in small structures has been investigated from several points of view: a first approach is that proposed by Guyer and Krumhansl (see Chap. 9), revisited by Tzou (1996) who introduces a phase lag for the temperature gradient besides the time lag of the heat flux. However, in both formalisms, the temperature equation is of the Jeffrey's parabolic time and does not allow for finite propagation of heat. Direct computer simulations have also been proposed (e.g. Giardina et al. 2000; Garrido et al. 2001) but they will not be discussed further in this chapter focused on thermodynamic developments. Zhang (2007) has written a wide comprehensive monograph on several approaches and applications of heat transport in nano-systems to which the reader is referred for a wide information. Rather, our purpose is here to privilege descriptions deeply rooted in physics, and more particularly in thermodynamics and (or) the kinetic theory. In a first section, we present a macroscopic model based on EIT (Jou et al. 2001; Alvarez and Jou 2007), expressions for the heat conductivity matching satisfactorily experimental data in micro and macro devices have been derived and in parallel, the more general problem of transient heat conduction in thin films is investigated. A microscopic method referring to Boltzman's equation in conjunction with the relaxation time approximation has been preferred by Majumdar (1993) and Joshi and Majumdar (1993), their model is known as the equation of phonon radiative transfer (EPRT) and is discussed in Sect. 10.2. However, solving the Boltzmann equation is not an easy task and, so far, the solution of Boltzmann's equation has been limited to rather simple and academic geometrical configurations. This has motivated Chen (2001, 2002) to propose an interesting mixed ballistic–diffusion equation (BDE), consisting in a coupling between Boltzmann's kinetic and Cattaneo's macroscopic equations. The essence of Chen's description is to split the distribution function into two parts, a diffusive and a ballistic one, the consequences of which are examined in Sect. 10.3.

10.1 EIT Description of Heat Conduction at Micro- and Nano-scales

It was soon recognized that Fourier's and Cattaneo's equations are not applicable at micro-and nano-scales when the Knudsen number Kn becomes comparable or larger than unity. To formulate the problem in simple terms, let us consider a one-dimensional system of thickness L whose opposite boundaries are at temperatures T and $T - \Delta T$. Depending on the values of Kn, experimental investigations have evidenced that the heat flux q takes the following limiting forms:

$$q = \lambda_0 \frac{\Delta T}{L} \text{ (for } Kn \ll 1, \text{ diffusive transport)}, \tag{10.1}$$

or

$$q = \Lambda \Delta T \text{ (for } Kn \gg 1, \text{ ballistic transport)} \tag{10.2}$$

The factor λ_0 designates the heat conductivity and Λ a heat transfer coefficient; both quantities are generally temperature dependent. In the diffusive limit, the heat flux is proportional to the temperature gradient as reflected by the law of Fourier; in the ballistic regime, it depends on the temperature difference only but not on the length L of the device. Explicit expressions of λ_0 and Λ have been derived in the kinetic theory. For a monatomic ideal gas in the diffusive regime, it is found that the heat conductivity is $\lambda_0 = \frac{5}{2} n k_B (k_B T/m)^{1/2} \ell$ with n the particle number density, m the mass of the particles and ℓ the mean free path; in the rarefied gas regime, the coefficient Λ is given by $\Lambda = \frac{1}{2} n k_B (k_B T/m)^{1/2} = \frac{1}{5}\lambda/\ell$ which, unlike the heat conductivity, does not depend on ℓ. Expression (10.1) is a little bit too restrictive, as computer simulations on heat transport in harmonic and anharmonic lattices suggest that Fourier's law should be generalised in the form

$$q = \lambda_0 \frac{\Delta T}{L^\alpha}, \tag{10.3}$$

with α an exponent depending on the characteristics of the system, for instance $\alpha = 0.63$ for some systems, $\alpha = 0.5$ for disordered chains with free boundaries and $\alpha = 3/2$ for anharmonic chains with fixed boundaries (Lepri et al. 2003). However, we shall not further discuss these particularities.

A simplified description of the transition from diffusive to ballistic regime may be achieved by introducing an effective heat conductivity $\lambda(T, \ell/L)$ in such a way that in whole generality

$$q = \lambda(T, \ell/L) \frac{\Delta T}{L}. \tag{10.4}$$

The limiting values of this generalised conductivity should be

$$\lambda(T, \ell/L) \to \lambda_0(T) \text{ for } \ell/L \to 0, \tag{10.5}$$

$$\lambda(T, \ell/L) \to \frac{\lambda_0(T)}{a} \frac{L}{\ell} \equiv \Lambda(T) L \quad \text{for} \quad \ell/L \to \infty, \tag{10.6}$$

where a is a constant depending on the system.

10.1.1 Effective Heat Conductivity

At nanoscales, heat transport is mostly influenced by non-local effects. It was shown in Sect. 4.4 that EIT incorporates non-local effects by appealing to a hierarchy of fluxes $\boldsymbol{J}^{(1)}, \boldsymbol{J}^{(2)}, \ldots, \boldsymbol{J}^{(n)}$ with the vector $\boldsymbol{J}^{(1)}$ denoting the heat flux $\boldsymbol{q}$, the second-order tensor $\boldsymbol{J}^{(2)}$ the flux of the flux $\boldsymbol{q}$, etc. From the kinetic point of view, this corresponds to selecting higher-order moments of the distribution function as variables. In the linear approximation consisting to neglect second and higher-order terms in the fluxes, the hierarchy of evolution equations can be written as

$$\nabla T^{-1} - \alpha_1 \dot{\boldsymbol{J}}^{(1)} + \beta_1 \nabla \cdot \boldsymbol{J}^{(2)} = \mu_1 \boldsymbol{J}^{(1)}, \tag{10.7}$$

$$\beta_{n-1} \nabla \boldsymbol{J}^{(n-1)} - \alpha_n \dot{\boldsymbol{J}}^{(n)} + \beta_n \nabla \cdot \boldsymbol{J}^{(n+1)} = \mu_n \boldsymbol{J}^{(n)}, \tag{10.8}$$

wherein α_i, β_i and μ_i are phenomenological coefficients related to the relaxation times, correlation lengths and transport coefficients, respectively. By considering an infinite number of flux variables and after applying the Fourier transform to the set (10.7)–(10.8), one obtains the following expression of the heat flux:

$$\hat{\boldsymbol{q}}(\omega, \boldsymbol{k}) = -\mathrm{i}\boldsymbol{k}\lambda(\omega, \boldsymbol{k})\hat{T}(\omega, \boldsymbol{k}), \tag{10.9}$$

where upper hats designate Fourier's transforms and $\lambda(\omega, \boldsymbol{k})$ the continued-fraction for the $\omega, \boldsymbol{k}$ -dependent effective thermal conductivity:

$$\lambda(T, \omega, \boldsymbol{k}) = \cfrac{\lambda_0(T)}{1 + \mathrm{i}\omega\tau_1 + \cfrac{k^2 l_1^2}{1 + \mathrm{i}\omega\tau_2 + \cfrac{k^2 l_2^2}{1 + \mathrm{i}\omega\tau_3 + \cfrac{k^2 l_3^2}{1 + \mathrm{i}\omega\tau_4 + ...}}}}, \tag{10.10}$$

$\lambda_0(T)$ is the classical bulk thermal conductivity, $\tau_n = \alpha_n/\mu_n$ the relaxation time, and l_n the correlation length defined through $l_n^2 = \beta_n^2/\mu_n\mu_{n+1}$. Limiting expansion (10.10) to the second-order approximation, one has simply

$$\lambda(T, \omega, \boldsymbol{k} = \cfrac{\lambda_0(T)}{1 + \mathrm{i}\omega\tau_1 + \cfrac{l_1^2 k^2}{1 + \mathrm{i}\omega\tau_2}}. \tag{10.11}$$

To examine the transition to a ballistic regime in the steady case, put $\omega = 0$ and assume that k is of the order of l/L so that (10.11) becomes

$$\lambda(T, l/L) = \frac{\lambda_0(T)}{1 + a(l/L)^2}. \tag{10.12}$$

This relation reduces to $\lambda_0(T)$ for small values of l/L but behaves as L^2 for large values of l/L, in contradiction with experimental data showing that λ is proportional to L in the ballistic regime. Therefore, limiting the expansion (10.11) to second-order non-local terms is not sufficient to describe the transition, third and higher order contributions have been shown to be no more satisfactory, suggesting that an infinite number of terms are necessary. By assuming that all the relaxation times and correlation lengths are equal ($\tau_1 = \cdots = \tau_n = \tau$, $l_1 = \cdots = l_n = l/2$) independently of the order of approximation, the continued fraction (10.10) reduces to the asymptotic limit

$$\lambda(T, \omega, \boldsymbol{k}) = \lambda_0(T)\frac{-(1 + \mathrm{i}\omega\tau) + \sqrt{(1 + \mathrm{i}\omega\tau)^2 + k^2 l^2}}{(1/2)k^2 l^2}. \tag{10.13}$$

The equality of all the relaxation times and mean free paths is rather natural in the relaxation-time approximation. Deeper analyses of the full Boltzmann equation

(Hess 1977) suggest different values of the relaxation times and consequently more sophisticated expressions of the heat conductivity. Here, we restrict the analysis to the simplest possibility. In the steady state approximation, one has $\omega = 0$ and expression (10.13) reads simply

$$\lambda(T, k) = \frac{2\lambda_0(T)}{l^2k^2}\left(\sqrt{1 + l^2k^2} - 1\right). \tag{10.14}$$

In the present one dimensional problem, there is only one characteristic length L and it is natural to identify k with $2\pi/L$ so that from (10.14) one gets

$$\lambda(T, l/L) = \frac{2\lambda_0(T)L^2}{4\pi^2 l^3}\left[\left(1 + \frac{4\pi^2 l^2}{L^2}\right)^{1/2} - 1\right], \tag{10.15}$$

which exhibits the required asymptotic behaviours expressed by (10.5) and (10.6). The result (10.15) is in agreement with experimental data for nanotubes and some theoretical models of heat transport in micro and nanodevices (Alvarez and Jou 2007). The above considerations confirm that EIT provides a consistent modelling of heat transfer processes not only at short times but also at small length scales. Expression (10.15) may be used both in nanowires and in thin layers by defining an effective size L as $L^{-2} = L_x^{-2} + L_y^{-2} + L_z^{-2}$. For thin layers, $L_x = L_y = \infty$ and $L = L_z$ is simply the width of the layer; for nanowires, $L_x = L_y = r$, $L_z = \infty$, and $L = r/\sqrt{2}$, with r the radius of the nanowire.

When the mean free path is shorter than the dimensions of the sample, one has $\lim_{l\to 0} \lambda(L) = \lambda_0$ and in the opposite limit of nanodistances,

$$\lim_{l\to\infty} \lambda(L) = \frac{L}{l}\frac{\lambda_0}{\pi}. \tag{10.16}$$

The behaviour of the heat conductivity as a function of the size of the device is plotted in Fig. 10.1. It is seen that expression (10.16) fits satisfactorily to the experimental data obtained by Liu and Asheghi (2004) in thin silicon films, the agreement is also good by comparing with the experimental values on nanotubes reported by Li (2003). When the dimensions of the material are much larger than the mean free path, the conductivity is no longer dependent on the size and is equal to the classical bulk viscosity $\lambda_0(T)$. In contrast, when the dimensions are comparable or smaller than the mean free path, the effective conductivity starts to decrease and tends to zero when the size goes to zero. Such a reduction of the conductivity was still observed by Larson et al. (1986). For very high values of Kn, the conductivity behaves linearly with the dimension as indicated by expression (10.16), this result confirms that the heat flux depends only on the temperature difference between the wall and not on the temperature gradient. A more sophisticated model of the effective heat conductivity wherein the bulk and size effects are explicitly separated is presented in the Box 10.1.

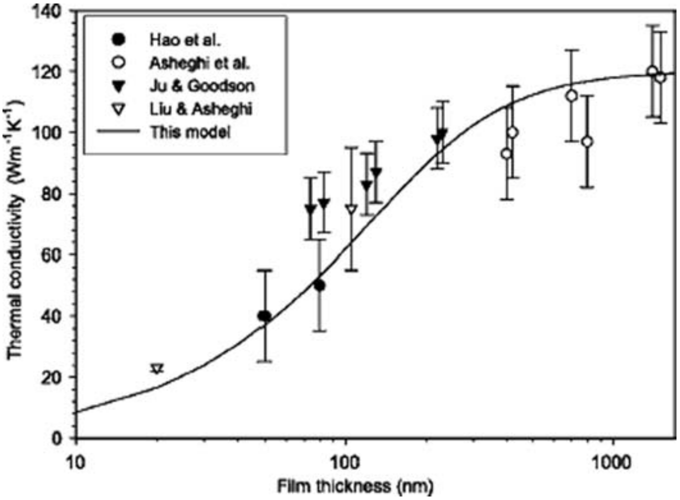


Fig. 10.1 The effective thermal conductivity λ given by (10.15) as a function of the dimension L of the system, λ is expressed in W/mK and L in nm. The values used in the graph are 120 W/mK for λ_0 and 40 nm for l for Si. The different symbols refer to experimental data in layers of different thicknesses (reprinted with permission from Álvarez FX, Jou D (2007) Appl Phys Lett 90:083109)

Box 10.1 Bulk and boundary effects We have seen that expression (10.15) describes in a satisfactory way the transition between diffusive and ballistic regimes but it does not reflect explicitly the role played by the boundaries. We know in particular, that specific boundary effects, like temperature jumps at the surfaces, penetrate into the material at a depth of the order of the mean free path and therefore, become especially pervasive in systems whose dimensions are comparable to the mean free path. In that respect, we mention an interesting result established by Lepri et al. (2003) who propose the following simple model for the effective heat conductivity:

$$\lambda_s(l, L) = \frac{\lambda_0}{1 + 2\varepsilon(l/L)}, \tag{10.1.1}$$

where ε is a dimensionless phenomenological coefficient. In analogy with relation (10.15), the above expression tends to λ_0 in the diffusive regime $(L/l \gg 1)$ and to $\lambda_0(L/l)$ in the ballistic regime. The result (10.1) is easily derived by considering temperature jumps $\pm\delta T$ at the hot and cold boundaries of the material in contact with thermostats. It is assumed that $\delta T = \varepsilon l \nabla T$ with ε a dimensionless phenomenological coefficient, l the mean free path, and ∇T the value of the temperature gradient extrapolated at the boundaries. Near equilibrium, the temperature difference between the two thermostats may be written as

$$\Delta T = L\nabla T + 2\varepsilon l \nabla T = (L + 2\varepsilon l)\nabla T, \tag{10.1.2}$$

wherein the first term accounts for the temperature difference between the boundaries of the device and the second one for the temperature jumps system-thermostats. Defining the effective thermal conductivity by

$$\lambda_s(l,L) \equiv \frac{qL}{\Delta T} = \frac{(\lambda_0 \nabla T)L}{(L+2\varepsilon l)\nabla T} = \frac{\lambda_0}{1+2\varepsilon(l/L)}, \tag{10.1.3}$$

one recovers back the formula (10.1.1). In this model, the contribution to the heat conductivity is essentially of ballistic origin and is due to the presence of the boundaries. In absence of temperature jumps ($\varepsilon = 0$), the process is dominated by diffusive scattering and λ_s is equal to its bulk value λ_0. The value of ε is obtained by fitting experimental observations data; $\varepsilon = 1/2$ and $\varepsilon = 4/3$ are the most frequently found values. Although expression (10.15) as well as Lepri's formula (10.1.1) cannot pretend to provide a definite final answer, they grasp in a relatively simple way the physical essence of heat transfer processes in nano systems. To combine both bulk and boundary effects, we suggest substituting in (10.1.3) the quantity λ_0 by the "bulk" conductivity as given by (10.15) so that the final formula is

$$\lambda_{\text{bb}}(l,L) = \frac{\lambda_{\text{bulk}}(l,L)}{1+2\varepsilon(l/L)}, \tag{10.1.4}$$

with index bb recalling that both bulk and boundary effects are taken into account. The boundary effects, also known as thermal boundary resistance, are especially relevant in multilayer systems.

10.1.2 Transient Temperature Distribution in a Micro Film

Our aim is twofold, firstly, to use the effective heat conductivity discussed in the previous section to determine the transient temperature profile in a one-dimensional micro film as a function of the Knudsen number; secondly, to compare the results with these obtained not only from Fourier's and Cattaneo's laws but also from two more recent models described in the foregoing sections. Initially, the film is at ambient temperature T_0 and the two faces are kept at temperatures $T_1(0,t)$ and $T_0(L,t)$ respectively. The relevant differential equation is the telegrapher's equation (9.5) established in Chap. 9 with $\lambda_{\text{eff}}(l,L)$ given by the general relation (10.15) and $\tau_{\text{eff}} = \tau(1 - l^2\omega/4\pi\tau) = \tau/4$; as shown in Chap. 4, the bulk conductivity λ_0 is expressed by $\lambda_0 = (1/3)c_v l v$, with v the average velocity of the phonons. Introducing the dimensionless time $t^* = t/\tau_{\text{eff}}$, distance $x^* = x/L$, and temperature $T^* = (T - T_0)/(T_1 - T_0)$, the hyperbolic equation (9.5) will take the dimensionless form

$$\frac{1}{4}\frac{\partial^2 T^*}{\partial t^{*2}} + \frac{\partial T^*}{\partial t^*} = \frac{1}{6\pi^2}\left(\sqrt{1+4\pi^2 Kn^2} - 1\right)\frac{\partial^2 T^*}{\partial x^{*2}}. \tag{10.17}$$

For low values of *Kn*, this expression reduces to

$$\frac{1}{4}\frac{\partial^2 T^*}{\partial t^{*2}}+\frac{\partial T^*}{\partial t^*}=\frac{Kn^2}{3}\frac{\partial^2 T^*}{\partial x^{*2}}. \tag{10.18}$$

Usually, instead of the normalized time τ_{eff}, it is customary to work with the relaxation time τ and the factor $\frac{1}{4}$ does not appear in the first term of the left-hand-side. This factor was first introduced by Anile and Pluchino (1984) to fit experimental ultrasound propagation in gases. One takes as initial condition $T(x,0)=0$. At $t=0^+$, one suddenly imposes $T(0,0)=1$ at one end of the sample and one keeps $T(1,0)=0$ fixed at the other extremity. The evolution of the heat flux in the course of time at the face $x=0$ is shown in Fig. 10.2. One observes that in the long-time limit, the value of the heat flux is the same in the Cattaneo and the Fourier description but that it is significantly lower in EIT. The flux reduction is similar to that predicted by Chen's ballistic–diffusion model (see Sect. 10.3) and agrees with Larson et al. (1986) experimental data. The advantage of the present one-constituent model with a generalised heat conductivity is that the equations are simpler to solve because there is no need to use different temperatures according the heat carriers are of ballistic or diffusive nature. The results of EIT are also rather close to these of Joshi and Majumdar (see Sect. 10.2) based on the direct resolution of Boltzmann's equation. When the Knudsen number becomes smaller and smaller, the results become similar to these of the Cattaneo description and are therefore not represented. We finally mention an alternative proposed by Naqvi and Waldenstrom (2005) who introduced a time-dependent heat conductivity and solved the

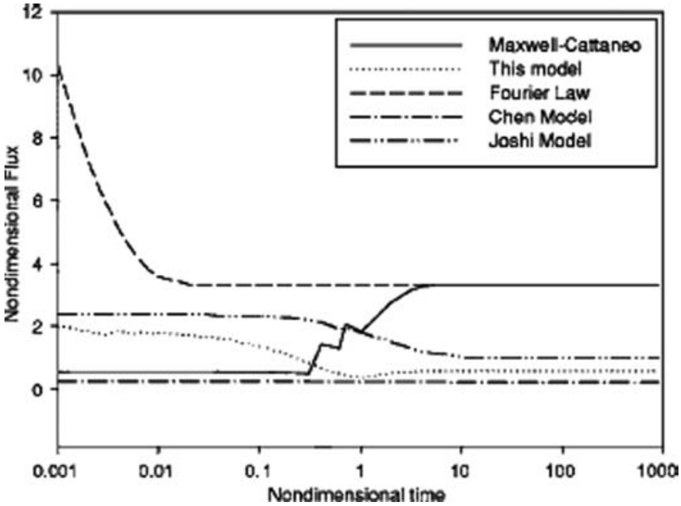


Fig. 10.2 Time evolution of the heat flux through the $x=0$ wall in a device with $Kn=10$ for five different models: Fourier, Maxwell-Cattaneo, Joshi and Majumdar, Chen, EIT (this model) (reprinted with permission from Álvarez FX, Jou D (2007) Appl Phys Lett 90:083109)

following temperature equation

$$\frac{\partial T^*}{\partial t^*} = (1 - e^{-t/\tau}) \frac{Kn^2}{3} \frac{\partial^2 T^*}{\partial x^{*2}}, \tag{10.19}$$

with uniform initial temperature and fixed temperatures at both ends of the material. The difference with the EIT description is that the heat conductivity is explicitly time-dependent instead of being expressed as a function of the length of the system. Naqvi and Solderhom's model predicts a lowering of the temperature compared to the results provided by Fourier's and Cattaneo's laws. The shortcoming of this description is its inability to cope with the reduction of conductivity in steady-state situations.

The EIT approach is not a first-principles theory but it is practically useful as it presents the advantages

1. To use one single partial differential equation
2. Not to make explicitly appeal to a distinction between ballistic and diffusive phonons
3. To fit the experimentally observed behaviour of heat conductivity in nano-devices as a function of their dimensions
4. To predict the reduction of the temperature and heat flux distributions as a consequence of a reduction of thermal conductivity
5. To be applicable to transient and steady problems.

10.2 The Equation of Phonon Radiative Transfer

The previous section was dedicated to a macroscopic description of heat transfer in micro and nanodevices. Here we present the problem under a completely different angle, namely a microscopic approach based on the linearized Boltzmann equation in conjunction with the relaxation time approximation. This model was originally proposed by Majumdar (1993) and Joshi and Majumdar (1993) and is known as the Equation of Phonon Radiative Transfer (EPRT). In the case of the one-dimensional heat transport, Boltzmann's equation takes the form

$$\frac{\partial f_\omega}{\partial t} + v_x \frac{\partial f_\omega}{\partial x} = \frac{f_\omega - f_\omega^0}{\tau}, \tag{10.20}$$

in the relaxation-time approximation with f_ω, the distribution function with frequency ω and f_ω^0 its equilibrium value, v_x is the velocity of heat carriers in the direction x and τ the relaxation time, here identified as the mean free time during phonon scattering and generally frequency-dependent; heat sources are assumed to be absent.

Rather than working with the distribution function, it is more convenient to use the phonon intensity whose modulus I_ω is defined as the energy of the phonon flow

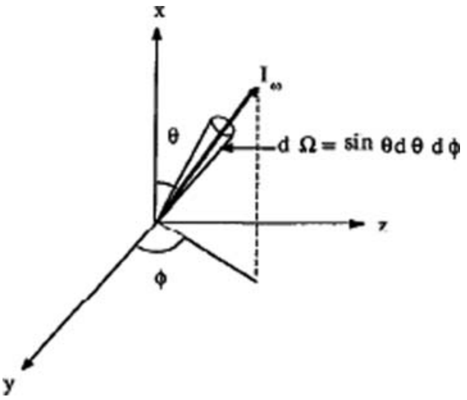


Fig. 10.3 Spherical coordinates showing the vectorial intensity I_ω

per unit time, unit solid angle Ω and unit frequency:

$$I_\omega(\theta, \varphi, x, t) = \hbar\omega f_\omega(x, t)\,|v(\theta, \varphi)|\,D(\omega), \tag{10.21}$$

where $v(\theta, \varphi)$ is the group velocity related to v_x by $v_x = |\boldsymbol{v}|\cos\theta$, θ and φ are the polar and azimuthal angles as shown in Fig. 10.3, $\hbar\omega$ the quantum of phonon energy of frequency ω, $\mathrm{d}\Omega = \sin\theta\ \mathrm{d}\theta\ \mathrm{d}\varphi$ the corresponding differential of the solid angle, and $D(\omega)$ the density of states per unit volume. The direction of the intensity is that of the phonon velocity $\boldsymbol{v}$.

Multiplying (10.20) by $|v|\hbar\omega D(\omega)/(4\pi)$ and in virtue of the definition (10.21), one obtains for the intensity in the x-direction

$$\frac{1}{|v|}\frac{\partial I_\omega}{\partial t} + \cos\theta\frac{\partial I_\omega}{\partial x} = \frac{I_\omega^0 - I_\omega}{|v|\tau}, \tag{10.22}$$

wherein the equilibrium value I_ω^0 is independent of the direction. In terms of I_ω, the corresponding heat flux q and internal energy density u are given by

$$q = \int_\omega \int_\Omega I_\omega \cos\theta \mathrm{d}\Omega \mathrm{d}\omega, \tag{10.23a}$$

$$u = \int_\omega \int_\Omega |v|^{-1} I_\omega \mathrm{d}\Omega \mathrm{d}\omega. \tag{10.23b}$$

When the phonon intensity is independent of the azimuthal angle φ, the above relations take the form

$$q = 2\pi \int_0^\pi \int_\omega I_\omega \cos\theta \sin\theta \mathrm{d}\theta \mathrm{d}\omega, \tag{10.24a}$$

$$u = 2\pi \int_0^\pi \int_\omega |v|^{-1} I_\omega \sin\theta \mathrm{d}\theta \mathrm{d}\omega. \tag{10.24b}$$

Integrating the differential equation (10.22) over θ and ω over the range $0 < \omega < \omega_D$, where ω_D is the Debye cutoff frequency, and making use of (10.24a and b) one is led to

$$\frac{\partial u}{\partial t} + \frac{\partial q}{\partial x} = 2\pi \int_0^{\pi} \int_0^{\omega_D} (I_\omega^0 - I_\omega)(\tau|v|)^{-1} \sin\theta \mathrm{d}\theta \mathrm{d}\omega, \tag{10.25}$$

where $\tau|v| = l$ represents the phonon mean free path. Simplifications of Eq. (10.22) are obtained by observing, first, that I_ω^0 is independent of the direction and thus only temperature-dependent; second, that the left-hand-side of (10.25) vanishes, as it represents the classical law of conservation of energy. As a consequence, the right-hand-side of (10.25) is zero and one is led to

$$\int_0^{\omega_D} I_\omega^0 \mathrm{d}\omega = \tfrac{1}{2} \int_0^{\omega_D} \int_0^{\pi} I_\omega \sin\theta \mathrm{d}\theta \mathrm{d}\omega, \tag{10.26}$$

which, substituted in (10.22), gives the final form of the basic equation of the EPRT model,

$$\frac{1}{|v|}\frac{\partial I_\omega}{\partial t} + \cos\theta \frac{\partial I_\omega}{\partial x} = \frac{I_\omega^0 - I_\omega}{\tau|v|} = \frac{\frac{1}{2}\int_0^{\pi} I_\omega \sin\theta \mathrm{d}\theta - I_\omega}{\tau|v|}. \tag{10.27}$$

This integro-differential equation is similar to the one describing photon radiation transfer (Ozisik and Tzou 1994) and has been solved numerically by Joshi and Majumdar (1993). Once that the phonon intensity is known, the temperature field is obtained from (10.26) by using for the equilibrium distribution I_ω^0 the Bose–Einstein statistics so that finally, the temperature can be calculated from

$$\int_0^{\omega_D} \frac{\hbar\omega^3\, D(\omega)}{8\pi^3 v^2 \exp\left[\hbar\omega/(k_\mathrm{B}T) - 1\right]} \mathrm{d}\omega = \tfrac{1}{2} \int_0^{\omega_D} \int_0^{\pi} I_\omega \sin\theta \mathrm{d}\theta \mathrm{d}\omega. \tag{10.28}$$

Note that I_ω may be very different from the equilibrium distribution, in such a way that (10.28) defines in fact an effective non-equilibrium temperature, rather than a strict equilibrium temperature.

The transient EPRT model was applied by Joshi and Majumdar (1993) to calculate the temperature distribution in a thin diamond film with the following boundary conditions:

$$T = T_1 \quad \text{at } x = 0, \qquad T = T_0 \quad \text{at } x = L, \tag{10.29}$$

with $\Delta T = T_1 - T_0 = 0.1$ K; the associated boundary conditions for the phonon intensity are

$$I_\omega = I_\omega^0(T_1) \text{ at } x = 0, \; I_\omega = I_\omega^0(T_0) \text{ at } x = L. \tag{10.30}$$

The material is assumed to be disturbed from the uniform initial temperature field $T(x, 0) = 300$ K with a zero rate temperature change $\partial T(x, 0)/\partial t = 0$. The film thickness of 0.10 μm is smaller than the mean free path, which is 0.45 μm, and therefore ballistic heat transfer is expected to be dominant. The results are reproduced in Fig. 10.4a–c and compared with the profiles predicted by the Fourier (diffusive limit), and Cattaneo (hyperbolic) laws, all the results are given in terms of the dimensionless temperature $T^* = (T - T_0)/(T_1 - T_0)$ shown as θ in Figure 10.4, length and time are scaled by L and ℓ/v respectively.

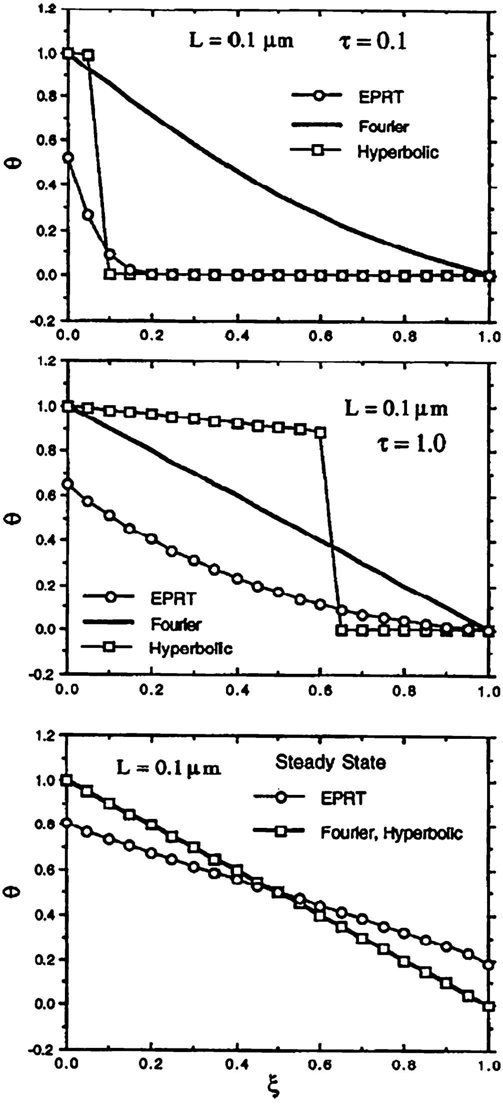


Fig. 10.4 Transient temperature profiles predicted by the Fourier, Cattaneo (hyperbolic) and EPRT models at three different dimensionless times (reprinted with permission from Joshi AA, Majumdar A (1993) J Appl Phys 74: 31). Here ξ is the dimensionless length $\xi = x/L$, with L the length of the system

Fourier's description predicts a well established temperature profile throughout the film while a sharp wave front is the salient feature of Cattaneo's model. Both Fourier's and Cattaneo's laws overestimate the values obtained from EPRT. The EPRT distribution is smoother that Cattaneo's because the phonons relaxation times $\tau(\omega)$ are very short at some frequencies so that diffusive effects may become more important than in Cattaneo's description. If the regime is purely ballistic, $t^* = 1$ is the time required to travel from one boundary to the other. Note that with Cattaneo's equation (see Fig. 10.4b) the temperature is only felt up to the value $x^* = 0.6$ because the speed of the wave is $v/\sqrt{3}$ as shown in Chap. 2. Another difference between the EPRT and the two other models is that the former predicts a temperature jump at the boundaries; it is observed that at $x^* = 0$, the jump decreases with time as a consequence of appearance of diffusion. The jump becomes less important for a larger thickness, due to increasing diffusive motions. In the steady state, the sharp wave front of Cattaneo's model vanishes and both Fourier's and Cattaneo's descriptions exhibit the same linear temperature profile. Note that EPRT does not reduce to Fourier's and Cattaneo's results in the steady state: as shown in Fig. 10.4c, EPRT leads to a lower temperature at the hot side $x^* = 0$ and a higher temperature at the cold side $x^* = 1$. By increasing the thickness of the sample, the three profiles tend to coalesce in the steady state. When the film thickness becomes comparable to the mean free path, it was shown by Majumdar (1993) that in the steady state, the heat flux is given by

$$q = \frac{\sigma(T_1^4 - T_0^4)}{(3/4)(L/l) + 1}, \tag{10.31}$$

where σ is the Stefan–Boltzmann constant (see Problem 10.1). In the so-called Casimir limit $L/l \to 0$, corresponding to purely ballistic transport, expression (10.31) is the same as the Stefan–Boltzmann's law in radiative heat transfer. The main drawback of EPRT is its excessive time consumption when it is solved numerically.

10.3 The Ballistic Diffusion Equation

This model can be considered as half the way between the EPRT microscopic and the EIT macroscopic descriptions. A first version was proposed by Chen (2001) in the line of thought of the kinetic theory and EPRT; here we develop a model more axed on thermodynamics and EIT. The originality of BDE is to split the distribution function f into two parts: a diffusive f_d and a ballistic f_b one; the latter is the transport originating from the boundaries of the material while the former originates from the phonons multiple collisions occurring inside the system (see Fig. 10.5). As a consequence, the internal energy density u will be split into a diffusive u_d and a ballistic contribution u_b, so that $u = u_\mathrm{d} + u_\mathrm{b}$, and similarly, the heat flux vector will be decomposed in such a way that $\boldsymbol{q} = \boldsymbol{q}_\mathrm{d} + \boldsymbol{q}_\mathrm{b}$.

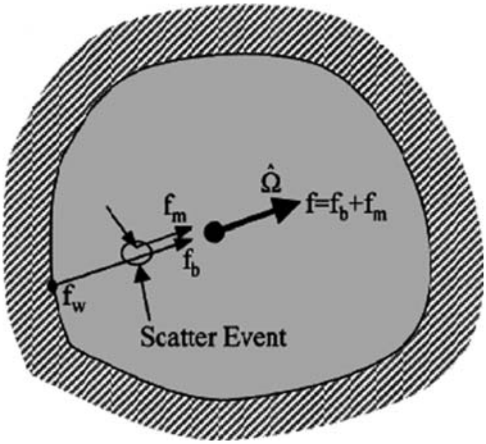


Fig. 10.5 Distinction between the ballistic phonons originating from the boundary with distribution f_b and the diffusive phonons scattered from the inside of the body with distribution f_d (denoted by f_m in the figure) (reprinted with permission from Chen G (2001) Phys Rev Lett 86:2297)

10.3.1 The Model Equations

The essence of Chen's ballistic–diffusion model is to split the phonon intensity into a diffusive and a ballistic part

$$I_\omega(\boldsymbol{r},t) = I_\mathrm{d}(\boldsymbol{r},t) + I_\mathrm{b}(\boldsymbol{r},t). \tag{10.32}$$

By following the same procedure which led to the establishment of Eq. (10.22) in the EPRT model, it is shown that the governing equation of the diffusive part I_d which describes the scattered phonons from the inner region is

$$\frac{1}{|\boldsymbol{v}|}\frac{\partial I_\mathrm{d}}{\partial t} + \frac{|\boldsymbol{v}|}{|\boldsymbol{v}|}\cdot\nabla I_\mathrm{d} = \frac{I_\mathrm{d}^0 - I_\mathrm{d}}{|\boldsymbol{v}|\tau}. \tag{10.33}$$

Since there is no equilibrium state associated with the ballistic phonons, the corresponding equation satisfied by I_b will be of the form

$$\frac{1}{|\boldsymbol{v}|}\frac{\partial I_\mathrm{b}}{\partial t} + \frac{\boldsymbol{v}}{|\boldsymbol{v}|}.\nabla I_\mathrm{b} = -\frac{I_\mathrm{b}}{|\boldsymbol{v}|\tau}. \tag{10.34}$$

An equation similar to (10.34) was solved in the theory of radiation hydrodynamics (Pomraning 1977) and its solution is given by

$$I_\mathrm{b} = I_\mathrm{bw}\left[t - \frac{s-s_0}{|\boldsymbol{v}|}, \boldsymbol{r} - (s-s_0)\boldsymbol{e}\right]\exp\left(-\int_{s_0}^{s}\frac{\mathrm{d}s}{|\boldsymbol{v}|\tau}\right), \tag{10.35}$$

wherein I_{bw} is the value of I_{b} at the boundary point $\boldsymbol{r} - (s - s_0)\boldsymbol{e}$, $\boldsymbol{e}$ denoting the unit vector $\boldsymbol{e} = \boldsymbol{v}/|\boldsymbol{v}|$ and $(s - s_0)$ the distance along the propagation distance $\boldsymbol{e}$.

Based on the decomposition (10.32) of the intensity, one can define ballistic and diffusive heat fluxes and internal energies according to

$$\boldsymbol{q} = \iint I_\omega \boldsymbol{v} |\boldsymbol{v}|^{-1} \mathrm{d}\Omega \mathrm{d}\omega = \boldsymbol{q}_{\mathrm{b}} + \boldsymbol{q}_{\mathrm{d}}, \tag{10.36a}$$

$$u = \iint I_\omega |\boldsymbol{v}|^{-1} \mathrm{d}\Omega \mathrm{d}\omega = u_{\mathrm{b}} + u_{\mathrm{d}} \tag{10.36b}$$

with respectively

$$\boldsymbol{q}_{\mathrm{b}} = \iint I_{\mathrm{b}} \boldsymbol{v} |\boldsymbol{v}|^{-1} \mathrm{d}\Omega \mathrm{d}\omega, \tag{10.37a}$$

$$u_{\mathrm{b}} = \iint I_{\mathrm{b}} |\boldsymbol{v}|^{-1} \mathrm{d}\Omega \mathrm{d}\omega, \tag{10.37b}$$

and similar expressions for $\boldsymbol{q}_{\mathrm{d}}$ and u_{d}. The total internal energy u and the corresponding total temperature T are defined through

$$\mathrm{d}u = \mathrm{d}u_{\mathrm{b}} + \mathrm{d}u_{\mathrm{d}} = c_v \mathrm{d}T, \tag{10.38}$$

with c_v the heat capacity per unit volume. Since in the ballistic regime the distribution of phonons deviates significantly from that of equilibrium, the definition of temperature becomes ambiguous, and this is the reason why in the following, T represents essentially a measure of energy.

The evolution equation (10.34) for I_{b} is now used to obtain the balance law of internal energy u_{b}. It is directly checked from the definitions (10.37) and Eq. (10.34) after integration over frequency and solid angle that

$$\frac{\partial u_{\mathrm{b}}}{\partial t} + \nabla \cdot \boldsymbol{q}_{\mathrm{b}} = -\frac{u_{\mathrm{b}}}{\tau_{\mathrm{b}}}, \tag{10.39}$$

wherein the minus sign indicates that ballistic carriers can be converted into diffusive ones but that the converse is not possible. Moreover, for a body at rest and absence of internal heating, the total energy conservation law writes as

$$\frac{\partial u_{\mathrm{d}}}{\partial t} + \frac{\partial u_{\mathrm{b}}}{\partial t} = -\nabla \cdot \boldsymbol{q}_{\mathrm{d}} - \nabla \cdot \boldsymbol{q}_{\mathrm{b}}, \tag{10.40}$$

from which follows, after making use of (10.38), that the evolution equation for u_{d} is

$$\frac{\partial u_{\mathrm{d}}}{\partial t} + \nabla \cdot \boldsymbol{q}_{\mathrm{d}} = \frac{u_{\mathrm{b}}}{\tau_{\mathrm{b}}}. \tag{10.41}$$

Referring to the general statements of EIT, the ballistic and diffusive energy fluxes may, in a first approximation, be cast in the form of Cattaneo equations, namely

$$\tau_{\mathrm{b}} \frac{\partial \boldsymbol{q}_{\mathrm{b}}}{\partial t} + \boldsymbol{q}_{\mathrm{b}} = -\lambda \mathrm{b} \nabla T_{\mathrm{b}}, \tag{10.42a}$$

$$\tau_{\mathrm{d}} \frac{\partial \boldsymbol{q}_{\mathrm{d}}}{\partial t} + \boldsymbol{q}_{\mathrm{d}} = -\lambda_{\mathrm{d}} \nabla T_{\mathrm{d}}. \tag{10.42b}$$

Note that in (10.42a, b) the relaxation times of the ballistic and diffusive phonons are supposed to take different values; moreover all the coefficients τ_{b}, τ_{d}, λ_{b} and λ_{d} are positive definite as a consequence of the laws of thermodynamics. Expressions (10.39), (10.41) and (10.42) provide the basic set of eight scalar evolution equations for the eight unknowns u_{b}, u_{d}, $\boldsymbol{q}_{\mathrm{b}}$ and $\boldsymbol{q}_{\mathrm{d}}$. The validity of Cattaneo's law (10.42b) for the diffusive carriers was confirmed by Chen (2002) as a consequence of the differential equation (10.33) satisfied by I_{d}. Elimination of $\boldsymbol{q}_{\mathrm{d}}$ and $\boldsymbol{q}_{\mathrm{b}}$ yields two second-order uncoupled differential equations:

$$\tau_{\mathrm{b}} \frac{\partial^2 u_{\mathrm{b}}}{\partial t^2} + 2\frac{\partial u_{\mathrm{b}}}{\partial t} + (1/\tau_{\mathrm{b}}) u_{\mathrm{b}} = \nabla \cdot [(\lambda_{\mathrm{b}}/c_{v\mathrm{b}}) \nabla u_{\mathrm{b}}], \tag{10.43}$$

$$\tau_{\mathrm{d}} \frac{\partial^2 u_{\mathrm{d}}}{\partial t^2} + \frac{\partial u_{\mathrm{d}}}{\partial t} - (\tau_{\mathrm{d}}/\tau_{\mathrm{b}}) \frac{\partial u_{\mathrm{b}}}{\partial t} - (1/\tau_{\mathrm{b}}) u_{\mathrm{b}} = \nabla \cdot [(\lambda_{\mathrm{d}}/c_{v\mathrm{d}}) \nabla u_{\mathrm{d}}]. \tag{10.44}$$

Expressions (10.42) and (10.43) are the key relations of our model. Assuming that $\tau_{\mathrm{b}} = \tau_{\mathrm{d}} \equiv \tau$, $\lambda_{\mathrm{b}} = \lambda_{\mathrm{d}} \equiv \lambda$, $c_{v\mathrm{b}} = c_{v\mathrm{d}} \equiv c_v$, and eliminating u_{b} with the help of (10.39), one recovers from (10.44) Chen's main result (2001, 2002)

$$\tau \frac{\partial^2 u_{\mathrm{d}}}{\partial t^2} + \frac{\partial u_{\mathrm{d}}}{\partial t} + \nabla \cdot \boldsymbol{q}_{\mathrm{b}} = -\nabla \cdot [(\lambda/c_v) \nabla u_{\mathrm{d}}]. \tag{10.45}$$

This expression differs from the telegraph equation by the term in $\nabla \cdot \boldsymbol{q}_{\mathrm{b}}$ which accounts here for the presence of non-local effects. This contribution is the essence of BDE and will deeply influence the final results, as shown in the next section. The approach leading to expressions (10.43) and (10.44) is more general than Chen's original model (Chen 2001), as the heat capacities, the heat conductivities and the relaxation time of the diffusive and ballistic phonons are left unequal. The price to be paid is that it implies the determination of these various coefficients, a task which at the present state of our knowledge is not completed yet due to lack of experimental data. This is the reason why we prefer in the foregoing to concentrate our attention on Eq. (10.45). Its resolution demands the preliminary derivation of $\boldsymbol{q}_{\mathrm{b}}$, which is obtained by substitution of solution (10.31) for I_{b} into the definition of $\boldsymbol{q}_{\mathrm{b}}$ (10.37a), the result is

$$\boldsymbol{q}_{\mathrm{b}} = \iint \left\{ I_{\mathrm{bw}} \left[t - |\boldsymbol{v}|^{-1}(s - s_0), \boldsymbol{r} - (s - s_0)\boldsymbol{e} \right] \exp\left[-\int_{s_0}^{s} \boldsymbol{e} |\boldsymbol{v}|^{-1} \tau^{-1} \mathrm{d}s \right] \right\} \mathrm{d}\Omega \mathrm{d}\omega, \tag{10.46}$$

with I_{bw} the intensity of phonons at the specified time at the wall.

Equation (10.45) represents a good approximation of Boltzmann equation but it is simpler to solve numerically because it contains only the time and spatial variables, but not the momentum variables which appear in Boltzmann's equation. In the next section, Eq. (10.45) will be applied to solve the problem of transient heat transport across micro films.

10.3.2 Illustration: Transient Heat Transport in Thin Films

BDE will be applied to the study of heat conduction in a one-dimensional thin film of thickness L smaller than the mean free path ℓ, heat capacity and heat conductivity are assumed to be constant and internal energy sources are absent. The system is initially at uniform temperature T_0. The lower surface $x=0$ is suddenly brought to temperature $T_0+\Delta T$ with $\Delta T = T_1 - T_0$, while the surface $x=L$ is kept at temperature T_0. Since the ballistic phonons originate from the walls, their energy is the prescribed energy at the boundaries, i.e. $c_v T_0$ and $c_v T_1$ respectively. Assuming that the boundaries are only undergoing incident diffusive phonons, and making use of a result derived by Marshak (1967) in the limit of black walls for thermal radiation, the heat flux at the walls corresponding to diffusive phonons can be cast in the form

$$\boldsymbol{q}_{\mathrm{d}} \cdot \boldsymbol{n} = -\tfrac{1}{2} v u_{\mathrm{d}}, \tag{10.47}$$

where $\boldsymbol{n}$ is the unit normal to the boundary pointing positively outwards. After substitution of (10.47) in Cattaneo's law (10.42b), one obtains the following boundary condition for the diffusive component:

$$\tau \frac{\partial u_{\mathrm{d}}}{\partial t} + u_{\mathrm{d}} = \frac{2}{3} \ell \nabla u_{\mathrm{d}} \cdot \boldsymbol{n}, \tag{10.48}$$

where ℓ denotes the mean free path defined through $\lambda = \frac{1}{3} c_v v \ell$. The basic relation (10.45) of the ballistic–diffusion model takes the simplified form

$$\tau \frac{\partial^2 u_{\mathrm{d}}}{\partial t^2} + \frac{\partial u_{\mathrm{d}}}{\partial t} = \frac{\lambda}{c_v} \frac{\partial^2 u_{\mathrm{d}}}{\partial x^2} - \frac{\partial q_{\mathrm{b}}}{\partial x}, \tag{10.49}$$

with the initial and boundary conditions given by

$$t=0: \quad u(x,0) = u_{\mathrm{d}}(x,0) + u_{\mathrm{b}}(x,0) = c_v T_0, \ \left(\frac{\partial u(x,t)}{\partial t} \right)_{t=0} = 0, \tag{10.50}$$

$$x=0: \ u_{\mathrm{b}}(0,t) = c_v T_1, \tag{10.51}$$

$$\tau \left(\frac{\partial u_{\mathrm{d}}}{\partial t} + u_{\mathrm{d}} \right)_{x=0} = \frac{2\ell}{3} \left(\frac{\partial u_{\mathrm{d}}}{\partial x} \right)_{x=0}, \tag{10.52}$$

$$x=L: \ u_{\mathrm{b}}(L,t) = c_v T_0, \tag{10.53}$$

$$\tau\left(\frac{\partial u_\mathrm{d}}{\partial t}+u_\mathrm{d}\right)_{x=L}=-\frac{2\ell}{3}\left(\frac{\partial u_\mathrm{d}}{\partial x}\right)_{x=L}. \tag{10.54}$$

To solve (10.49), one needs to determine the ballistic heat flux q_b which, in the present geometry, is given by (Chen 2002)

$$q_\mathrm{b}(x,t)=\tfrac{1}{2}c_v v\Delta T\int_{\mu_t}^{1}\xi\exp[-x/(\xi l)]\,\mathrm{d}\xi+q_{\mathrm{b}0}(x,0)\ \text{for}\ 0\le\mu_t\le 1, \tag{10.55a}$$

$$q_\mathrm{b}=q_0(x,0)\ \text{for}\ -1\le\mu_t\le 0, \tag{10.55b}$$

wherein $\mu_t = x/vt$. This result is a confirmation of the property that the heat flux depends on the difference of temperatures ΔT between the two extremities and not on the temperature gradient. The problem has been solved numerically by Chen (2002) in terms of the non-dimensional quantities temperature $T^* = (u - u_0)/(c_v\Delta T)$, heat flux $q^* = (q - q_0)/(c_v v\Delta T)$, time $t^* = t/\tau$, and space coordinate $x^* = x/L$. Chen has determined the temperature and heat flux distribution and compared his results with these obtained from Fourier's, Cattaneo's and Boltzmann's equations. The results for the temperature are plotted in Fig. 10.6a and b and indicate clearly that Fourier's and Cattaneo's laws break down to describe heat conduction at small space scales (large Kn numbers) and short time scales. On the other hand, comparison of the results of the BDE with these derived by direct integration of the Boltzmann equation shows a close agreement. At small Kn's and large t^* -values, the four models tend to deliver similar results as seen in Fig. 10.6b. Whatever the values of Kn, the Boltzmann and BDE formalisms exhibit a temperature jump at the boundaries, a feature still observed in EPRT. Chen has also calculated the behaviours of the heat flux at $x^* = 0$ as a function of time, as shown in Fig. 10.2. Fourier's description predicts a unrealistic infinite value as time goes to zero. Cattaneo's law leads to artificial heat flux oscillations; the results of BDE are similar to these obtained from Boltzmann's equation while a good agreement

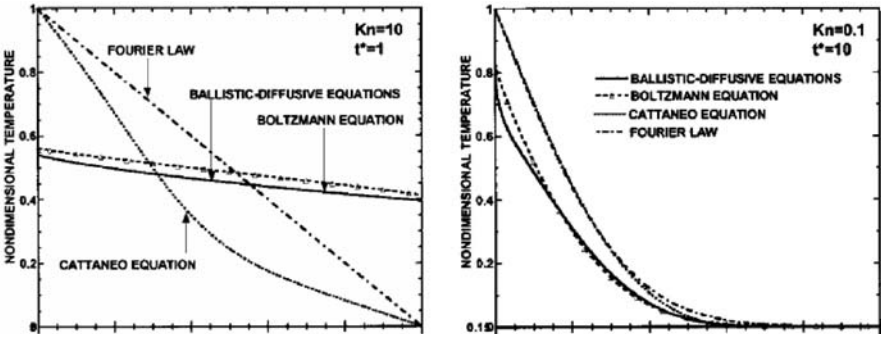


Fig. 10.6 Comparison of temperature profiles obtained from Fourier's, Cattaneo's, Boltzmann's, BDE models at two different Knudsen numbers and two different times (reprinted with permission from Chen G (2002) J Heat Transf 124:320)

is reached between the EIT and BDE approaches especially in the long time limit ($t^* > 1$). Chen and collaborators (Yang et al. 2005) have extended the BDE to the study of transient heat conduction in two-dimensional structures in presence of internal heat generation. In spite of its interest and success, the BDE contains an inconsistency when applied to the equilibrium limit. Assuming that the system is in equilibrium with the environment at temperature T_0, one is able to calculate the equilibrium values of $u_{\mathrm{d}0}$ and $u_{\mathrm{b}0}$ but the sum $u_0 = u_{\mathrm{d}0} + u_{\mathrm{b}0}$ does not make restitution of the equilibrium value $c_v T_0$, thus temperature T_0. The reasons may be found in the relaxation time hypothesis and the use of Cattaneo's equation (10.42b) which represent only rough approximations of the true behaviour of the diffusive phonons.Moreover, Chen introduces the simplifying assumptions that the heat capacities $c_{\mathrm{d}} = c_{\mathrm{b}} \equiv c_v$, the heat conductivities $\lambda_{\mathrm{d}} = \lambda_{\mathrm{b}} \equiv \lambda$, and the relaxation times $\tau_{\mathrm{d}} = \tau_{\mathrm{b}} \equiv \tau$ are equal for both the diffusive and ballistic phonons. Although for reasons of simplifications, such an hypothesis may be relevant concerning the heat capacity and the heat conductivity which describe mean macroscopic properties, it is not acceptable for the relaxation times; indeed, at large *Kn* and short times, the frequency of collisions $1/\tau_{\mathrm{b}}$ of phonons with the boundaries is largely dominant and this means that the corresponding relaxation time should be smaller than the diffusive one: $\tau_{\mathrm{b}} \ll \tau_{\mathrm{d}}$. Finally, the BDE constitutes a rather complex approach as it mixes macroscopic considerations, via the use of Cattaneo's law for the diffusive part, and microscopic aspects, through the resolution of Boltzmann's equation for the ballistic motion. The model requires also the resolution of twice the number of equations compared to the EPRT and EIT models.

In summary, the use of a phenomenological effective thermal conductivity depending on the size of the system, as described in Sect. 10.1 may be especially useful for an initial exploration of the general trends of the behaviour of the system, as it requires a reduced computational effort. After the most promising configurations of a device have been identified, one could proceed to a more detailed microscopic exploration by using, for instance, the EPRT or BDE approaches or some more detailed Monte Carlo simulations. One of the merits of EIT is to provide a practical first description of heat transport in small length and short time scales which would not have been possible in the frame of the local-equilibrium approach.

10.4 Problems

10.1. Consider a 1-D thin film of thickness L subject to a temperature difference $T_1 - T_0$. Using the EPRT model, show that in the steady state, the heat flux is given by

$$q = \frac{\sigma(T_1^4 - T_0^4)}{1 + \frac{3}{4}(L/\ell)},$$

wherein σ is Stefan–Boltzmann's constant and ℓ the mean free path of phonons (Majumdar 1993). Show that in the limiting cases of purely diffusive and purely ballistic transport, one recovers respectively the Fourier's law and the so-called Casimir limit $q = \sigma(T_1^4 - T_0^4)$.

10.2. Show that by considering only the first truncation approximation in the continued-fraction expansion (10.10), i.e. by assuming that $\ell_1 = 1$, $\ell_i = 0$ for $i > 1$ together with $\omega = 0$, one finds, in the limit of large Kn values, that

$$\lambda_1(L) = \frac{\lambda_0}{4\pi^2\ell^2} L^2,$$

which is not satisfactory, as experiments indicate that λ is proportional to L instead of to L^2.

10.3. Determine the temperature distribution in a 1-D thin slab of length L from Naqvi and Waldenstrom's equation (10.19) for $Kn = 10,\ 1,\ 0.01$ and the following initial and boundary conditions:

$$\begin{aligned} t &= 0: \ T(x,0) = T_0, \\ x &= 0: \ T = T_1 \ x = L: \ T = T_0. \end{aligned}$$

Compare with the results obtained from the classical Fourier's law.

10.4. Starting from the equation for steady-state phonon hydrodynamics

$$\nabla^2 \boldsymbol{q} = \frac{k_0}{\ell^2} \nabla T,$$

and assuming that the heat flux along the walls is not zero, but given by the slip condition

$$q_{\text{wall}} = C\ell \left(\frac{\partial q}{\partial r} \right)_{\text{wall}}$$

obtain the profile $q(r)$ of the heat flux in a thin layer of width R, and show that the effective thermal conductivity has the form

$$\lambda_{\text{eff}} = \lambda_0 \left[1 - \left(\frac{2\ell}{R} - C \right) \tanh\left(\frac{R}{2\ell} \right) \right].$$

(See Álvarez, Jou, Sellito (2009).)

10.5. To apply (10.15) to a nanowire the effective size L must be $L^{-2} = r^{-2} + r^{-2}$, i.e. $L = r/\sqrt{2}$. (a) Compare the effective conductivity of a thin layer of width r with that of a nanowire of radius r. (b) Obtain the effective size of a tubular nanowire of external and internal radii given by r_1 and r_2.

Chapter 11
Waves in Fluids: Sound, Ultrasound, and Shock Waves

The presence of relaxation terms and higher-order gradients in the dynamical equations makes it very difficult to solve them because they require the introduction of supplementary boundary and initial conditions compared to classical thermo-hydrodynamics. Instead of trying to solve the whole mathematical problem, it is more fruitful to concentrate on the analysis of waves in infinite media, as their speed and attenuation are directly measurable and of great practical interesting in the determination of the constitutive properties of the materials.

As the relaxation times of the fluxes are usually very small, it is rather difficult to observe their effects in transient processes. However, such effects may be made perceptible in high-frequency phenomena, like sound and ultrasound propagation when the frequency becomes comparable to the inverse of the relaxation times of the fluxes. At high frequencies, the influence of the relaxational terms becomes decisive, as they imply a finite propagation speed instead of a divergent speed, as it was already mentioned in the context of thermal waves. Another situation of interest is provided by shock waves, where the gradients and the speeds are very high, this implying a relevant role of non-local contributions.

Classical hydrodynamics is described by five independent variables (mass, energy, and the three components of velocity), to which correspond five hydrodynamic modes. In EIT, additional independent variables are incorporated and thus the number of independent modes will increase accordingly. In this chapter we shall focus on the influence of these extra variables on propagation of waves and shocks in ordinary fluids. This topic finds also several applications in complex fluids, as for instance laminar or turbulent superfluids (Mongiovì 1993, Mongiovì and Jou 2007), where a higher number of independent waves may arise.

11.1 Sound Propagation in Fluids: Linear Waves

Wave propagation in fluids, and more particularly ultrasound propagation in monatomic gases, was one of the main tools used to study the properties of fluids before the development of new techniques based on light and neutron scattering. Wave propagation in gases has been examined from the point of view of the kinetic

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_11,

theory of gases to explain experimental results by Greenspan (1956) and Meyer and Sessler (1957). A macroscopic interpretation in terms of EIT was proposed by Carrassi and Morro (1973), Anile and Pluchino (1984), and others, who based their analyses on the relaxational equations (2.70–2.72). These works were generalised by Lebon and Cloot (1989), who introduced non-local higher-order terms, and by Chu (1999), by using discrete kinetic models..

Consider a perturbation around a reference equilibrium state with pressure p_0, density ρ_0, temperature T_0, and velocity zero, so that $\rho = \rho_0 + \delta\rho$, $p = p_0 + \delta p$, $T = T_0 + \delta T$, and $\boldsymbol{v} = \mathbf{0} + \delta\boldsymbol{v}$. The linear form of the balance equations of mass, momentum and energy is

$$\frac{\partial \delta\rho}{\partial t} + \rho_0 \nabla \cdot \delta\boldsymbol{v} = 0, \tag{11.1a}$$

$$\rho_0 \frac{\partial \delta\boldsymbol{v}}{\partial t} = -\nabla \delta p - \nabla \cdot \delta\mathbf{P}^v, \tag{11.1b}$$

$$\rho_0 \frac{\partial \delta u}{\partial t} = -p_0 \nabla \cdot \delta\boldsymbol{v} - \nabla \cdot \delta\boldsymbol{q}. \tag{11.1c}$$

The perturbation of the internal energy in terms of the perturbation in density and temperature can be written as

$$\delta u = c_v \delta T + \frac{1}{\rho_0}\left(\frac{p_0}{\rho_0} - \frac{c_p - c_v}{\alpha}\right)\delta\rho, \tag{11.2}$$

when non-linear terms in the fluxes have been omitted.

Consider one-dimensional perturbations of the form $\delta\phi = \delta\phi' \exp[\mathrm{i}(\omega t - kx)]$, with amplitude $\delta\phi'$, real frequency ω and complex wavevector k. Inserting these into (11.1a–c), one obtains

$$\mathrm{i}\omega\delta\rho' - \mathrm{i}k\rho_0\delta v_x' = 0, \tag{11.3a}$$

$$-\mathrm{i}k\delta p' - \mathrm{i}k\delta P_{xx}^{v\prime} + \mathrm{i}\omega\rho_0\delta v_x' = 0, \tag{11.3b}$$

$$\mathrm{i}\omega\rho_0 c_v\delta T' - \mathrm{i}k\delta q_x' - \frac{p_0}{\alpha}\left(c_p - c_v\right)\mathrm{i}k\delta v_x' = 0, \tag{11.3c}$$

where δT can be expressed in terms of $\delta\rho$ and δp by means of $\alpha\rho_0\delta T = (\gamma/c_s^2)\delta p - \delta\rho$, with α the coefficient of thermal expansion, $\gamma = c_p/c_v$, and $c_s^2 = (\partial p/\partial\rho)_s$ the Laplace sound velocity.

11.1.1 The Classical Theory

In this section we reproduce the classical theory, and for pedagogical reasons we have given the details of the calculations.

For fluids described by the Newton and Fourier equations with zero bulk viscosity one has

$$\delta P'_{xx^v} = \frac{4}{3}\mathrm{i}k\eta\delta v'_x,\ \delta q'_x = \mathrm{i}k\lambda\delta T'. \tag{11.4}$$

Combination of (11.3) and (11.4) yields

$$\mathbf{A}_c \cdot \boldsymbol{b}_c = \mathbf{0}, \tag{11.5}$$

where

$$\mathbf{A}_c = \begin{pmatrix} \mathrm{i}\omega & -\mathrm{i}k\rho_0 & 0 \\ 0 & \mathrm{i}\omega\rho_0 + \frac{4}{3}\eta k^2 & -\mathrm{i}k \\ -\frac{1}{\alpha\rho_0}(\mathrm{i}\omega\rho_0 c_v + \lambda k^2) & -\frac{\rho_0}{\alpha}(c_p - c_v)\mathrm{i}k & \frac{\gamma}{\rho_0 c_s^2 \alpha}(\mathrm{i}\omega\rho_0 c_v + \lambda k^2) \end{pmatrix}, \tag{11.6a}$$

$$\boldsymbol{b}_c = \begin{pmatrix} \delta\rho' \\ \delta v'_x \\ \delta p' \end{pmatrix} \tag{11.6b}$$

$$\mathbf{0} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \tag{11.6c}$$

The corresponding dispersion relation given by the vanishing of the determinant of $\mathbf{A}_c$ is

$$\frac{\lambda}{c_s\rho_0 c_p}k^4\left(-\frac{\mathrm{i}c_s}{\omega} + \frac{4}{3}\frac{\eta\gamma}{c\rho_0}\right) + k^2\left[1 + \frac{i\omega}{c_s^2\rho_0}\left(\frac{4}{3}\eta + \frac{\lambda\gamma}{c_p}\right)\right] - \frac{\omega^2}{c_s^2} = 0. \tag{11.7}$$

This is the well-known Kirchhoff equation for acoustic waves. For small values of k and ω one finds for the phase velocity v_p and the absorption coefficient Γ'

$$v_p = \frac{\omega}{\mathrm{Re}\,k}, \tag{11.8a}$$

$$\Gamma' = -\mathrm{Im}\,k = \frac{\omega^2}{2c_s^3}\left[\frac{4}{3}\frac{\eta}{\rho_0} + \chi(\gamma - 1)\right], \tag{11.8b}$$

with $\chi = \lambda/\rho_0 c_p$ the heat diffusivity. These are the classical results for sound propagation and absorption at low frequencies. At high frequencies, the asymptotic solution of (11.7) behaves as

$$k^2 \approx a + \mathrm{i}\left[b(\omega/c_s) + \mathcal{O}(1/\omega)\right], \tag{11.9}$$

wherein a and b are functions of $l_1 = \chi/c_s$ and $l_2 = \frac{4}{3}\eta/(c\rho_0)$ (Problem 11.1). In the high-frequency limit, the imaginary part of k^2 dominates, so that $k^2 = \mathrm{i}b(\omega/c)$; it is easily checked (see Problem 11.1) that

$$\mathrm{Re}\,k \approx \mathrm{Im}\,k \approx \omega^{1/2}. \tag{11.10}$$

Consequently, the phase velocity behaves as

$$v_p = \frac{\omega}{\operatorname{Re} k} \approx \omega^{1/2}, \tag{11.11}$$

which is unbounded as ω tends to infinity. This remains true for the absorption coefficient. The above results indicate clearly that the classical approach is not valid at high frequencies.

11.1.2 Extended Thermodynamic Theory

For a vanishing bulk viscous pressure, the one-dimensional linearized equations (2.70) and (2.72) can be expressed as

$$\tau_1 \frac{\partial q_x}{\partial t} + q_x = -\lambda \frac{\partial T}{\partial x} + \beta \lambda T^2 \frac{\partial P^v_{xx}}{\partial x}, \tag{11.12a}$$

$$\tau_2 \frac{\partial P^v_{xx}}{\partial t} + P^v_{xx} = -\frac{4}{3}\eta \frac{\partial v_x}{\partial x} + \frac{4}{3}\eta T \beta \frac{\partial q_x}{\partial x}. \tag{11.12b}$$

These equations, together with (11.3), can be cast in the form $\mathbf{A} \cdot \boldsymbol{b} = \mathbf{0}$, where

$$\mathbf{A} = \begin{pmatrix} \mathrm{i}\omega & -\mathrm{i}k\rho_0 & 0 & 0 & 0 \\ 0 & \mathrm{i}\omega\rho_0 & -\mathrm{i}k & -\mathrm{i}k & 0 \\ -\mathrm{i}\omega c_v/\alpha & -\mathrm{i}k\rho_0(c_p - c_v)/\alpha & \mathrm{i}\omega c_p/(\alpha c^2) & 0 & -\mathrm{i}k \\ 0 & -\frac{4}{3}\mathrm{i}k\eta & 0 & 1 + \mathrm{i}\omega\tau_2 & \frac{4}{3}\mathrm{i}k\eta\beta T \\ \mathrm{i}k\lambda/(\rho_0\alpha) & 0 & \mathrm{i}k\lambda/(c^2\rho_0\alpha) & \mathrm{i}k\lambda\beta T^2 & 1 + \mathrm{i}\omega\tau_1 \end{pmatrix},$$

$$\boldsymbol{b} = \begin{pmatrix} \delta\rho' \\ \delta v'_x \\ \delta p' \\ \delta P^{v\prime}_{xx} \\ \delta q'_x \end{pmatrix}. \tag{11.13}$$

We now neglect for simplicity the cross terms on the right-hand side of (11.12) and (11.13), i.e. we assume that $\beta = 0$. The dispersion relation corresponding to this simplified version turns out to be

$$l_1 \left[\gamma l_2 - \mathrm{i}\frac{c_s}{\omega}(1 + \mathrm{i}\omega\tau_2)\right] k^4 + \left\{ f(\omega) + \mathrm{i}\frac{\omega}{c_s}\left[(1 + \mathrm{i}\omega\tau_1) l_2 + (1 + \mathrm{i}\omega\tau_2)\gamma l_1\right] \right\} k^2 - \left(\frac{\omega}{c_s}\right)^2 f(\omega) = 0, \tag{11.14}$$

with $f(\omega) = (1 + \mathrm{i}\omega\tau_1)(1 + \mathrm{i}\omega\tau_2)$. When $\tau_1 = \tau_2 = 0$, one recovers the Kirchhoff equation (11.7). The corresponding phase velocities are calculated in Box 11.1.2

Box 11.1 Phase Velocities at High Frequencies If (11.14) is multiplied by $(1 - \mathrm{i}\omega\tau_1)(1 - \mathrm{i}\omega\tau_2)$ to make the last term a real one, we may write it as

$$Ak^4 + Bk^2 - C = 0, \tag{11.1.1}$$

with

$$A = (a_1 + a_1'\omega^2) - \mathrm{i}(1/\omega)(a_2 + a_2'\omega^2), \tag{11.1.2}$$
$$B = (1 + b_1'\omega^2 + b_1''\omega^4) + (b_2 + b_2'\omega^2), \tag{11.1.3}$$
$$C = c_1\omega^2 + c_1'\omega^4 + c_1''\omega^6. \tag{11.1.4}$$

The coefficients in (11.1.2)–(11.1.4) are

$$\begin{gathered}
a_1 = c_s l_1[\gamma(l_2/c_s) - \tau_1], \quad a_1' = -c_s l_1 \tau_1^2[\gamma(l_2/c_s) + \tau_2], \quad a_2 = c_s l_1, \\
a_2' = c_s l_1 \left[\tau_2^2 + \gamma(l_2/c_s)(\tau_1 + \tau_2)\right], \quad b_1' = \tau_1^2 + \tau_2^2 + (l_2/c_s)\tau_2 + \gamma(l_1/c_s)\tau_1, \\
b_1'' = \tau_1\tau_2\left[\tau_1\tau_2 + (l_2/c_s)\tau_1 + \gamma(l_1/c_s)\tau_2\right], \quad b_2 = (l_2 + \gamma l_1)c_s^{-1}, \\
b_2' = (l_2\tau_1^2 + \gamma l_1\tau_2^2)c_s^{-1}, \quad c_1 = c_s^{-2}, \quad c_1' = (\tau_1^2 + \tau_1^2)c_s^{-2}, \quad c_1'' = \tau_1^2\tau_2^2 c_s^{-2}.
\end{gathered}$$

At high frequencies, (11.1.1) leads after rather lengthy calculations to

$$\begin{aligned}
k^2 = \frac{\omega^2}{2a_1'^2}\Big\{& a'\left[-b_1'' \pm (b_1''^2 + 4a_1'c_1'')^{1/2}\right] \\
&+ \frac{1}{\omega}\left[(a_1'b_2' + a_2'b_1'')[(b_1''^2 + 4a_1'c_1'')^{1/2} \mp b_1''] \mp 2a_1'a_2''c_1''\right] \\
&(b_1''^2 + 4a_1'c_1'')^{-1/2}\Big\}
\end{aligned} \tag{11.1.5}$$

This relation shows that at high frequencies the imaginary part of k^2 is negligible with respect to the real part.

Within the same high-frequency limit, one obtains two waves with constant phase velocities given by

$$v_p = \frac{\omega}{\mathrm{Re}\,k} = \frac{(2a_1')^{1/2}}{\left[-b_1'' \pm (b_1''^2 + 4a_1'c_1'')^{1/2}\right]^{1/2}}, \tag{11.1.6}$$

The result (11.1.6) shows that within the limit of high frequencies, the phase velocities tend to coincide with the characteristic values of matrix A given in (11.13).

11.1.3 Particular Results for Monatomic Gases

Expression (11.1.6) may be calculated explicitly by using kinetic theory results; accordingly, $\lambda = \frac{5}{2}(k_B^2 Tn/m)\tau_1,\ \eta = p\tau_2,\ \gamma = \frac{5}{3},\ c_v = \frac{3}{2}k_B/m,\ \tau_1 = \frac{3}{2}\tau_2,\ p = nk_B T$, and the Laplace sound velocity $c_s^2 = \frac{5}{3}k_B T/m$. With these values it is found that

$$\lim_{\omega\to\infty} v_p^{(1)} = 1.65\, c_s,\ \lim_{\omega\to\infty} v_p^{(2)} = 0.63\, c_s, \tag{11.15}$$

where superscripts 1 and 2 denote the two wave velocities. In the low-frequency limit, the corresponding values for the phase velocity are respectively $\lim_{\omega\to 0} v_p^{(1)} = c_s$, and $\lim_{\omega\to 0} v_p^{(2)} = 0$. The results are shown in Fig. 11.1 (Müller 1984). The first wave is the usual acoustic wave, with velocity equal to c_s at small frequencies and $1.65\, c_s$ at high frequencies, in contrast with the classical prediction of an infinite speed in this limit. The second wave corresponds to a diffusive wave which is strongly damped at low frequencies and is therefore not observed. This is no longer true however at high frequencies, at which the absorption coefficients $\Gamma^{(}2)$ and $\Gamma^{(}1)$ remain finite and almost constant when ω is varied

A numerical comparison between the respective phase velocities in the classical Kirchhoff and the relaxational theory may be found in Table 11.1, where values of v_p/c_s are reported as functions of l/λ' where $l = \eta(\rho_0 c_s)^{-1}$ is the mean free path of the molecules and λ' the wavelength, given by $\lambda' = 2\pi$ The numerical values in the relaxational case have been calculated by assuming that $\tau_1 = \tau_2 = l/(c_s\pi)$ (Carrassi and Morro 1973). It is evident that the classical theory deviates appreciably

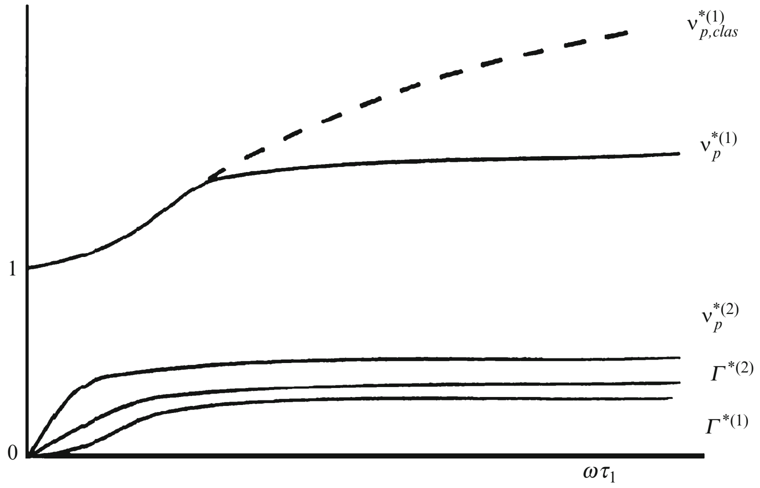


Fig. 11.1 Non-dimensional phase speeds $v_p^*\,(= v_p/c_s)$ and absorption coefficients $\Gamma^*\,(= \tau_1 c_s \Gamma')$ of the acoustic wave 1 and the extra wave 2 as a function of the non-dimensional frequency $\omega\tau_1$ for EIT. The dashed curve represents the phase speed for the classical theory increasing without bound

Table 11.1 Numerical values of v_p/c_s as a function of l/λ' (Carassi and Morro 1973)

l/λ'	0.25	0.50	1.00	2.00	4.00	7.00
$(v_p/c_\mathrm{s})_{\text{(Kirchhoff)}}$	2.50	3.84	5.26	7.69	40	100
$(v_p/c_\mathrm{s})_{\text{(relaxational)}}$	1.92	2.32	2.27	2.52	2.08	2.09
$(v_p/c_\mathrm{s})_{\text{(experimental)}}$	1.96	2.17	2.00	2.17	2.17	2.17

from the experimental results as l/λ' increases, whereas the introduction of the relaxation times makes the comparison much more accurate in the domain of short wavelengths.

The degree of agreement with the experimental data is very sensitive to the choice of the values of τ_1 and τ_2 (Carrassi and Morro 1973). It is true that from a macroscopic point of view one is free to choose τ_1 and τ_2 as phenomenological parameters maximizing the agreement with experiments, but the kinetic theory of gases (Chap. 4) and the fluctuation theory (Chap. 5) predict definite relations between τ_1 and λ and between τ_2 and η, so that the macroscopic freedom is only apparent. When the kinetic results are taken into account, as in (11.15), the predicted values of the high-frequency speed do not agree with the experimental ones. This is not surprising, because the relaxation times of heat flux and of viscous pressure are of the order of the collision time. This means that, at frequencies comparable to the inverse of the relaxation times, it is necessary to include in the macroscopic description not only the dissipative fluxes but also higher-order fluxes, as explained in Sect. 4.7. This improves considerably the agreement with experimental data.

Lebon and Cloot (1989) suggested to replace the Maxwell–Cattaneo's laws (2.70) and (2.72) by

$$\tau_1 \frac{\partial \boldsymbol{q}}{\partial t} = -(\boldsymbol{q} + \lambda \nabla T) + \nabla \cdot \mathbf{Q}, \tag{11.16}$$

$$\tau_2 \frac{\partial \mathbf{P}^v}{\partial t} = -(\mathbf{P}^v + 2\eta \mathbf{V}) + \nabla \cdot \mathbb{Q}, \tag{11.17}$$

wherein $\mathbf{Q}$ and $\mathbb{Q}$ are second and third-order fluxes respectively, which satisfy evolution equations of the form:

$$\tau_3 \frac{\partial \mathbf{Q}}{\partial t} = -\nabla \cdot \mathbb{R} - \mathbf{Q}, \tag{11.18}$$

$$\tau_4 \frac{\partial \mathbb{Q}}{\partial t} = -\nabla \cdot \mathfrak{R} - \mathbb{Q}. \tag{11.19}$$

It is assumed that the third-order $\mathbb{R}$ and fourth-order $\mathfrak{R}$ flux tensors are given by the following constitutive relations:

$$\mathbb{R} = \lambda_1 \boldsymbol{q} \mathbf{U}, \quad \mathfrak{R} = \eta_1 \mathbf{U} \mathbf{P}^v, \tag{11.20}$$

wherein λ_1 and η_1 are constant phenomenological coefficients. Letting the relaxation times τ_3 and τ_4 tend to zero and substituting (11.18-11.20) in (11.16) and (11.17) respectively, leads to

$$\tau_1 \dot{\boldsymbol{q}} = -(\boldsymbol{q} + \lambda \nabla T) + \beta \lambda T^2 \nabla \cdot \mathbf{P}^v + \lambda_1 \nabla \cdot (\nabla \boldsymbol{q}), \tag{11.21}$$

$$\tau_2 \dot{\mathbf{P}}^v = -(\mathbf{P}^v + 2\eta \mathbf{V}) + 2\eta\beta T(\nabla \boldsymbol{q}) + \eta_1 \nabla \cdot (\nabla \mathbf{P}^v). \tag{11.22}$$

This weakly non-local model involves seven unknown parameters τ_1, τ_2, λ, η, β, λ_1, and η_1. Instead of selecting τ_1 and τ_2 as free parameters,as done earlier by Carrassi and Morro (1973) and Anile and Pluchino (1984), Lebon and Cloot (1989) prefer to choose λ_1 and η_1, because of the uncertainty about the theoretical value of these two quantities. In view of the kinetic theory, the other parameters are related to λ_1 and η_1 by $\lambda = \frac{15}{4}[k_\mathrm{B}/(Tm)]^{1/2} p\eta_1$, $\beta = -2(\eta_1)^{-1/2}/(5pT)$, $\eta = p\eta_1(k_\mathrm{B}T/m)^{-1/2}$, $\tau_1 = \frac{3}{2}\eta_1(k_\mathrm{B}T/m)^{-1/2}$, and $\tau_2 = \eta_1(k_\mathrm{B}T/m)^{-1/2}$, in the case of monatomic Maxwell molecules. Instead of (11.14) one obtains now the more complicated dispersion relation

$$\begin{aligned}
\rho_0 A_2 A_3 + \left(\frac{k}{\omega}\right)^2 &\left[\mathrm{i}\rho_0\omega\left(\frac{\lambda}{c_v}A_2 + \frac{1}{3}\eta A_3\right) + \rho_0^2 A_2 A_3 \left(\frac{c_s^2}{\chi}\right)\left(1 + \frac{k_\mathrm{B}}{mc_v}\right)\right] \\
-\left(\frac{k}{\omega}\right)^4 &\left[\frac{\omega\lambda c_s^2}{c_v}\left(\frac{\eta\omega}{3c^2} + \frac{1}{\gamma}\rho_0 A_1\right) - \frac{2\rho_0 c_s^2}{c_p}\lambda^2\eta\beta T\omega^2\right. \\
&\left.+\frac{2\rho_0}{3}\eta^2\beta T\omega^2\left(\frac{k_\mathrm{B}}{mc_v} - \frac{2\eta\beta T\omega}{A_2}\right)\right] = 0,
\end{aligned} \tag{11.23}$$

with $A_1 = 1 - \mathrm{i}\omega\tau_1 + \lambda_1 k^2$, $A_2 = 1 - \mathrm{i}\omega\tau_2 + \eta_1 k^2$, and $A_3 = A_1 + \frac{4}{3}(\eta\lambda\beta^2 T^3/A_2)k^2$. This equation has been solved numerically (Lebon and Cloot 1989) and compared with the experimental data by Greenspan (1956) and Meyer and Sessler (1957). In Figs. 11.2 and 11.3, c_s/v_p and the dimensionless absorption coefficient $\Gamma^* = \tau c_s \Gamma'$ are shown as a function of the dimensionless frequency $\omega^* = \tau^*\omega$ with $\tau^* = 2\eta(p\gamma)^{-1}$. It is noticed that the dimensionless wave speed v_p/c_s attains a finite value (approximately 2) at high frequency ($\omega^* > 10$).

As for the damping, it is seen that the absorption coefficient increases at small frequencies up to a maximum value at $\omega^* = 1$ and then decreases slowly for high frequencies. As pointed out by Woods and Troughton (1980), at high values of ω^* there may be a contribution to the absorption arising from diffusion in the piezoelectric receiver, so that the experimental result for the absorption factor should be considered as an upper limit to the actual value.

In brief, it is observed that, whereas the Navier–Stokes approach provides a good modelling at low frequencies, it is definitively not adequate at high frequencies, say $\omega^* > 2$. By using extended irreversible thermodynamics in its simplest version, i.e. with the heat flux and the viscous pressure tensor as the only extra variables, Anile and Pluchino (1984) obtained a more satisfactory result for the phase speed. Unfortunately, the results for the absorption coefficients are even worse than those based on the Navier–Stokes theory as soon as ω^* becomes larger than unity.

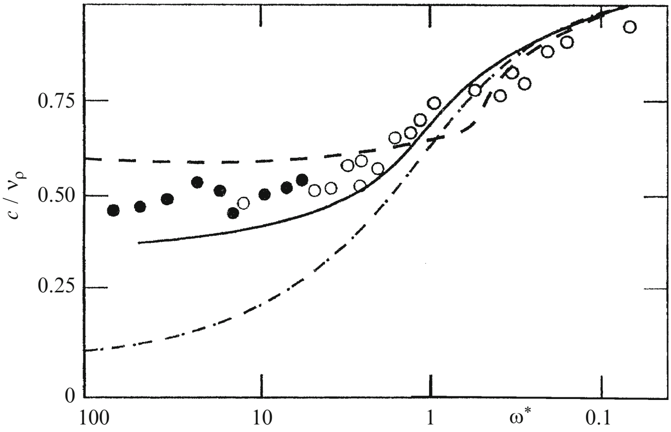


Fig. 11.2 The quantity c_s/v_p versus dimensionless frequency ω^*. Experimental data: *black circles*, Meyer and Sessler; *white circles*, Greenspan. Theoretical results: — — — Navier–Stokes; — — — Anile and Pluchino; —— Lebon and Cloot (reprinted with permission from Lebon G, Cloot A (1989) Wave Motion 11: 23)

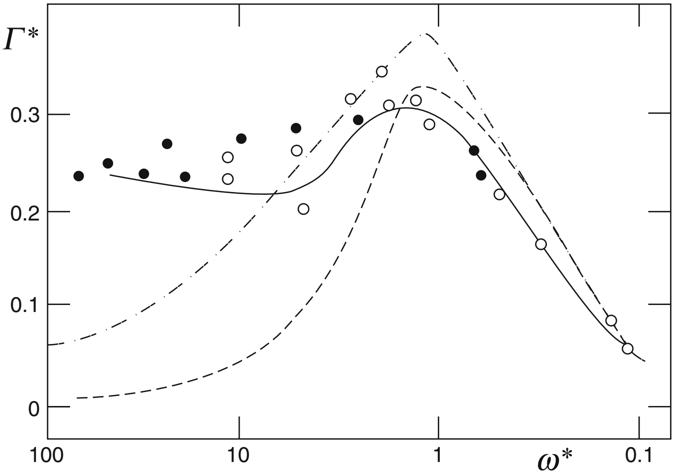


Fig. 11.3 Dimensionless absorption coefficient $\Gamma^* = \tau^* c_s \Gamma'$ versus dimensionless frequency $\omega^* (= \tau^* \omega)$. Experimental data: *black circles*, Meyer and Sessler; *white circles*, Greenspan. Theoretical results: — — — Navier–Stokes; — — — Anile–Pluchino; —— Lebon–Cloot (reprinted with permission from Lebon G, Cloot A (1989) Wave Motion 11: 23)]

Better results are obtained with the strongly non-local model with $\lambda_1 \neq 0$ and $\eta_1 \neq 0$. As shown in Fig. 11.2, the theoretical curve for the phase velocity matches reasonably well the experimental observations by Greenspan and by Meyer and Sessler, even in the high-frequency range ($\omega^* > 2$). Moreover, an excellent agreement between theory and experiment is achieved for the absorption coefficient over the whole range of frequencies (Fig. 11.3). It follows from the previous analysis that, in order to match the high-frequency experimental data, it is necessary to include, in addition to the usual heat flux and viscous pressure tensor, supplementary variables of the form of fluxes of the fluxes.

Here we are concerned with simple monoatomic gases. Other causes of relaxational effects are found when the molecules have internal degrees of freedom, or when a chemical reaction takes place in the gas. Such relaxation effects have been observed, and analysed by Bauer (1965) and Knesser (1965). Sound propagation in the framework of EIT in elastic dielectrics and metals has been studied by Kranys (1977) and Jou et al. (1982).

11.2 Non-linear Acceleration Waves in Monatomic Ideal Gases

We here follow the same procedure as in Chapter 9 about non-linear heat wave propagation in rigid solids. Let us recall that acceleration waves (or weak discontinuities) propagate in such a way that the field variables remain continuous through the discontinuity surface, but their first derivatives undergo a jump. For simplicity, consider a monoatomic ideal gas without bulk viscosity and assume that the motion is one-dimensional in the direction x. The field variables ρ (mass density), v (x-component of the velocity), T (temperature), q (x-component of the heat flux), and P_{xx} (xx-component of the viscous pressure tensor) obey the following evolution equations:

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} + \rho\frac{\partial v}{\partial x} = 0, \tag{11.24}$$

$$\rho\frac{\mathrm{d}v}{\mathrm{d}t} + \frac{\partial p}{\partial x} + \frac{\partial P_{xx}}{\partial x} = 0, \tag{11.25}$$

$$\rho\frac{\mathrm{d}u}{\mathrm{d}t} + \frac{\partial q}{\partial x} + p\frac{\partial v}{\partial x} + P_{xx}\frac{\partial v}{\partial x} = 0, \tag{11.26}$$

$$\tau_1\frac{\mathrm{d}q}{\mathrm{d}t} + q + \lambda\frac{\partial T}{\partial x} - \beta\lambda T^2\frac{\partial P_{xx}}{\partial x} = 0, \tag{11.27}$$

$$\tau_2\frac{\mathrm{d}P_{xx}}{\mathrm{d}t} + P_{xx} + \frac{4}{3}\eta\frac{\partial v}{\partial x} - \frac{4}{3}\beta\eta T\frac{\partial q}{\partial x} = 0. \tag{11.28}$$

These equations are completed by the constitutive relations $p = \rho RT$, $u = c_v T = \frac{2}{3}RT$, $\beta = -\frac{2}{5}(pT)^{-1}$. To determine the characteristic velocities, we apply the classical correspondence rule

$$\frac{\partial}{\partial x} \to \delta,\ \frac{d}{dt}\left(= \frac{\partial}{\partial t} + v\frac{\partial}{\partial x}\right) \to -\tilde{w} = -(w - v), \tag{11.29}$$

with δ denoting the jump of the derivatives of the variables across the wave front $\varphi(x,t)$, $\tilde{w} = w - v$ is the relative velocity of the wave with respect to the fluid. After application of the transformations (11.29) to equations (11.24)–(11.28), one obtains the algebraic system

$$\tilde{w}\delta\rho + \rho\delta v = 0, \tag{11.30}$$

$$-\rho\tilde{w}\delta v + \rho R\delta T + RT\delta\rho + \delta P_{xx} = 0, \tag{11.31}$$

$$-\frac{3}{2}\rho R\tilde{w}\delta T + \delta q + \rho RT\delta v + P_{xx}\delta v = 0, \tag{11.32}$$

$$-\tau_1\tilde{w}\delta q + \lambda\delta T - \beta\lambda T^2\delta P_{xx} = 0, \tag{11.33}$$

$$-\tau_2\tilde{w}\delta P_{xx} + \frac{4}{3}\eta\delta v - \frac{4}{3}\eta T\delta q = 0. \tag{11.34}$$

Taking into account that $\lambda/\tau_1 = \frac{5}{2}\rho R^2 T$, $\eta/\tau_2 = p$, the set (11.30)–(11.34) may be written under the form

$$(\mathrm{A} - \tilde{w}\mathbf{U}) \cdot \boldsymbol{b} = 0, \tag{11.35}$$

with

$$\mathbf{A} = \begin{pmatrix} 0 & \rho & 0 & 0 & 0 \\ RT\rho^{-1} & 0 & R & 0 & \rho^{-1} \\ 0 & \frac{3}{2}(T + P_{xx}R^{-1}) & 0 & \frac{2}{3}(\rho R)^{-1} & 0 \\ 0 & 0 & \frac{5}{2}\rho R^2 T & 0 & RT \\ 0 & \frac{4}{3}\rho RT & 0 & \frac{8}{15} & 0 \end{pmatrix} \tag{11.36a}$$

$$\boldsymbol{b} = \begin{pmatrix} \delta\rho \\ \delta v \\ \delta T \\ \delta q \\ \delta P_{xx} \end{pmatrix}. \tag{11.36b}$$

The condition that $\det(\mathbf{A} - \tilde{w}\mathbf{U}) = 0$ provides the following fifth-order characteristic polynomial

$$\overline{w}\left[\overline{w}^4 - \overline{w}^2\left(\frac{2}{3}\overline{P}_{xx} + \frac{78}{25}\right) - \frac{8}{25}\overline{P}_{xx} + \frac{27}{25}\right] = 0, \tag{11.37}$$

wherein the following non-dimensional quantities have been introduced

$$\overline{w} = \frac{\tilde{w}}{c_s}, \quad \overline{q} = \frac{q}{\rho c_s^3}, \quad \overline{P}_{xx} = \frac{P_{xx}}{\rho c_s^2}. \tag{11.38}$$

Besides the trivial solution $\overline{w} = 0$, i.e. $w = v$, we have four thermo-viscous sound wave solutions. Note that the characteristic equation is independent on q because in monatomic ideal gases, the internal energy u is only function of the temperature. In more complex systems, u may depend on q, for instance, in dielectric crystals or in more general gases described for instance by Grad's model, wherein the evolution equation of q contains a term in $\boldsymbol{q} \cdot \nabla \boldsymbol{v}$ (see Chapter 4). A similar term occurs also if the material time derivative is substituted by more general objective time derivatives, as in polymers.

In equilibrium, for which $q = P_{xx} = 0$, the characteristic equation (11.37) simplifies as

$$\overline{w}^4 - \frac{78}{25}\overline{w}^2 + \frac{27}{25} = 0, \tag{11.39}$$

whose four solutions are given by

$$\overline{w}_{1,2} = \pm 1.65\, c_s, \quad \overline{w}_{3,4} = 0.63\, c_s \tag{11.40}$$

and coincide with the phase velocities at high frequencies as derived in Section 11.3.2. Hyperbolicity requires that the roots of the characteristic equation (11.37) are real, which implies that the discriminant

$$\Delta = \frac{1}{9}P_{xx}^2 + \frac{102}{25}P_{xx} + \frac{846}{625} > 0 \tag{11.41}$$

be positive. For $P_{xx} > 0$, this is unconditionally satisfied while for $P_{xx} < 0$, hyperbolicity is fulfilled everywhere except in the region where $-11.16 < P_{xx} < -1.08$.

11.3 Shock Waves

This section is concerned with propagation of shock waves in a fluid at equilibrium. In shock waves, the density, temperature or pressure, and velocity are experiencing discontinuities across thin layers. Physically, such a discontinuity layer is not a geometrical surface but a material surface with a small but non-vanishing thickness, of the order of a few mean free paths. In the foregoing, it is shown that the presence of relaxation terms in the field equations has a non-negligible influence of the propagation and structure of shocks. In a first subsection, it will be assumed that the discontinuity is modelled by a geometric surface of zero thickness before discussing the problem of shock's structure. To better apprehend the importance of EIT in the study of shock waves, we briefly recall the main results obtained from a classical approach.

11.3.1 The Classical Navier–Fourier–Stokes Approach

In a one-dimensional description, the relevant balance equations written in conservative form are

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho v) = 0, \tag{11.42}$$

$$\frac{\partial}{\partial t}(\rho v) + \frac{\partial}{\partial x}(\rho v^2 + p + P_{xx}) = 0, \tag{11.43}$$

$$\frac{\partial}{\partial t}\left(u + \frac{\rho}{2}v^2\right) + \frac{\partial}{\partial x}\left(\frac{1}{2}\rho v^3 + uv + pv + P_{xx}v + q\right) = 0, \tag{11.44}$$

wherein u is measured per unit volume. For a shock moving at velocity Σ, the relative velocity of the fluid is $w = v - \Sigma$. In the moving reference frame where the discontinuity is at rest, the Rankine–Hugoniot equations (e.g. Landau and Lifshitz 1985) expressing the compatibility conditions for the existence of shocks take the form

$$[\rho w] = 0, \tag{11.45}$$

$$\left[\rho w^2 + P_{xx} + p\right] = 0, \tag{11.46}$$

$$\left[\frac{1}{2}\rho w^3 + uw + P_{xx}w + pw + q\right] = 0, \tag{11.47}$$

wherein $[\Phi]$ denotes the jump $[\Phi] = \Phi_1 - \Phi_0$, Φ_0 and Φ_1 are the limiting values of Φ across the surface of discontinuity respectively in the unperturbed equilibrium state (ahead of the front) and the perturbed state (behind the front) (see Fig. 11.4).

Our next task is to relate the values of ρ, w, T (and accessory p) behind and ahead of the shock. In the classical Navier–Fourier–Stokes theory, equilibrium is reached at long distances, so that the dissipative fluxes P_{xx} and q in (11.46) and (11.47) are negligible. Denoting by J the mass flux at the surface of discontinuity, one obtains from (11.45)

$$w_0 = \frac{J}{\rho_0},\ w_1 = \frac{J}{\rho_1}, \tag{11.48}$$

and, after introducing these results in (11.46),

$$p_1 + \frac{J^2}{\rho_1} = p_0 + \frac{J^2}{\rho_0}, \tag{11.49}$$

or

$$J^2 = \frac{p_1 - p_0}{1/\rho_0 - 1/\rho_1}. \tag{11.50}$$

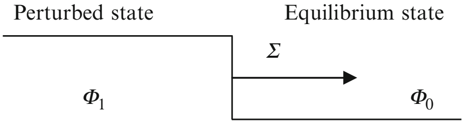


Fig. 11.4 In the reference frame where the shock wave is at rest, the gas flows from the region in equilibrium (Φ_0) to the region perturbed by the shock motion (Φ_1). In the frame at rest with respect to the gas, the shock wave moves from the left to the right

In terms of J and making use of $q = P_{xx} = 0$, the energy balance (11.47) can be written as

$$u_1 + \frac{p_1}{\rho_1} + \frac{J^2}{2\rho_1^2} = u_0 + \frac{p_0}{\rho_0} + \frac{J^2}{2\rho_0^2}, \tag{11.51}$$

and, in virtue of (11.50),

$$u_1 - u_0 + \frac{1}{2}\left(\frac{1}{\rho_1} - \frac{1}{\rho_0}\right)(p_1 + p_0) = 0. \tag{11.52}$$

For given values of ρ_0 and p_0, this equation links ρ_1 and p_1. Such an expression is known as the shock adiabatic line or the Hugoniot adiabatic line: it relates the thermodynamic quantities on both sides of the shock surface. For an ideal gas described by the state equations

$$u = \frac{3}{2\rho\, p} = \frac{c_s^2}{\gamma(\gamma-1)}, \qquad p = \rho RT = \frac{c_s^2}{\gamma}, \tag{11.53}$$

where $c_s = \left(\frac{5}{3}RT\right)^{1/2}$ is the Laplace sound velocity, with $\gamma = c_p/c_v$, the ratios of the densities, velocities, pressures and temperatures, when expressed in terms of the unperturbed Mach number,

$$M_0 = \frac{w - v_0}{c_s} = \frac{\Sigma}{c_s}, \tag{11.54}$$

are given by

$$\frac{\rho_1}{\rho_0} = \frac{v_0}{v_1} = \frac{(\gamma+1)M_0^2}{(\gamma-1)M_0^2 + 2}, \tag{11.55a}$$

$$\frac{p_1}{p_0} = \frac{2\gamma M_0^2 - (\gamma+1)}{\gamma^2 + 2(\gamma+1)}, \tag{11.55b}$$

$$\frac{\theta_1}{\theta_0} = \frac{\left[2\gamma M_0^2 - (\gamma-1)\right]\left[(\gamma-1)M_0^2 + 2\right]}{(\gamma+1)^2 M_0^2}. \tag{11.55c}$$

These results are well known (e.g. Landau and Lifshitz 1985) and they are independent of the dissipative fluxes.

11.3.2 The Extended Irreversible Thermodynamics Approach

Up to now, we have deliberately omitted the influence of the dissipative fluxes. In EIT, these quantities are associated to relaxation effects and are governed by evolution equations which complement the classical balance laws (11.42)–(11.44). In the present section, we assume that the evolution equations of the momentum and energy fluxes are the non-linear expressions (4.39) and (4.40) obtained from Grad's formalism for ideal monatomic gases with zero bulk viscosity. They present the advantage to be easily expressed in conservative form. It is easily checked (Ruggeri 1993, Problem 11.8) that the one-dimensional expressions of (4.39) and (4.40) may be written as

$$\frac{\partial}{\partial t}\left(\frac{2}{3}\rho v^2 + P_{xx}\right) + \frac{\partial}{\partial x}\left(\frac{2}{3}\rho v^3 + \frac{4}{3}pv + \frac{7}{3}P_{xx}v + \frac{8}{15}q\right) = -\frac{1}{\tau_2}P_{xx}, \tag{11.56}$$

$$\begin{aligned}\frac{\partial}{\partial t}\left(2q + 5pv + 2P_{xx}v + \rho v^3\right) + \frac{\partial}{\partial x}\Bigg[\rho v^4 + 5\frac{p^2}{\rho} + \frac{P_{xx}p}{\rho}\\ + \frac{32}{5}qv + v^2(8p + 5P_{xx})\Bigg] = -\frac{1}{\tau_1}q - \frac{2}{\tau_2}P_{xx}v\end{aligned} \tag{11.57}$$

With a shock front propagating at the velocity Σ and a fluid moving with the relative velocity $w = v - \Sigma$, the compatibility Rankine–Hugoniot equations corresponding to the set of equations (11.42–11.44), (11.56) and (11.57) are given by

$$[\rho w] = 0, \tag{11.58}$$

$$\left[\rho w^2 + p + P_{xx}\right] = 0, \tag{11.59}$$

$$\left[5pw + 2P_{xx}w + \rho w^3 + 2q\right] = 0, \tag{11.60}$$

$$\left[\frac{4}{3}pw + \frac{7}{3}P_{xx}w + \frac{2}{3}\rho w^3 + \frac{8}{15}q\right] = 0, \tag{11.61}$$

$$\left[\rho w^4 + 5p^2\rho^{-1} + 7p\rho^{-1}P_{xx} + 32wq + w^2(8p + 5P_{xx})\right] = 0, \tag{11.62}$$

with the brackets defined after expression (11.47). Let us introduce the non-dimensional quantities expressed in terms of the equilibrium values ρ_0, p_0 and w_0 (recall that $v_0 = q_0 = (P_{xx})_0 = 0$):

$$M_0 = \frac{\Sigma}{c_s},\ W = \frac{w_1}{w_0},\ Q = \frac{q_1}{p_0 c_s},\ P = \frac{(P_{xx})_1}{p_0}. \tag{11.63}$$

It is easily checked that the solutions of the Rankine–Hugoniot equations can be cast in the form

$$\frac{\rho_1}{\rho_0} = \frac{1}{W}, \tag{11.64}$$

$$\frac{p_1}{p_0} = 1 - \frac{5}{27}M_0^2\frac{W^2 - 1}{W}, \tag{11.65}$$

$$P = \frac{10}{27}M_0^2\frac{(W-1)(7W-2)}{W}, \tag{11.66}$$

$$Q = -\frac{15}{18}M_0(W-1)\,(10M_0^2W - 5M_0^2 - 9), \tag{11.67}$$

wherein W is solution of

$$5M_0^4(693\,W^3 - 710\,W^2 + 143\,W + 8) - 2106\,M_0^2 W(2W - 1) + 729\,W = 0. \tag{11.68}$$

Expressions (11.64–11.68) constitute a set of five equations with the five unknowns ρ_1, p, P, Q, W. Given a unperturbed Mach number M_0, one obtains directly from (11.68) the value of the corresponding W, which substituted in (11.64–11.67) leads to the values of ρ_1/ρ_0, p_1/p_0, P and Q in the perturbed region. The results for the temperature and velocity fields are straightforward and given by

$$\frac{T_1}{T_0} = W\frac{p_1}{p_0}, \; \frac{v_1}{c_s} = (1 - w)M_0, \tag{11.69}$$

after use is made of the state equation (11.53b) and the definition of w. Within the limit of a null shock defined by $v_1 = v_0 = 0$, whence $W = 1$, relation (11.68) simplifies as

$$M_0^4 - \frac{78}{25}M_0^2 + \frac{27}{25} = 0, \tag{11.70}$$

whose solutions are $M_0 = \pm 0.63$, $M_0 = \pm 1.65$. It is worth to note that these values are the same as the characteristic values (11.15) obtained in the problem of high-frequency wave propagation. When M_0 approaches 1.65 (respectively 0.63), one speaks about fast shock (respectively slow shock). Solving (11.68) yields the four solutions $M_0(W)$ as a function of W. After substitution in the set (11.64)–(11.67), one obtains the expressions of the mass density, pressure, temperature, pressure tensor and heat flux jumps across the front in terms of Mach's number M_0 or the velocity Σ of the shock. Numerical calculations have been performed by Muller and Ruggeri (1998).

In addition, it is well known that among the mathematical solutions of the Rankine–Hugoniot equations, only the stable ones are physically admissible. Several criteria of selection have been put forward. Among them, Lax's criterion (1957) is unanimously accepted. It states that the admissible shocks are these for which the shock velocity is greater than the unperturbed characteristic velocity and smaller than the perturbed one

$$v_0 < \Sigma < v_1. \tag{11.71}$$

When applied to the fastest wave, one notices that the Lax condition is satisfied under the condition $M_0 > 1.65$ and that, after the passage of the front, the ensemble of variables, and in particular temperature and heat flux, jump up. Such a shock is called a *hot shock*. In contrast, for slow shocks, Lax's criterion implies that $0.63 < M_0 < 0.908$ and that in this case, numerical analyses indicate that the shock wave produces a cooling of the gas, with temperature and heat flux jumping down after the passage of the wave. Such a shock is referred to as a *cold shock*. Existence of cold shocks has also been predicted in dielectric crystals as NaF, Bi (Valenti et al. 2002, Lebon et al. 2008). The occurrence of cold shocks is clearly linked to the introduction of the fluxes in the space of state variables, with the consequence that temperature looses its privilege to be the only relevant thermal parameter. It may seem paradoxical that temperature jumps down after the passage of the shock, but this is not unusual. Although it is true that for compressive waves in ordinary gases at room temperature, the latter is increased when the gas particles flow across the shock, this is no longer verified for rarefaction flows characterized by a negative jump of the temperature. This is interesting as it allows comparing a cold shock with a kind of thermal rarefaction. Moreover, it is noted that in the case of cold shocks, entropy is decreased when passing from the front to the back side of the shock (Valenti et al. 2002). If it is admitted that entropy is a measure of disorder, we may understand that the occurrence of cold shocks is accompanied by less disorder, whence a lowering of temperature.

11.3.3 Shock Structure

In the previous analyses, it was admitted that the shock wave is mimicked by a geometrical surface with zero thickness. Actual shocks are of course characterized by a finite thickness of the order of magnitude of a few mean free paths in the fluid. The thickness decreases with the magnitude of the discontinuity; for huge discontinuities, the change occurs so sharply that the concept of thickness becomes meaningless. The problem of shock structure has been a subject of active research and debate during the two last decades; however, because the problem involves heavy numerical developments, we shall not enter into the details and propose only a qualitative analysis. The shock thickness is conveniently defined as

$$L = \frac{\rho_1 - \rho_0}{(\partial \rho / \partial x)_{\max}}, \tag{11.72}$$

and depends generally on the value of the Mach number M_0. The classical description based on Navier–Fourier–Stokes (NFS) equations predicts a regular structure, which means a smooth profile without singularity whatever the value of M_0. Nevertheless, the NFS model does not predict results which are in satisfactory agreement with experience (e.g. Alsemeyer 1976) and this has prompted the emergence of other approaches. In Grad's thirteen-moment method of resolution of Boltzman's equation, no regular solution is found for Mach's numbers exceeding $M_0 = 1.65$. This was confirmed by a first analysis by Ruggeri (1993) and later refined by Weiss (1996), who showed that the upper bound beyond which no shock‘s structure solution exists is given by $v_0 = \lambda_0^{\max}$, where v_0 is the velocity ahead of the front and $\lambda_0^{\max}$ the highest characteristic velocity in the equilibrium state. Referring to Grad's model, it was shown in the preceding subsection that $\lambda_0^{\max} = 1.65\, c_s$ so that a singularity will occur for $M_0 > 1.65$.

In Table 11.2 are reported the values of the ratio L/l where L is the shock's width and l the mean free path for three different models, namely NFS, Grad's thirteen moment and a EIT model proposed by Anile and Majorana (1981). These

Table 11.2 Ratio L/l between the shock's width L and the mean free path l in monatomic ideal gases, calculated by means of three different models

Mach number	NFS model	Grad's 13-moments	EIT model (Anile–Majorana)
1.1	28.90	28.90	28.81
1.2	14.79	14.81	14.79
1.3	10.17	10.19	10.15
1.6	6.55	6.54	5.64
1.8	4.63		4.58
1.9	4.28		4.24

authors used a model based on equations (11.24–11.28) with the relaxation times for q and P_{xx} given by $\tau_1 = \frac{4}{25}\rho\lambda T/p^2$ and $\tau_2 = \frac{3}{5}\eta/(\pi p)$ respectively; these values were obtained by fitting the linear dispersion relation (11.14) with experimental data in the high frequency limit. This particular model accepts regular structures up to $M_0 = 2.96$. As indicated by Table 11.2, the three models agree fairly well for all the Mach's numbers for which a regular solution exists. The values reported in Table 11.2 indicate also that for weak shocks (i.e. M_0 values close to 1), relaxation effects have little influence on the shock's thickness. Because of the differences between the Grad's-models and experience for $M_0 > 1.65$, it was suggested to increase the number of moments appearing in the expansion of the distribution function in terms of Hermite polynomials. By increasing the number of moments, Weiss (1990) was able to show that the loss of structure is pushed to higher Mach's numbers: for 14 moments, the critical Mach number is $M_0 = 1.76$ and for 35 moments, $M_0 = 2.21$. Although the shock's structure improves with the number of moments, this amelioration is very slow and not monotonous. Weiss conjectured also that the limit value should be higher and higher by including more and more moments. This argument is however in contradiction with an earlier work by Holway (1964) wherein it is shown that, no matter how many moments are used, there exists a bound of the Mach number beyond which no structure is possible. According to Holway, this value is $M_0 = 1.851$. Weiss pointed out that the correct value should instead be 1.938, and that, in his opinion, Holway's argument is erroneous because of a confusion between the front and the back sides of the shock. Nevertheless, the general opinion is that these results constitute a drawback of EIT. To circumvent the problem, two routes have been opened. First, it was suggested to depart from Grad's moment method and to base the analysis on other field equations. This was precisely the attitude of Anile and Majorana (1981), who modified the linear part of Grad's equations (11.56) and (11.57). Another option is to formulate non-linear evolution equations for the fluxes more general than Grad's. This was achieved by Jou and Pavón (1991) who found that the critical Mach number was pushed to $M_0 = 4.67$. This result was however contested by Ruggeri (1993) who argued that the limiting value of M_0 should depend on the highest characteristic velocity of the linear problem and could therefore not be modified by non-linear contributions. The debate is not closed yet; the problem of the shock wave structure raises a number of questions which are still waiting for a definite answer. As most of the aforementioned difficulties find their roots in Grad's formalism, it would be interesting to explore descriptions not based on the moments' approach.

11.4 Problems

11.1. In the classical study of wave motion in fluids (see Section 11.1.1), it was shown that in the case $\omega \to \infty$, the dispersion relation is given by $k^2 = a + \mathrm{i}b(\omega/c_s)$ (see Eq. (11.9)). Check that a and b are respectively given by

$$a = \frac{1}{2\gamma l_1 l_2}\left[\frac{(1-\gamma)l_2 + \gamma l_1}{\gamma l_2} \pm \frac{(2-\gamma)l_1 - l_2}{l_2 - \gamma_1}\right],$$
$$b = \frac{1}{2\gamma l_1 l_2}\left[(l_2 + \gamma l_1) \pm (l_2 - \gamma l_1)\right].$$

Since $\sqrt{\mathrm{i}} = (1/\sqrt{2})(1+\mathrm{i})$ show that

$$\mathrm{Re}\,k \approx \mathrm{Im}\,k \approx \left[\frac{(l_2 + \gamma l_1) \pm (l_2 - \gamma l_1)}{8\gamma l_1 l_2}\right]^{1/2} \omega^{1/2}$$

and that the phase velocity is given by

$$v_p = \frac{\omega}{\mathrm{Re}\,k} \approx \left[\frac{\gamma l_1 l_2}{(l_2 - \gamma l_1) \pm (l_2 - \gamma l_1)}\right]^{1/2} \omega^{1/2}.$$

11.2. In order to fit the experimental data for the ultrasonic speed presented in Table 11.1., Carrassi and Morro took $\tau_1 = \tau_2 = l/(c_s\pi)$ with l the mean free path, and c_s the Laplace sound velocity. (a) Compare these values for τ_1 and τ_2 with those obtained from the kinetic theory of gases, for which $\lambda = \frac{5}{2}(k_B^2 Tn/m)\tau_1$ and $\eta = p\tau_2$. (b) Obtain the value of the high-frequency limit of the phase speed v_p and compare with the values $M_0 = \pm 0.63$ and ± 1.65.

11.3. (a) Show that if one imposes the requirement that plane waves must propagate with speed lower than the speed of light c, the inequality $\beta^2 \leq c^2\alpha_1\alpha_2$ must be obeyed. (b) Check that this inequality is true for the coefficients listed in Table 17.1 for relativistic gases. (*Hint*: Obtain the high-frequency limit of the perturbations of δq_x, δP^v_{xz} for a wave vector $\boldsymbol{k}$ in the z direction according to (2.70–2.72))

11.4. The criterion that wave speeds should be lower than the speed of light c is used to develop constraints on possible models for the equations of state of nuclear matter. As a simple illustration, we consider the equations of state in the low-temperature limit:

$$\rho = n\,[m_0 + E_0(n)]\,,\ p = n^2\,[\mathrm{d}E_0(n)/\mathrm{d}n]\,,$$

with $E_0(n)$ being the ground-state energy per nucleon, m_0 the nucleon rest mass, n the number density of particles, and ρ the mass-energy density. (a) Calculate the adiabatic sound speed $c_s = [(\partial p/\partial \rho)_s]^{1/2}$ for this system. (b) One usual equation for $E_0(n)$ is

$$E_0(n) = E_0(n_0) + \frac{K}{18\,nn_0}(n-n_0)^2,$$

with $E_0(n_0) = -16\,\mathrm{MeV}$, $K = 210\,\mathrm{MeV}$ and $n_0 = 0.160\,\mathrm{fm}^{-3}$. Find the range of values of n/n_0 for which this equation satisfies $c_s \leq c$. (Olson, Hiscock (1989))

11.5. The experimental results for ultrasonic absorption in metals have been described phenomenologically by taking for the viscosity η of the electron gas the expression $\eta = \frac{1}{5}nmv_{\mathrm{F}}^2\tau$, with v_{F} being the Fermi velocity, n the electron number density, and m the electron mass. Assume for $\mathbf{P}^v$ the evolution equation

$$\tau\dot{\mathbf{P}}^v + \mathbf{P}^v = -2\eta V + A\nabla^2\mathbf{P}^v,$$

where A is a coefficient which has the dimensions of (length)^2. In contrast with classical gases, where the relaxational effects are more important than the non-local ones, in Fermi gases the latter are more important and the former may be neglected. (a) Using the balance laws of mass, momentum and energy and the corresponding simplified equation for $\mathbf{P}^v$, show that the inverse attenuation time $\alpha_t = -\operatorname{Im}\omega$ of longitudinal waves is

$$\alpha_t = \frac{2}{3}\eta\omega^2(\rho_0 c_s^3)^{-1}(1 - Ak^2).$$

(b) Compare with the second-order form of the general microscopic expression

$$\frac{2\alpha\rho c_s\tau}{nm} = \frac{1}{3}\frac{(kl)^2\tan^{-1}(kl)}{kl - \tan^{-1}(kl)} - 1$$

with l the mean free path and obtain the value of coefficient A (Jou, Bampi, Morro (1982)).

11.6. The profile of the pressure p across the layer of a weak shock may be written as

$$p - \frac{p_0 + p_1}{2} = \frac{p_0 - p_1}{2}\tanh\left(\frac{2x}{L}\right),$$

with

$$L = \frac{16av^2}{(p_0 - p_1)(\partial^2 v/\partial p^2)_s},$$

where v the specific volume and $a = (2\rho c^3)^{-1}[(4/3)\eta + (\lambda/c_p)(\gamma - 1)]$, c_p being the heat capacity at constant pressure per unit mass. Obtain the relation between the thickness of the shock layer L and the mean free path ℓ for a monatomic perfect gas for the Mach number $M_0 = 1.2$. (*Hint*: Use the following results: (1) $\eta = \frac{1}{3} nm\langle v\rangle \ell$, with $\langle v\rangle = [8k_B T/(\pi m)]^{1/2}$; (2) $\lambda = \frac{5}{2}\eta c_v$, with c_v being the heat capacity at constant volume per unit mass; (3) for a perfect gas $(\partial^2 v/\partial p^2)_s = (\gamma + 1)v(\gamma p)^{-2}$; and (4) the relation p_1/p_0 in (11.55b).)

11.7. The viscous pressure in a one-dimensional flow is given by $P^v_{xx} = \frac{4}{3}\eta(\partial v_x/\partial x)$. One may estimate the viscous pressure in the shock as $P^v_{xx} = \frac{4}{3}\eta[(v_1 - v_0)/L]$, with L the thickness of the shock layer. (a) By using the value of L derived in the previous problem, determine the ratio P^v_{xx}/p for a shock wave with $M_0 = 1.2$. (b) Using an analogous procedure, evaluate the heat flux across a shock wave with $M_0 = 1.2$.

11.8. Show that for monatomic ideal gases, Grad's equations (4.39) and (4.40) can be cast in the conservative form as expressed by (11.56) and (11.57).

11.9. Transverse viscoelastic waves correspond to the propagation of oscillatory perturbations of the transversal components of the viscous pressure tensor. Their description is obtained by starting from the linear momentum balance equation

$$\rho\frac{\partial \boldsymbol{v}}{\partial t} = -\nabla\cdot\mathbf{P}^v - \nabla p,$$

and the coupled evolution equations for $\boldsymbol{q}$ and $\mathbf{P}^v$ (2.70) and (2.72), namely

$$\begin{aligned}\tau_1\frac{\partial \boldsymbol{q}}{\partial t} + \boldsymbol{q} &= \lambda T^2\beta\nabla\cdot\mathbf{P}^v - \lambda\nabla T,\\ \tau_2\frac{\partial \mathbf{P}^v}{\partial t} + \mathbf{P}^v &= -2\eta(\nabla\boldsymbol{v})^s + \beta\eta T(\nabla\boldsymbol{q})^s.\end{aligned}$$

Show that the high-frequency speed for transverse viscoelastic waves involving perturbations of P^v_{xy} and q_y at constant T is

$$v_p = \left(\frac{\eta}{\rho_0\tau_2}\right)^{1/2}\left[1 + \frac{\lambda\beta^2T^3}{\tau_1}\right]^{1/2}.$$

Note the influence of the coupling term in β, and the fact that when the relaxation times τ_1 or τ_2 tend to zero, this speed diverges.

Chapter 12
Generalised Hydrodynamics

In ordinary fluids, the relaxation times of the fluxes are usually very small. One could therefore ask whether the relaxational effects considered in extended irreversible thermodynamics are observable. The answer is affirmative: it is possible to obtain information on such effects either from experiments or numerical simulations. Computer simulations were analysed in Chap. 8; in this chapter, we discuss several experimental aspects.

Experimental information has been obtained from light- and neutron-scattering, which allows not only to measure the relaxation times of the fluxes, but also to determine their frequency and wavelength dependences through a discipline known as generalised hydrodynamics. In this approach, the relaxation times, which play a central role in EIT, enjoy the status of relevant experimental quantities. On the other hand, computer simulations have opened the road to situations not directly accessible to experiments.

One of the most unexpected results of the light and neutron experiments and related computer simulations is that the behaviour of a fluid at microscopic scales may still be described by means of hydrodynamical equations, provided that the transport coefficients are assumed to be functions of the frequency and the wavevector. This has a special relevance in the context of EIT, as it shows that the extension of hydrodynamic concepts to a regime of high frequencies and short wavelengths is relevant. An analogous situation has been seen in nanosystems (see Chap. 10), where the transport coefficients become a function of the size of the system. Extended thermodynamics appears as the thermodynamic framework consistent with generalised hydrodynamics, in the same way that classical irreversible thermodynamics subtends classical hydrodynamics.

12.1 Density and Current Correlation Functions

Spontaneous microscopic fluctuations are present in any macroscopic system. It is generally assumed that their decay parallels the decay of external perturbations. This means that the analysis of fluctuations may provide as much information on the dynamics of the system as the study of external perturbations.

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_12,

Velocity fluctuations are intimately related to the time correlation function of the density and the momentum of the system. In general terms, a time correlation function is defined as the thermodynamic average of the product of two dynamical variables, each of them expressing at any time and any position in space the spontaneous deviation of a fluid property from its equilibrium average. The time correlation function of the density is important to investigate the non-equilibrium properties of fluids, because it contains most of the relevant information about the dynamics of the system. In that respect, the importance of the density time-correlation function for transport properties is comparable to that of the partition function for equilibrium properties in statistical mechanics.

The time correlation function of the density may be directly derived from light and neutron inelastic spectroscopy or from computer simulations. The ability to perform experiments or simulations at high-frequency and short-wavelength regimes has motivated a very strong interest for that field (Berne and Pecora 1976; Boon and Yip 1980). In the above-mentioned experiments, it is possible to work at frequencies so high that they become comparable to the inverse of the relaxation times of fluxes in liquids. Therefore, generalised hydrodynamics constitutes a stimulating basement for checking and discussing the hypotheses and results of EIT.

As mentioned earlier, one of the basic ideas behind generalised hydrodynamics is to keep as far as possible the structure of the classical hydrodynamics transport equations by allowing the usual transport coefficients to depend on the frequency and the wavelength; in physical space, these coefficients take the form of memory functions reflecting the spatial and temporal non-locality of the transport equations. To evaluate these transport coefficients and the corresponding memory functions is among the most challenging problems in modern non-equilibrium statistical mechanics.

The central quantities for a fluid are, from the point of view of generalised hydrodynamics, the density correlation function and the momentum or current correlation function. They are respectively defined as

$$C_{nn}(\boldsymbol{r}', t', \boldsymbol{r}'', t'') = V\left\langle \delta n(\boldsymbol{r}', t')\delta n(\boldsymbol{r}'', t'')\right\rangle, \tag{12.1a}$$

$$C_{v_i v_j}(\boldsymbol{r}', t', \boldsymbol{r}'', t'') = V\left\langle \delta[\rho v_i(\boldsymbol{r}', t')]\delta[\rho v_j(\boldsymbol{r}'', t'')]\right\rangle, \tag{12.1b}$$

with $\delta A(\boldsymbol{r}, t) = A(\boldsymbol{r}, t) - \langle A(\boldsymbol{r}, t)\rangle$, A being a dynamical variable such as n, ρ or $\boldsymbol{v}$, and $\langle A\rangle$ standing for the equilibrium average; V is the total volume and n the number of particles per unit volume. At equilibrium, which means a homogeneous and stationary state, expressions in (12.1a) may only depend on the relative distance $r = |\boldsymbol{r}' - \boldsymbol{r}''|$ and the time interval $t = t' - t''$.

We introduce the Fourier transforms of (12.1a):

$$S(\boldsymbol{k}, t) = \int d\boldsymbol{r} \exp(i\boldsymbol{k} \cdot \boldsymbol{r} C_{nn}(\boldsymbol{r}, t), \tag{12.2a}$$

$$J_{ij}(\boldsymbol{k}, t) = \int d\boldsymbol{r} \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}) C_{v_i v_j}(\boldsymbol{r}, t). \tag{12.2b}$$

From symmetry requirements, the current time correlation function (12.2b) may be written as

$$J_{ij} = \frac{k_i k_j}{k^2} J_l(k,t) + \left(\delta_{ij} - \frac{k_i k_j}{k^2}\right) J_t(k,t), \tag{12.3}$$

where $J_l(k,t)$ and $J_t(k,t)$ are the longitudinal and transverse current correlation functions, respectively, and $k^2 = \boldsymbol{k} \cdot \boldsymbol{k}$, with $\boldsymbol{k}$ being the wavevector.

Furthermore, one denotes the Laplace transform of (12.2) as

$$\tilde{S}(k,\omega) = \int_{-\infty}^{\infty} \mathrm{d}t \ \exp(-\mathrm{i}\omega t) S(\boldsymbol{k},t), \tag{12.4a}$$

$$\tilde{J}_{ij}(k,\omega) = \int_{-\infty}^{\infty} \mathrm{d}t \ \exp(-\mathrm{i}\omega t) J_{ij}(\boldsymbol{k},t), \tag{12.4b}$$

where $\tilde{S}(\boldsymbol{k},\omega)$ and $\tilde{J}_{ij}(\boldsymbol{k},\omega)$ are known respectively as the spectral density of the density and velocity fluctuations.

From the continuity equation (1.12) it follows that

$$\frac{\partial n_{\boldsymbol{k}}(t)}{\partial t} = \mathrm{i}\boldsymbol{k} \cdot \boldsymbol{j}_{\boldsymbol{k}}(t), \tag{12.5}$$

where $n_{\boldsymbol{k}}(t)$ and $\boldsymbol{j}_{\boldsymbol{k}}(t)$ denote the Fourier transform of the number density n and the current density $n\boldsymbol{v}$, respectively. From (12.5) one obtains the basic relation between $\tilde{S}(\boldsymbol{k},\omega)$ and $\tilde{J}_{ij}(\boldsymbol{k},\omega)$, namely

$$\tilde{J}_l(\boldsymbol{k},\omega) = \frac{\omega^2}{k^2} \tilde{S}(\boldsymbol{k},\omega). \tag{12.6}$$

Although the correlation functions $\tilde{J}_l(\boldsymbol{k},\omega)$ and $\tilde{S}(\boldsymbol{k},\omega)$ contain the same information, some spectral characteristics are displayed more clearly by considering one quantity rather than the other, as will be outlined below. The limiting value of $\tilde{S}(\boldsymbol{k},\omega)$ for $\omega = 0$ is the so-called static structure factor $\tilde{S}(\boldsymbol{k})$, a frequently used quantity in the study of equilibrium properties of fluids.

12.2 Spectral Density Correlation

12.2.1 The Classical Hydrodynamical Approximation

Let us start with the classical hydrodynamical description. The spectral density of the density fluctuations at low ω and $\boldsymbol{k}$ is easily derivable from the expressions of the linearized hydrodynamical equations (1.12–1.14) coupled with the classical Fourier-Stokes-Newton constitutive equations. After application of Laplace and Fourier transforms to the balance equations of mass, momentum and energy (1.12–1.14), one obtains

$$s\delta\tilde{\rho}_k(s) + \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{j}_k(s) = \delta\tilde{\rho}_k(0), \tag{12.7a}$$

$$(s + \nu_l k^2)\tilde{\mathbf{j}}_k(s) + \frac{c^2}{\gamma}\mathrm{i}\boldsymbol{k}\,[\delta\tilde{\rho}_k(s) + \alpha\tilde{g}_k(s)] = \boldsymbol{j}_k(0), \tag{12.7b}$$

$$(s + \gamma\chi k^2)\tilde{g}_k(s) + \frac{\gamma - 1}{\alpha}\mathrm{i}\boldsymbol{k}\cdot\tilde{\boldsymbol{j}}_k(s) = \tilde{g}_k(0), \tag{12.7c}$$

where s stands for $\mathrm{i}\omega$ a usual notation in generalised hydrodynamics and which cannot in this chapter be confused with the entropy, $g(s)$ is the Laplace–Fourier transform of $\rho_0\delta T(\boldsymbol{r}, t)$, and ν_l is the longitudinal viscosity, given by $\nu_l = \left(\frac{4}{3}\eta + \zeta\right)\rho^{-1}$. Eliminating $\tilde{\boldsymbol{j}}_k(s)$ and $\tilde{g}_k(s)$ from (12.7a), one is led to

$$\delta\tilde{\rho}_k(s) = \frac{N(\boldsymbol{k}, s)}{M(\boldsymbol{k}, s)}, \tag{12.8}$$

where

$$M(\boldsymbol{k}, s) = \det\begin{vmatrix} s & \mathrm{i}k_x & \mathrm{i}k_y & \mathrm{i}k_z & 0 \\ \gamma^{-1}c^2\mathrm{i}k_x & s + \nu_l k^2 & 0 & 0 & \gamma^{-1}\alpha c^2\mathrm{i}k_x \\ \gamma^{-1}c^2\mathrm{i}k_y & 0 & s + \nu_l k^2 & 0 & \gamma^{-1}\alpha c^2\mathrm{i}k_y \\ \gamma^{-1}c^2\mathrm{i}k_z & 0 & 0 & s + \nu_l k^2 & \gamma^{-1}\alpha c^2\mathrm{i}k_z \\ 0 & \alpha^{-1}(\gamma-1)\mathrm{i}k_x & \alpha^{-1}(\gamma-1)\mathrm{i}k_y & \alpha^{-1}(\gamma-1)\mathrm{i}k_z & s + \gamma\chi k^2 \end{vmatrix}$$

$$N(\boldsymbol{k}, s) = \det\begin{vmatrix} \delta\tilde{\rho}_k(0) & \mathrm{i}k_x & \mathrm{i}k_y & \mathrm{i}k_z & 0 \\ \tilde{j}_{kx}(0) & s + \nu_l k^2 & 0 & 0 & \gamma^{-1}\alpha c^2\mathrm{i}k_x \\ \tilde{j}_{ky}(0) & 0 & s + \nu_l k^2 & 0 & \gamma^{-1}\alpha c^2\mathrm{i}k_y \\ \tilde{j}_{kz}(0) & 0 & 0 & s + \nu_l k^2 & \gamma^{-1}\alpha c^2\mathrm{i}k_z \\ \tilde{g}_k(0) & \alpha^{-1}(\gamma-1)\mathrm{i}k_x & \alpha^{-1}(\gamma-1)\mathrm{i}k_y & \alpha^{-1}(\gamma-1)\mathrm{i}k_z & s + \gamma\chi k^2 \end{vmatrix} \tag{12.9}$$

From this result, it is easy to construct the correlation function $\langle\delta\tilde{\rho}^*_k(0)\delta\tilde{\rho}_k(s)\rangle$ by taking into account that cross correlations involving $\boldsymbol{j}_k(0)$ and $g_k(0)$ do not appear, as ρ, T, and $\boldsymbol{v}$ are here statistically independent variables. A superscript asterisk denotes the complex conjugate. In this way one finds that

$$\langle\delta\tilde{\rho}^*_k(0)\delta\tilde{\rho}_k(s)\rangle = \frac{(s + \nu_l k^2)(s + \gamma\chi k^2) + (1 - \gamma^{-1})(ck)^2}{(s - s_0)(s - s_-)(s - s_+)}\langle\delta\tilde{\rho}^*_k(0)\delta\tilde{\rho}_k(0)\rangle, \tag{12.10}$$

where s_0, $s_\pm$ are the roots of the determinant $M(\boldsymbol{k}, s)$, i.e. solutions of

$$z^3 + z^2(\gamma a + b) + z(1 + \gamma ab) + a = 0, \tag{12.11}$$

with $a = \chi k/c$, $b = \nu_l k/c$, and $z = s/ck$, where c is the Laplace sound velocity and k is the magnitude of wavevector $\boldsymbol{k}$. The quantities a and b are small for typical light-scattering experiments in an ordinary liquid, where $k \approx 10^5\ \mathrm{cm}^{-1}$ and $c \approx 10^5\ \mathrm{cm\,s}^{-1}$. Up to the first order in a and b, which means the first order in k^2, the solutions of (12.11) are given by

$$z_0 = -a, \quad z_\pm = \pm\mathrm{i} - (1/2)[b + (\gamma - 1)a], \tag{12.12}$$

or, in terms of s,

$$s_0 = -\chi k^2, \quad s_\pm = \mathrm{i}ck - \Gamma k^2, \tag{12.13}$$

where $\Gamma = \frac{1}{2}[\nu_l + (\gamma - 1)\chi]$ is related to the sound absorption coefficient $\Gamma' = -\mathrm{Im}\, k$ by $\Gamma = \Gamma' c/k^2$.

It is then easy to calculate the spectral density of the density fluctuations, defined as

$$\frac{\tilde{S}(k,\omega)}{\tilde{S}(k)} = 2\mathrm{Re}\frac{\left\langle \delta\tilde{\rho}_k^*(0)\delta\tilde{\rho}_k(s = \mathrm{i}\omega)\right\rangle}{\left\langle \delta\tilde{\rho}_k^*(0)\delta\tilde{\rho}_k(0)\right\rangle}; \tag{12.14}$$

with $\tilde{S}(k)$, the static structure factor, given by $\tilde{S}(k) = \left\langle \delta\tilde{\rho}_k^*(0)\delta\tilde{\rho}_k(0)\right\rangle$. Using (12.10) and (12.13), one obtains for (12.14)

$$\begin{aligned}\frac{\tilde{S}(k,\omega)}{\tilde{S}(k)} &= \frac{\gamma - 1}{\gamma}\frac{2\chi k^2}{\omega^2 + (\chi k^2)^2}\\ &+ \frac{1}{\gamma}\left[\frac{\Gamma k^2}{(\omega + ck)^2 + (\Gamma k^2)^2} + \frac{\Gamma k^2}{(\omega - ck)^2 + (\Gamma k^2)^2}\right]\\ &+ \frac{k}{\gamma c}[\Gamma + (\gamma - 1)\chi]\left[\frac{\omega + ck}{(\omega + ck)^2 + (\Gamma k^2)^2} - \frac{\omega - ck}{(\omega - ck)^2 + (\Gamma k^2)^2}\right].\end{aligned} \tag{12.15}$$

This result is important because it shows the structure of the spectrum which can be measured by light-scattering spectroscopy of simple monatomic liquids. In most cases, the spectrum is well approximated by the first three terms in (12.15), which are a sum of three Lorentzians (Fig. 12.1).

The central (Rayleigh) peak arises from fluctuations at constant pressure and corresponds to the thermal diffusivity mode. The other two peaks, shifted in frequency by $-ck$ and $+ck$, are the Stokes and anti-Stokes components of the Brillouin

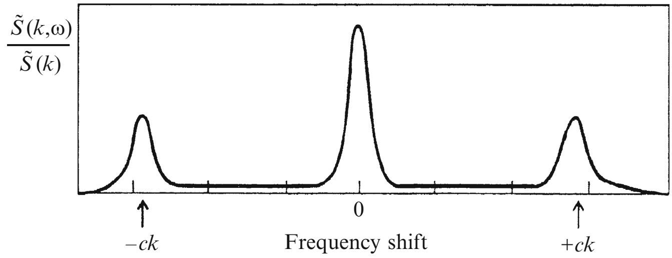


Fig. 12.1 Spectrum of the density fluctuations in a simple fluid. The central (Rayleigh) peak corresponds to the thermal diffusivity mode and the two lateral (Brillouin) peaks, shifted in frequency $\pm ck$, correspond to the acoustic modes. The height and width of the respective peaks are given by equation (12.15)

doublet, and they correspond to acoustic modes. The amplitude of the last two terms in (12.15) is several orders of magnitude smaller than the amplitude of the Lorentzians. A measurement of the position and widths of the Rayleigh and the Brillouin peaks allows one to determine the sound velocity c, thermal diffusivity χ, and sound absorption factor Γ. Note, finally, that because of (12.6) the longitudinal current correlation will lack the central Rayleigh peak owing to the ω^2 factor. The ratio of the integrated intensity of the Rayleigh peak, I_R, and the integrated intensities of the Brillouin peaks, I_B, is known as the Landau–Placzek ratio. Direct integration of (12.15) yields $I_R(2I_B)^{-1} = \gamma - 1$, so that this ratio provides a measurement of γ.

The frequency range of light-scattering experiments in liquids exceeds considerably that of ultrasonic experiments. Nevertheless, at still higher frequencies, like those found in neutron-scattering experiments in liquids or light-scattering experiments in gases, the above analysis based on classical hydrodynamics is no longer valid. New features appear, like, for instance, new propagation modes or dispersion effects in sound propagation and sound absorption. In the next sections we shall show that these features are well accounted for by EIT.

12.2.2 The EIT Description

In EIT, the linearized hydrodynamical equations (1.12–1.14) must be complemented by the Maxwell–Cattaneo equations (2.66–2.68) for the fluxes, which are uncoupled from the set (1.12–1.14). By substituting solutions of the form exp(–*st*) in (2.66–2.68), it is readily checked that the viscosity and the heat diffusivity coefficients take the form

$$\nu_l(s) = \frac{4}{3}\eta\frac{1}{1+s\tau_2} + \zeta\frac{1}{1+s\tau_0}, \qquad \chi(s) = \chi\frac{1}{1+s\tau_1}, \tag{12.16}$$

where τ_0, τ_1, and τ_2 are the respective relaxation times of the bulk viscous pressure, the heat flux and the viscous pressure tensor. After inserting these expressions into the dispersion relation (12.10), the resulting equation exhibits six roots, three more than the usual three longitudinal modes, and no simple analytic solution exists.

To explore the consequences of (12.16), consider a simple model in which $\tau_1 = \tau_2 = 0$. Such a model is useful for the description of thermal relaxation in molecular fluids, where there is a coupling between internal and translational degrees of freedom. This coupling becomes important when the energy fluctuations in the internal degrees of freedom relax on a time scale comparable to the hydrodynamic characteristic times $(\Gamma k^2)^{-1}$ and $(\chi k^2)^{-1}$. In such a case the first of expressions (12.16) can be written as (Boon and Yip 1980)

$$\nu_l(s) = \nu_l + \frac{c_\infty^2 - c_0^2}{1+s\tau_0}\tau_0, \tag{12.17}$$

where c_∞ and c_0 stand for the infinite and zero-frequency sound speed, respectively, and ν_l is the frequency-independent part of $\nu_l(s)$ associated with translational motion whereas the second term in (12.17) describes the contribution of the internal degrees of freedom to $\nu_l(s)$. The frequency domain for which $\nu_l(s = \mathrm{i}\omega)$ is the most sensitive to the frequency dependence is for $\omega \approx 10^{-10}$ s. When (12.17) is introduced into (12.11), the dispersion relation, under the restrictions $\nu_l k/c_0 \ll 1$ and $\chi k/c_0 \ll 1$, reads as

$$(s + \chi k^2)(s + \mathrm{i}\omega_s + \Gamma_s k^2)(s + c_0^2 c_s^{-2} \tau_0^{-1}) = 0 \tag{12.18a}$$

with

$$\omega_s \equiv c_s k = c_0 k \left\{ B + \left[B^2 + (c_0 k \tau_0)^{-2} \right]^{1/2} \right\}^{1/2}, \tag{12.18b}$$

$$B = \frac{1}{2} \left[\left(\frac{c_\infty}{c_0} \right)^2 - \left(\frac{1}{c_0 \tau_0 k} \right)^2 \right], \tag{12.18c}$$

$$\Gamma_s = \Gamma + \frac{1}{2} \chi \left[1 - \left(\frac{c_0}{c_s} \right)^2 \right] + \frac{1}{2} \left(1 - \gamma \chi \tau_0 k^2 \right) \frac{c_\infty^2 - c_0^2}{1 + \omega_s^2 \tau_0^2} \tau_0. \tag{12.18d}$$

Making use of (12.9) and (12.17), we see that the spectral distribution may be expressed as a sum of four Lorentzians, namely

$$\begin{aligned} \frac{\tilde{S}(k,\omega)}{\tilde{S}(k)} &= (1 - \gamma^{-1}) \frac{2\chi k^2}{\omega^2 + (\chi k^2)^2} + R_C \frac{2(c_0/c_s)^2 \tau_0^{-1}}{\omega^2 + (c_0^2 c_s^{-2} \tau_0^{-1})^2} \\ &\quad + R_B \left[\frac{\Gamma_s k^2}{(\omega + c_s k)^2 + (\Gamma_s k^2)^2} + \frac{\Gamma_s k^2}{(\omega - c_s k)^2 + (\Gamma_s k^2)^2} \right], \end{aligned} \tag{12.19a}$$

with

$$\begin{aligned} R_C = &\left\{ \left[1 - \left(\frac{c_s}{c_0} \right)^2 \right] \left[\left(1 - \gamma^{-1} \right) c_0^2 k^2 + \left(\frac{c_0}{c_s} \right)^4 \tau_0^{-2} \right] + \left(c_\infty^2 - c_0^2 \right) k^2 \right\} \\ &\times \left[\omega_s + \left(\frac{c_0}{c_s} \right)^4 \tau_0^{-2} \right]^{-1}, \end{aligned} \tag{12.19b}$$

$$\begin{aligned} R_B = &\left\{ \left[1 - \left(\frac{c_s}{c_0} \right)^2 \left(1 - \gamma^{-1} \right) \right] \left[\omega_s^2 + \left(\frac{c_0}{c_s} \right)^4 \tau_0^{-2} \right] + \left(c_\infty^2 - c_0^2 \right) k^2 \right\} \\ &\times \left[\omega_s + \left(\frac{c_0}{c_s} \right)^4 \tau_0^{-2} \right]^{-1} \end{aligned} \tag{12.19c}$$

A first difference between (12.15) and (12.19a–c), except for neglecting the last two terms of (12.15), is a change in position and width of the Brillouin peaks, given now respectively by c_s and Γ_s instead of c and Γ But more important is the presence of a new central peak of width τ_0^{-1}. Such a peak is difficult to detect, since it appears as a broad background between the Rayleigh and the Brillouin peaks. Note that $c_s > c$ and $\Gamma_s > \Gamma$, so that the Brillouin peaks are pushed away from the Rayleigh line and become wider than in the absence of relaxational effects. Observe finally that when $c_\infty = c_0 = c$, expression (12.19) reduces to the classical result (12.15), except for the last two terms of (12.15), which have been neglected in (12.19) for simplicity.

12.3 The Transverse Velocity Correlation Function: The EIT Description

Although not directly observable by means of light- or neutron-scattering experiments, the transverse velocity correlation function is worth studying from a fundamental point of view. On the one hand, its mathematical analysis is much simpler than that of the longitudinal velocity correlation function and, on the other hand, much effort has been devoted to its study through computer simulations and molecular dynamics.

The transverse velocity correlation function is defined as

$$C_t(\boldsymbol{r}, t, \boldsymbol{r}', t') = \langle \delta v_t(\boldsymbol{r}, t) \delta v_t(\boldsymbol{r}', t') \rangle, \tag{12.20}$$

where $\delta v_t = v_t - \langle v_t \rangle$ is the fluctuation of the component of the velocity transverse to the wavevector of the perturbation. From now on, to fix the ideas, we consider the wavevector in the x direction and the transverse velocity in the y direction. The Fourier transform of $C_t(\boldsymbol{r}-\boldsymbol{r}', t-t')$ will be denoted $J_t(k, t)$. The equation satisfied by $J_t(k, t)$ is derived from the linearized equation of motion (11.1b), which for the transverse velocity component is given by

$$\rho_0 \frac{\partial v_y}{\partial t} = -\frac{\partial P_{iy}^v}{\partial x_i}, \tag{12.21}$$

wherein the evolution of $\mathbf{P}^v$ (in absence of bulk effects) is governed by (2.72), namely

$$\tau_2 \frac{\partial P_{ij}^v}{\partial t} + P_{ij}^v + 2\eta V_{ij} - 2\beta^2 \eta \lambda T^3 \frac{\partial^2 P_{ij}^v}{\partial x_k \partial x_k} = 0. \tag{12.22}$$

Combination of (12.21) and (12.22) and application of a Fourier transform leads to

$$\tau_2 \frac{\partial^2 J_t}{\partial t^2} + \left(1 + l^2 k^2\right) \frac{\partial J_t}{\partial t} + \nu k^2 J_t = 0, \tag{12.23}$$

with $l^2 = 2\eta\lambda T^3 \beta^2$. A Laplace transform with respect to time allows to write (12.23) as

$$\frac{\tilde{J}_t(k,0)}{\tilde{J}_t(k,s)} = \frac{s + (1 + l^2k^2)\tau_2^{-1}}{s^2 + (1 + l^2k^2)\tau_2^{-1} + \nu\tau_2^{-1}k^2}. \tag{12.24}$$

When $\tau_2 = 0$ and $l = 0$, one recovers the transverse correlation function of classical hy-drodynamics. When $l = 0$ and $\tau_2 \neq 0$, one obtains the results of the Maxwell viscoelastic model. Expression (12.24) may be formulated in terms of the frequency by taking into account that $\tilde{J}_t(k,\omega) = 2\,\mathrm{Re}\left[\tilde{J}_t(k, s = \mathrm{i}\omega)\right]$ and noting that $J_t(k, t = 0) = v_0^2 = k_\mathrm{B}T/m$. The result is

$$\tilde{J}_t(k,\omega) = \frac{2v_0^2\tau_2^{-2}\nu k^2(1 + l^2k^2)}{\left\{\omega^2 - \left[\frac{\nu k^2}{\tau_2} - \frac{(1+l^2k^2)^2}{2\tau_2^2}\right]\right\}^2 + \left[\frac{\nu k^2}{\tau_2} - \frac{(1+l^2k^2)^2}{4\tau_2^2}\right]\left[\frac{(1+l^2k^2)^2}{\tau_2^2}\right]}. \tag{12.25}$$

When $l = 0$, this expression reduces to

$$\tilde{J}_t(k,\omega) = \frac{2v_0^2\nu k^2}{\tau_2^2\omega^4 + (1 - 2\nu\tau_2k^2)\omega^2 + (\nu k^2)^2}, \tag{12.26}$$

which is represented in Fig. 12.2. When $\tau_2 = 0$ and $l = 0$, (12.25) simplifies to

$$\tilde{J}_t(k,\omega) = \frac{2v_0^2\nu k^2}{\omega^2 + (\nu k^2)^2}. \tag{12.27}$$

The most relevant property of (12.25) in comparison with (12.27), obtained from the classical Navier–Stokes theory, is the occurrence of a maximum of $\tilde{J}_t(k,\omega)$ at a non-zero frequency, given by

$$\omega_\mathrm{max} = \left[\frac{\nu k^2}{\tau_2} - \frac{(1 + l^2k^2)^2}{2\tau_2^2}\right]^{1/2}. \tag{12.28}$$

The condition for observing such a maximum is that k exceeds the critical value k_c defined by $2\nu\tau_2k_c^2 = (1+l^2k_c^2)^2$ and corresponding to $\omega_\mathrm{max} = 0$. In the low-k limit, the maximum of $\tilde{J}_t(k,\omega)$ is attained at zero frequency (Fig. 12.2), which means a purely diffusive mode. A maximum at $\omega \neq 0$ reflects the property of propagation of shear waves with speed k/ω_max and is a typical feature of elastic solids rather than viscous fluids. Molecular dynamics computations on argon confirms the presence of such a resonant value for $k > k_c = 0.63\,\mathrm{\mathring{A}}^{-1}$.

Another comment concerns the ratio ν/τ_2 that appears in the previous formula. Recall that for an ideal gas, we have found in (4.45b) that

$$\frac{\nu}{\tau_2} = \rho^{-1}p. \tag{12.29}$$

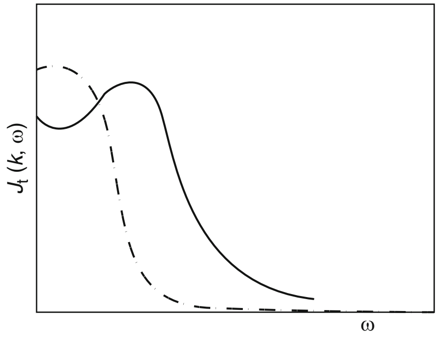


Fig. 12.2 Transverse velocity correlation function $J_t(k,\omega)$ in terms of the frequency for a given k: - - - - classical Navier–Stokes theory (12.27); —— extended theory (12.26)

For a liquid, this result must be replaced by (Boon and Yip 1980)

$$\frac{\nu}{\tau_2} = \rho^{-1} G_\infty(k), \tag{12.30}$$

where $G_\infty(k)$ is the wavenumber-dependent high-frequency shear modulus. Since (12.30) is exactly the same expression as that obtained in the theory of viscoelasticity, we may identify τ_2 with the relaxation time of viscoelastic materials.

The present macroscopic analysis may also be compared with the microscopic Mori–Zwanzig theory presented in Chap. 7. This formalism gives an exact equation for the time evolution of the correlation function in terms of a memory function, namely

$$\frac{\partial J_t(k,t)}{\partial t} = -\int_0^t \mathrm{d}t' K(k,t-t') J_t(k,t'); \tag{12.31}$$

$K(k,t)$ may be written as $K(k,t) = k^2 K'(k,t)$, with $K'(k,t)$ a generalised shear-viscosity function which depends on k and t. Usually the memory function is modelled mathematically because it is impossible to derive its explicit expression from the projection operator techniques. In the extended thermodynamic description (Jou et al. 1985; Pérez-García et al. 1986), the generalised shear viscosity $K'(k,t)$ may be obtained explicitly by taking the Laplace transform of (12.21) and by comparing with

$$P_{iy}^{v}(k,s) = -ikK'(k,s)v_y(s). \tag{12.32}$$

This procedure yields

$$K'(k,s) = \frac{\eta}{\tau_2} \frac{1}{s + (1 + l^2 k^2)\tau_2^{-1}}, \tag{12.33a}$$

from which it follows that

$$K(k,t) = \frac{\eta k^2}{\tau_2} \exp\left[-(1 + l^2 k^2)\tau_2^{-1} t\right]. \tag{12.33b}$$

This expression may be written in terms of a k -dependent relaxation time $\tau_2(k)$ defined by

$$\tau_2(k) = \frac{\tau_2}{1 + l^2 k^2}, \tag{12.34}$$

in the form

$$K(k,t) \sim \exp[-t/\tau_2(k)]. \tag{12.35}$$

An expression of the same form as (12.34) has been used by Chung and Yip (1969) to fit the computer simulation data for argon-like fluids. It was found that for argon at 85 K, $\tau_2 = 0.26 \times 10^{-12}$ s and $l = 4 \times 10^{-9}$ cm. It is worth emphasizing that (12.33) is precisely the exponential model for the memory function used in generalised hydrodynamics; however, in the present context it is not introduced ad hoc but arises naturally from the postulates of EIT. A more detailed model for $\tau_2(k)$ is discussed in Sect. 12.5.

The wavelength dependence of the relaxation time was also the subject of detailed investigations, because interesting experimental information is gained about it from the position of the maximum of the spectral function $\tilde{J}_t(k,\omega)$. Alley and Alder (1983) have used computer simulations to study the generalised shear viscosity coefficient $\eta(k,s)$ in a fluid of hard spheres. They have shown that for a zero frequency and small wave number, molecular dynamical data may be fitted by an expression of the form

$$\eta(k,0) = \frac{\eta}{1 + a^2 k^2}, \tag{12.36}$$

where a, which incorporates the effect of spatial inhomogeneities, is a measure of the deviation from the Stokes friction law. It is worth to notice that expression (12.36) is equivalent to the EIT result (12.33a) for $s = 0$.

12.4 The Longitudinal Velocity Correlation Function: The EIT Description

The longitudinal velocity correlation function is defined in a way similar to (12.20) and is measurable because of its coupling with density fluctuations. In an isothermal system, neglecting relaxational effects of the heat flux, and introducing (2.70) into (2.71) and (2.66), one is led to the following evolution equations for the bulk and shear viscous pressures:

$$\tau_0 \dot{p}^v = -(p^v + \zeta \nabla \cdot \boldsymbol{v}) + \lambda \zeta T^3 \beta'^2 \nabla^2 p^v + \lambda \zeta T^3 \beta' \beta'' \nabla(\nabla \cdot \overset{0}{\mathbf{P}}{}^v), \tag{12.37}$$

$$\tau_2 (\overset{0}{\mathbf{P}}{}^v)^{\cdot} = -(\overset{0}{\mathbf{P}}{}^v + 2\eta \overset{0}{V}) + 2\lambda \eta T^3 \beta''^2 \nabla(\nabla \cdot \overset{0}{\mathbf{P}}{}^v) + 2\lambda \eta T^3 \beta' \beta'' (\overset{0}{\nabla}\nabla\, p^v)^s. \tag{12.38}$$

These expressions when introduced in the longitudinal part of the linearized momentum balance equation give

$$\rho_0 \frac{\partial \boldsymbol{v}_l}{\partial t} = -\nabla(p + p^v) - (\nabla \cdot \overset{0}{\mathbf{P}}{}^{v})_l \tag{12.39}$$

In the absence of temperature fluctuations, one has $\nabla p = (\rho \kappa_T)^{-1} \nabla \rho$, where κ_T is the isothermal compressibility. If the cross terms $\beta' \beta''$ are neglected (Jou et al. 1985; Pérez-García et al. 1986), one obtains for $\tilde{J}_l(k, s)$ (the longitudinal correlation function)

$$\frac{\tilde{J}_l(k,0)}{\tilde{J}_l(k,s)} = s + \gamma c_T^2 \frac{k}{s} + \frac{k^2}{\rho_0} \left[\frac{\zeta}{\tau_0(k) s + 1} + \frac{4}{3} \frac{\eta}{\tau_2(k) s + 1} \right] \tag{12.40}$$

where c_T stands for the isothermal sound velocity and $\tau_i(k)$ for $\tau_i(0)[1 + l^2 k^2]^{-1}$, with $l_0^2 = \lambda \zeta T^3 \beta'^2$ and $l_2^2 = 2\eta \lambda T^3 \beta''^2$.

When $\tau_0 = \tau_2 = 0$, i.e. in the Navier–Stokes regime, (12.40) reduces to the classical result

$$\frac{\tilde{J}_l(k,0)}{\tilde{J}_l(k,s)} = s + \gamma c_T^2 \frac{k^2}{s} + \nu_l k^2. \tag{12.41}$$

The spectral distribution corresponding to (12.40) reads

$$J_l(k,\omega) = \frac{2 v_0^2 \omega^2 k^2 A}{\left\{ \omega^2 - \gamma c_T^2 k^2 - \omega^2 k^2 [A_0 \tau_0(k) + A_2 \tau_2(k)] \right\}^2 + (\omega k^2 \nu_l)^2}, \tag{12.42a}$$

with ν_l defined by (12.16) and $A = A_0 + A_2$ given by

$$A_0 = \frac{\zeta}{\rho_0 \tau_0} \frac{\tau_0(k)}{1 + \omega^2 \tau_0^2(k)}, \tag{12.42b}$$

$$A_2 = \frac{4}{3} \frac{\eta}{\rho_0 \tau_2} \frac{\tau_2(k)}{1 + \omega^2 \tau_2^2(k)}. \tag{12.42c}$$

In the limiting case $\tau_0 = \tau_2 = l = 0$, expression (12.42a) simplifies to

$$J_l(k,\omega) = \frac{2 v_0^2 \omega^2 k^2 \nu_l}{(\omega^2 - \gamma c_T^2 k^2)^2 + (\omega k^2 \nu_l)^2}. \tag{12.43}$$

The most relevant feature of (12.42a) compared to (12.43) is the presence of dispersion effects leading to a wavevector-dependent phase speed

$$v_p^2 = \frac{\omega^2}{k^2} = \gamma c_T^2 + A_0 \omega^2 \tau_0(k) + A_2 \omega^2 \tau_2(k). \tag{12.44}$$

At low frequencies (i.e. $\omega \tau_0 \ll 1$ and $\omega \tau_2 \ll 1$) one finds back the classical result $v_p^2 = \gamma c_T^2$, whereas in the high-frequency limit one gets

$$v_{p\infty}^2 = \frac{\zeta}{\rho_0 \tau_0} + \frac{4}{3} \frac{\eta}{\rho_0 \tau_2}. \tag{12.45}$$

Furthermore, the damping function is now

$$\Gamma(k,\omega) = \frac{1}{2}\left(\frac{\omega}{v_p}\right)^2 A, \tag{12.46}$$

which reduces to the classical expression for $\Gamma(k,\omega)$ at low frequencies but does not vanish at high frequencies, at variance with the classical approach.

It is of interest to connect these results with the memory function formalism. By analogy with (12.30), we introduce a memory function through

$$\frac{\partial J_l(k,t)}{\partial t} = -\int_0^t \mathrm{d}t' K_l(k,t-t') J_l(k,t'). \tag{12.47}$$

The memory function corresponding to the EIT equations (12.37–12.38) is

$$K_l(k,t) = k^2\left[\gamma c_T^2 + \frac{\zeta}{\rho_0\tau_0}\exp\left(-\frac{t}{\tau_0(k)}\right) + \frac{4}{3}\frac{\eta}{\rho_0\tau_2}\exp\left(-\frac{t}{\tau_2(k)}\right)\right], \tag{12.48}$$

which shows explicitly that, in absence of heat flow, there are two exponentially decaying modes associated with the bulk and shear viscosities. This equation is far simpler than the corresponding one proposed in generalised hydrodynamics, although the general idea that $K_l(k,t)$ is governed by a two-relaxation-times model is well accepted (Boon and Yip 1980).

By including thermal conductivity, expression (12.40) will contain a supplementary term and will take the form (Pérez-García et al. 1986)

$$\frac{\tilde{J}_l(k,0)}{\tilde{J}_l(k,s)} = s + \gamma c_T^2\frac{k^2}{s} + \frac{k^2}{\rho_0}\left[\frac{\zeta}{\tau_0(k)s+1} + \frac{4}{3}\frac{\eta}{\tau_2(k)s+1}\right] + \frac{c_T^2 k^2(\gamma-1)}{s+\chi k^2}, \tag{12.49}$$

which corresponds to a memory function

$$\begin{aligned} K_l(k,t) = k^2\Bigg\{&\gamma c_T^2 + \frac{\zeta}{\rho_0\tau_0}\exp\left[-\frac{t}{\tau_0(k)}\right] \\ &+\frac{4}{3}\frac{\eta}{\rho_0\tau_2}\exp\left[-\frac{t}{\tau_2(k)}\right] + c_T^2(\gamma-1)\exp(-\chi k^2 t)\Bigg\}. \end{aligned} \tag{12.50}$$

Some authors (Chung and Yip 1969; Akcasu and Daniels 1970) have proposed microscopic models where the dissipative fluxes (heat flux, viscous pressure) enter as independent variables (see Sect. 7.3). It is found that in the linear approximation these fluxes satisfy the phenomenological equations (2.70–2.72), with microscopic expressions for the coefficients. Although such models reproduce the predictions of EIT, it should be borne in mind that they are not backed by a thermodynamic theory, which is the main concern of the present book.

12.5 Influence of Higher-Order Fluxes

In Sect. 4.6 we discussed the role of higher-order fluxes in EIT and showed to what extent their inclusion modifies the values of the speed of wave propagation. When introduced into the context of generalised hydrodynamics, these higher-order fluxes will influence the position of the peaks and, furthermore, may give additional peaks in the spectra.

Velasco and García-Colin (1972, 1995) have computed the generalised transport coefficients as a function of the frequency and the wavelength, in the 13-, 20- and 26-moment approximations for hard spheres. Their results depend on the number of moments, but they exhibit a qualitatively similar behaviour.

In a series of papers, Weiss and Müller (1995) have gone beyond these lower-order approximations and have analysed very carefully the spectrum of light scattering in gases in the framework of EIT, by including more and more higher-order fluxes. Their approach is essentially based on the Boltzmann equation for Maxwellian molecules and a closure is achieved by maximizing the entropy.

The number of peaks in the density spectrum depends on the number of higher-order fluxes. It turns out that, to describe the experimental data, one needs a large number of fluxes, for instance, to reproduce accurately the experimental data by Clark in xenon some 300 moments are needed. Under these conditions, additional higher-order moments no longer modify the results.

Another aspect of higher-order fluxes refers to the dependence of the relaxation time on the wave vector. For instance, within the limit $kl \gg 1$, the gas behaves like a system of independent free particles. In this case, the position distribution function at time t of particles having left the origin at time $t = 0$ is given by

$$f(\boldsymbol{r}, t) = \int \mathrm{d}\boldsymbol{r} f_{\mathrm{eq}}(\boldsymbol{p}) \delta \left[r - (\boldsymbol{p}/m)t \right], \tag{12.51}$$

with $\boldsymbol{p}$ being the momentum of the particles. When the Maxwellian distribution function is introduced into this expression, one obtains after several calculations (see Problem 12.4),

$$J_t(k, t) = \exp\left[-\frac{1}{2}(kv_0 t)^2 \right], \tag{12.52}$$

where $v_0 = (k_\mathrm{B}T/m)^{1/2}$ is the root-mean-square thermal speed. Therefore, one may identify $2^{-1/2}kv_0$ as the inverse of a relaxation time corresponding to a Gaussian decay of the form

$$J_t(k, t) = \exp\left[-(t/\tau)^2 \right]. \tag{12.53}$$

Then, one has

$$\tau = 2^{1/2}(kv_0)^{-1}, \tag{12.54}$$

from which it follows that the relaxation time varies as k^{-1} in the high-wavevector limit. However, the relaxation time given by (12.34) behaves in this high-wavevector limit as k^{-2}. To solve this contradiction, let us include higher-order fluxes in the description; in this case, the k dependence of the relaxation time will take the form

$$\tau_2(k) = \frac{\tau_2(0)}{1 + \dfrac{l^2k^2}{1 + \frac{l^2k^2}{1+\cdots}}}, \tag{12.55}$$

which is a generalisation of (12.34). In the asymptotic limit, this fraction may be written as (see Problem 4.9)

$$\tau(k) = \frac{\tau_0}{l^2k^2}\frac{\sqrt{1+4l^2k^2}-1}{2}, \tag{12.56}$$

which for high values of k exhibits the required k^{-1} dependence. This shows how the introduction of a large number of higher-order fluxes may modify the scaling laws describing the behaviour of $\tau(k)$ from k^{-2} at the lowest-order approximation to k^{-1} in the asympotic limit of an infinite number of fluxes.

12.6 Problems

12.1. The wavelength of visible light ranges from 450 to 700 nm. (a) Determine $\omega\tau$ and kl for visible light in a typical monatomic gas (molecular radius $= 2 \times 10^{-10}$ m) at 273 K and 1 atm. (b) Evaluate $\omega\tau$ and kl in a liquid where $\tau = 2\times10^{-13}$ s and $l = 4\times10^{-11}$ m. (c) Find the energy of scattered neutrons such that $kl = 1$ in this liquid.

12.2. One of the consequences of higher-order hydrodynamics is that the shift of Brillouin peaks is related to the hypersound velocity rather than to the sound velocity. Consider, for instance, the following situation. The frequency shift corresponding to the Brillouin peaks in water for scattering at 90° for light of 0.6328 μm (this is the red light of a He–Ne laser) is 4.33×10^9 Hz. Obtain the hypersonic velocity of sound and compare it with the sound velocity 1491 m s^{-1}. (*Hint*: The frequency shift for scattering at an angle θ is given by $\omega = 2\omega_0 n(v/c)\sin(\theta/2)$, with v the hypersound velocity, c the speed of light, and n the index of refraction of the medium.)

12.3. Starting from expression (12.25) for the transverse velocity correlation function, find the critical wave number k_c at which propagating shear waves could be observed in a monatomic perfect gas instead of the usual diffusive behaviours predicted by the classical theory. Estimate k_c for He at 273 K and 1 atm (shear viscosity of He^4 is 1.87×10^{-5} kg m^{-1} s^{-1}; recall that $\eta = \frac{1}{3}nm\langle v\rangle l$ and $\tau = l/\langle v\rangle$).

12.4. Within the limit $kl \gg 1$, i.e. when the wavevector of the perturbation is much smaller than the mean free path, a gas behaves like a system of independent free particles because the spatial scale is so small that particles do not collide with each other. In this case the transverse velocity correlation function is given by (12.51). Show that when the Maxwellian distribution function is introduced into this expression one obtains

$$J_t(\boldsymbol{r}, t) = (\pi v_0^2 t^2)^{-3/2} \exp\left[-(\boldsymbol{r}/v_0)^2\right].$$

By using Fourier transform derive (12.52) showing that the relaxation time in this regime behaves as the reciprocal of the wavevector k.

12.5. Compare the behaviour of the k-dependent viscosity found from the following second-order expansions of the constitutive equation for the viscous pressure tensor:

(a) an expansion in the fluxes (as in the Grad method and extended thermodynamics)

$$\tau_2 \frac{\partial \mathbf{P}^v}{\partial t} + \mathbf{P}^v = -2\eta \mathbf{V} + \nabla \cdot \overset{0}{\mathbf{J}}{}^v,$$

$$\overset{0}{\mathbf{J}}{}^v = -\eta'' \langle \nabla \mathbf{P}^v \rangle,$$

with $\overset{0}{\mathbf{J}}{}^v$ the flux of the viscous pressure tensor, η'' a phenomenological coefficient and $\langle \ldots \rangle$ the completely symmetrized part of the corresponding third-order tensor;

(b) a gradient expansion, as in the Burnett approach of kinetic theory

$$\tau_2 \frac{\partial \mathbf{P}^v}{\partial t} + \mathbf{P}^v = -2\eta \mathbf{V} + \ell^2 \nabla^2 \mathbf{V};$$

(c) compare them with (12.36). Note that (b) yields an unstable behaviour for high values of k, since the generalized viscosity becomes negative. Since this behaviour is not observed, the expansion in the fluxes seems more suitable than the expansion in gradients. (For a wide discussion of the instabilities arising in the Burnett approach to generalized hydrodynamics see Karlin (2000)).

12.6 Compare the first and third order approximations of the continued fraction expansion (12.55) with the second and fourth-order approximations, especially in the regime of high values of lk. Compare them with the asymptotic expression (12.56). Note that odd approximations fall below (12.56) whereas even approximations fall above (12.56), thus providing lower and upper bounds to the values of the asymptotic expression, respectively, and that these bounds approach monotonically to the asymptotic expression for increasing orders of approximation.

Chapter 13
Non-classical Diffusion, Thermo-diffusion and Suspensions

Although under normal circumstances the classical Fick's law gives an excellent description of matter diffusion, it is however not appropriate for describing some particular features, like those concerned with inertial effects, strong non-homogeneities, or couplings between mass transport and viscous or thermal effects. A simple non-Fickian diffusion model including relaxation is presented in Sect. 13.1. A modified diffusion equation taking into account density gradients and generalizing Cahn–Hilliard's approach is also derived. Inertial effects are of importance some stochastic processes, as correlated random walks, discussed in Sect. 13.2. Furthermore, the coupling between diffusion flux and viscous pressure (a coupling between quantities of different tensorial order which is excluded by the classical theory of non-equilibrium thermodynamics) leads to several non-Fickian processes which are relevant in glasses and polymer solutions as shown in Sect. 13.3. Section 13.4 is devoted to the analysis of reaction–diffusion processes, where hyperbolic diffusion is combined with chemical reactions. All these aspects have considerable practical outputs: to mention only a few examples, shear-induced diffusion is at the basis of chromatographic techniques of separation of macromolecules and, on the other hand, it is important in macromolecular processing, where homogeneity is required. Reaction–diffusion coupling plays a central role in the study of spreading of epidemics, propagation of forest fires, human migration, among others. In the above sections, the temperature was assumed to be uniform. This restriction is relaxed in Sect. 13.5 wherein the coupling between matter and heat transport is investigated. Section 13.6 is concerned with the motion of suspensions of solid particles in fluids. A last Sect. 13.7 is devoted to inertial effects in fast solidification of binary alloys and their influence on the morphology of the solidification fronts. Other problems of interest, as shear-induced polymer diffusion or Taylor dispersion – diffusion combined with a velocity gradient – are dealt with in detail in the companion book *Thermodynamics of Fluids under Flow* (Jou et al. 2001).

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_13, © Springer Science+Business Media LLC 2010

13.1 Molecular Diffusion in Perfect Fluid Mixtures

In this section, we derive the basic equations of diffusion between perfect fluids in the framework of EIT, with especial emphasis on relaxation effects. The system is in mechanical equilibrium with zero barycentric velocity and zero acceleration, which is the case for mixtures confined in closed vessels; it follows that the mass density and pressure can be considered as uniform. Moreover, we restrict our attention to isothermal conditions with not only $\nabla T = 0$ but also $\boldsymbol{q} = 0$; external forces and chemical reactions are supposed to be absent; a more general analysis wherein all the above restrictions are relaxed can be found in Lebon et al. (2003). The fluid particles are assumed of molecular dimensions so that their volume is ignored. In multi-component systems, the concentration of the constituents must be included among the set of independent variables. According to Chap. 1, the evolution equations of the mass fractions $c_k = \rho_k/\rho$ are

$$\rho\dot{c}_k = -\nabla\cdot\boldsymbol{J}_k, \quad (k = 1, 2, \ldots, n), \tag{13.1}$$

with $\boldsymbol{J}_k$ the diffusion flux of component k. Since $\sum_k c_k = 1$ and $\sum_k \boldsymbol{J}_k = 0$, only $n-1$ of the mass fractions and diffusion fluxes are independent variables.

For an n-component mixture, the classical Gibbs equation expressed in terms of Helmholtz's free energy $\psi(T, \rho, c_k) = u - Ts$ is

$$d\psi = -s\mathrm{d}T - p\mathrm{d}\rho^{-1} + \sum_k \mu_k \mathrm{d}c_k. \tag{13.2}$$

According to the postulates of EIT, the diffusion fluxes $\boldsymbol{J}_k$ are considered as independent variables. By assuming that $\partial\psi/\partial\boldsymbol{J}_k$ is proportional to $\boldsymbol{J}_k$, the generalised Gibbs equation is given by

$$\mathrm{d}\psi = -s\mathrm{d}T - p\mathrm{d}\rho^{-1} + \sum_k \mu_k\mathrm{d}c_k + \rho^{-1}\sum_k \alpha_k\boldsymbol{J}_k\cdot d\boldsymbol{J}_k. \tag{13.3}$$

Writing the entropy balance (2.19) in terms of ψ, one obtains, at uniform temperature,

$$\rho\dot{u} - \rho\dot{\psi} + \nabla\cdot(T\boldsymbol{J}^s) = T\sigma^s \geq 0. \tag{13.4}$$

Making use of Gibbs' equation (13.3) and the balance laws (1.10) and (13.1) for u and c_k, respectively, relation (13.4) takes the form

$$-\nabla\cdot\left(\sum\nolimits_k \mu_k\boldsymbol{J}_k + T\boldsymbol{J}^s\right) - \sum\nolimits_k \boldsymbol{J}_k\cdot[\nabla(\mu_k)_{T,\rho} + \alpha_k\dot{\boldsymbol{J}}_k] = T\sigma^s \geq 0. \tag{13.5}$$

Positiveness of $T\sigma^s$ demands that the divergence term vanishes from which follows the usual result $\boldsymbol{J}^s = -(1/T)\sum_k \mu_k\boldsymbol{J}_k$ and, in addition, that

$$\alpha_i \dot{\boldsymbol{J}}_i + (\nabla \mu_i)_{T,\rho} = -\sum_k L_{ik} \boldsymbol{J}_k, \tag{13.6}$$

with L_{ik} a positive definite matrix; it is important to stress that the summation rule over repeated indices is not of application in this section, as they concern components and not Cartesian coordinates; by writing (13.6), non-linear contributions in the fluxes have been omitted. The evolution equations for $\boldsymbol{J}_i$ can still be written as

$$\alpha_i \dot{\boldsymbol{J}}_i = -\sum_k L_{ik} \boldsymbol{J}_k - (\nabla \mu_i)_{T,\rho} \quad (i, k = 1, 2, \ldots, n-1). \tag{13.7}$$

The analysis of the cross terms in (13.7) will be carried out later on. In the particular case of diffusion in a binary system, expression (13.7) reduces to

$$\alpha \dot{\boldsymbol{J}}_1 = -a \nabla c_1 - L \boldsymbol{J}_1, \tag{13.8}$$

where a stands for $(\partial \mu / \partial c_1)_{T,\rho} = \partial^2 \psi / \partial c_1^2$, the quantity μ being given by $\mu = \mu_1 - \mu_2$, while $\boldsymbol{J}_1$ is the diffusion flux of component 1 with respect to the barycentric motion. After dropping index 1, and setting $a/L = \rho D$, $\alpha / L = \tau$ or $\alpha = \tau a / (\rho D)$, relation (13.8) can be rewritten as

$$\tau \dot{\boldsymbol{J}} + \boldsymbol{J} = -\rho D \nabla c, \tag{13.9}$$

with D the diffusion coefficient and τ the relaxation time of $\boldsymbol{J}$. Letting τ tend to zero, one finds back Fick's law. With the above notation, the Gibbs equation (13.3) becomes

$$\mathrm{d}\psi = -s \mathrm{d}T - p \mathrm{d}\rho^{-1} + \mu \mathrm{d}c + \frac{\tau a}{\rho^2 D} \boldsymbol{J} \cdot \mathrm{d}\boldsymbol{J}. \tag{13.10}$$

The last term in the right-hand side of (13.10) is analogous to that found previously for heat conduction, with the flux multiplied by the relaxation time and divided by the transport coefficient. Integration of (13.10) leads to

$$\psi(T, \rho, c, \boldsymbol{J}) = \psi_{\mathrm{eq}}(T, \rho, c) + \frac{1}{2} \frac{\alpha}{\rho} \boldsymbol{J} \cdot \boldsymbol{J}. \tag{13.11}$$

In the steady state, or for slow variations of $\boldsymbol{J}$, for which $\boldsymbol{J} = -\rho D \nabla c$, expression (13.11) can be written as

$$\psi(T, \rho, c, \nabla c) = \psi_{\mathrm{eq}}(T, \rho, c) + \tfrac{1}{2} k_{\mathrm{B}} T l^2 (\nabla c) \cdot (\nabla c), \tag{13.12}$$

where $l = (\alpha D^2 \rho^2 / k_{\mathrm{B}} T)^{1/2}$ represents a correlation length. A free energy depending on the concentration gradient was proposed by Ginzburg and Landau; it is not only the basis of the Landau–Lifshitz analysis of spatial correlations of density fluctuations, and the Ginzburg–Landau–Wilson Hamiltonian description of critical points but also of the Cahn–Hilliard theory of spinodal decomposition, as shown below. However, it must be kept in mind that (13.12) is less general than (13.11), which remains true even for unsteady processes.

When the evolution equation for the flux (13.9) is introduced into the balance law (13.1), and the quantities τ and D are constant, one is led to the telegrapher's equation

$$\tau \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = D\nabla^2 c, \tag{13.13}$$

which was already obtained in Chaps. 9 and 10. The extension of the analysis to viscous and non-linear evolution equations in the fluxes is rather straightforward (e.g. Lebon et al. 2003) (see Box 13.1).

Box 13.1 Cahn–Hilliard's model and spinodal decomposition The main feature of Cahn–Hilliard's model is that it integrates non-local effects to take account of strong non-homogeneities of the mass concentrations. Non-localities are particularly important in rapid phase transformations taking place in diffuse interfaces with thicknesses comparable to the characteristic length of the considered phenomenon and more generally when a topology of the interface becomes complicated or multiply connected. A straightforward method to incorporate Cahn–Hilliard's description into the frame of EIT is to introduce the functional or variational derivative defined by

$$\frac{\delta y}{\delta x} = \frac{\partial y}{\partial x} - \nabla \cdot \left(\frac{\partial y}{\partial (\nabla x)} \right), \tag{13.1.1}$$

wherein y designates an arbitrary function of x and ∇x. In the case that y is only depending on x, the variational derivative coincides with the partial derivative $\partial y / \partial x$. To illustrate the use of the variational derivative, let us consider an isothermal and isobaric binary mixture with mass concentrations c_1 and c_2; assuming that Helmholtz's free energy ψ is depending on the concentration gradient, Gibb's equation (13.3) will take the form

$$\mathrm{d}\psi = \frac{\partial \psi}{\partial T}\mathrm{d}T + \frac{\partial \psi}{\partial \rho}\mathrm{d}\rho + \frac{\delta \psi}{\delta c}\mathrm{d}c + \frac{\partial \psi}{\partial \boldsymbol{J}} \cdot \mathrm{d}\boldsymbol{J}, \tag{13.1.2}$$

with c standing for $c_1(= -c_2)$, $\boldsymbol{J}$ for $\boldsymbol{J}_1(= -\boldsymbol{J}_2)$ and $\delta\psi/\delta c$ for the variational derivative

$$\frac{\delta \psi}{\delta c} = \frac{\partial \psi}{\partial c} - \nabla \cdot \left(\frac{\partial \psi}{\partial (\nabla c)} \right). \tag{13.1.3}$$

In the case that ψ is quadratic in ∇c,

$$\psi(T, \rho, c, \nabla c, \boldsymbol{J}) = \psi(T, \rho, c, \boldsymbol{J}) + \frac{1}{2}\varepsilon^2 \nabla c \cdot \nabla c, \tag{13.1.4}$$

with ε^2 a positive constant to guarantee stability of equilibrium, one obtains from (13.1.3) that the chemical potential $\mu = \delta\psi/\delta c$ can be written as

$$\mu = \mu_0 - \varepsilon^2 \nabla^2 c, \tag{13.1.5}$$

wherein $\mu_0(T, \rho, \boldsymbol{J})$ is the part of the chemical potential independent of the gradient of concentration. The result (13.1.5) was first derived by Cahn and Hilliard (1958) on completely different grounds. From now on, the same procedure as in Sect. 13.1 leads to the following evolution equation of $\boldsymbol{J}$:

$$\tau \dot{\boldsymbol{J}} + \boldsymbol{J} = -\frac{1}{L}\nabla\mu_0 + \frac{\varepsilon^2}{L}\nabla \cdot (\nabla^2 c), \tag{13.1.6}$$

which differs from (13.7) by the presence of the last term at the right-hand-side. After combining this expression with the mass fraction balance law (13.1), and omitting non-linear contributions in the flux $\boldsymbol{J}$, one obtains

$$\tau\ddot{c} + \dot{c} = D\nabla^2 c - \varepsilon^2 M \nabla^4 c, \tag{13.1.7}$$

with D the coefficient of diffusion and $M > 0$ given by $M = 1/(\rho L)$, M is generally referred to as the (positive) atomic mobility. In view of application to spinodal decomposition, the coefficient $D(= a\rho^{-1}L^{-1})$ will be written under the form

$$D = \psi'' M, \tag{13.1.8}$$

where $\psi''(= a)$ stands for $\psi'' = (\partial^2\psi/\partial c^2)_{T,\rho}$. In comparison with the classical diffusion equation, expression (13.1.7) contains two additional contributions: the first one in $\ddot{c}$ arises as a consequence of non-locality in time, the second in $\nabla^4 c$ is related to non-locality in space. As $\tau \to 0$, (13.1.8) transforms into the equation derived by Cahn and Hilliard (1958).

Application to spinodal decomposition in a binary system

Spinodal decomposition is the process whereby a system consisting of a single uniform phase fluid, when suddenly quenched, develops into distinct regions of coexisting equilibrium phases. Its main characteristic feature is that it is an unstable mechanism, generally assumed to occur isothermally. Typical examples which have been widely studied include alloys, glasses and fluid mixtures. Although this transformation has been theoretically described by means of Cahn–Hilliard's linear model, experimental data on light and X-ray scattering by phase-separated glasses (Andreev et al. 1970) have been shown to be in contradiction with the results obtained from this approach. As shown below, the Cahn–Hilliard's modified version (13.1.7) that takes into account the relaxation of the diffusion flux seems to be better suited. In this form, the modified Cahn–Hilliard equation is a linear partial differential equation of a hyperbolic type. To derive the corresponding dispersion relation between the rate of amplification ω and the wavenumber k, consider a perturbation with respect to an initial uniform concentration c_0 of the form

$$c'(x,t) = c(x,t) - c_0 = a \exp(\mathrm{i}kx - \omega t), \tag{13.1.9}$$

where x and t are the spatial and time coordinates respectively and a the amplitude. After substitution of (13.1.9) in (13.1.7) and taking into account that c_0 is in the unstable spinodal region, so that $\psi'' < 0$, one obtains the following dispersion relation

$$\omega(k) = \frac{1 \pm \sqrt{1+4k^2\tau M\,|\psi''|\,(1-\varepsilon^2\,|\psi''|^{-1}\,k^2)}}{2\tau} = \frac{1 \pm \sqrt{1+4l_D^2 k^2(1-l_c^2 k^2)}}{2\tau}, \tag{13.1.10}$$

with $l_c = \varepsilon/\,|\psi''|^{-1/2}$ the correlation length and $l_D = (\mathrm{M}\,|\psi''|\,\tau)^{1/2}$ the diffusion length, the upper and lower signs correspond to wave propagation in the positive and negative x directions respectively. Within the local equilibrium limit $\tau \to 0$, it is found that

$$\omega = M l_c^2 k^2 (k^2 - k_c^2), \tag{13.1.11}$$

where $k_c = \psi''/\varepsilon$. Disturbances with a wavenumber k in the region $0 < k < k_c$ are unstable, i.e. grow exponentially with time. The fastest mode obtained by setting $\partial\omega/\partial k = 0$ is that for which $k = k_c/\sqrt{2}$ and this was the mode that

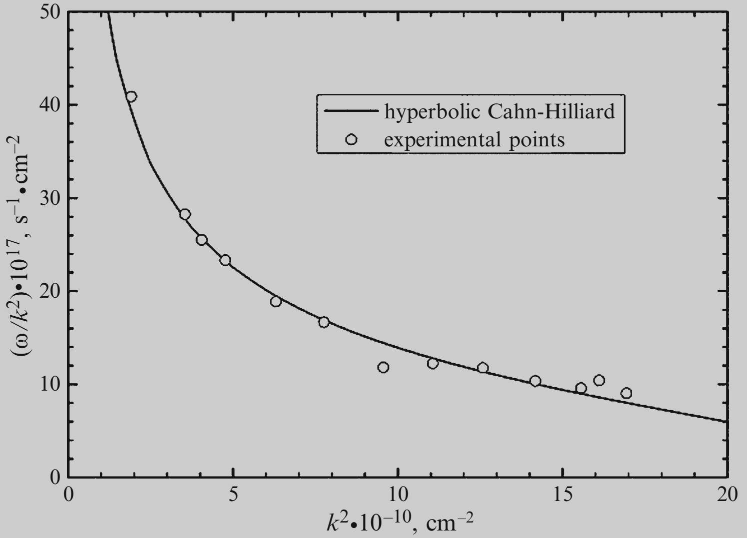


Fig. 13.1 Dependence ω/k^2 upon k^2 given by the hyperbolic model (Eq. (13.110)) and scattering data of visible light (Andreev et al. 1970). Experimental points were obtained on phase-separated SiO_2-12 wt.% Na_2O glass at temperature $T = 803K$ (reprinted with permission from Galenko P, Lebedev V (2008) Phys Lett A 372:985)

Cahn and Hilliard identified as responsible for the initial spinodal instability and determining the scale of the unstable structure consisting generally in disperse precipitates. The theoretical value of the most dangerous mode has the right order of magnitude compared to experimental data. Nevertheless, Cahn–Hilliard's theory suffers from several shortcomings. First, when the composition of the system tends to the value corresponding to the spinodal curve, $\psi'' = 0$, the critical wavelength $1/k_c$ tends to infinity. Moreover, the relationships between the function ω/k^2 and the square k^2 of the wavenumber, as predicted by (13.1.11), is linear while experiences (e.g. Binder and Fratzl 2001) exhibit a marked curvature. In contrast as indicated on Fig. 13.1.1, by comparing the result (13.1.10) obtained from EIT with experimental observations (Galenko and Lebedev 2008), the agreement is much more satisfactory, as shown in Sect. 13.7.

The conclusion is that the parabolic linear Cahn–Hilliard's model is missing several ingredients of the physics underlying spinodal decomposition but that the modified EIT version offers interesting improvements. These are in particular related to the presence of the two scaling lengths, the correlation l_c and the diffusion l_D ones, versus one single scaling length in Cahn–Hilliard's description. The relative importance of these two reference lengths determines the nature of the transition from the initially unstable homogeneous state to the final inhomogeneous state. At the earliest stages of the transition at which $l_D \gg l_c$ short range interactions play the dominant role in the selection of the mode of transition. and are responsible for the departure of the curve of Fig. 13.1 from a straight line. In the intermediate regime at which $l_D = l_c$, long range interactions become present while for $l_c \gg l_D$, they are dominant and the function ω/k^2 tends to the linear law predicted by Cahn–Hilliard's scenario.

13.2 Telegrapher's Equation and Stochastic Processes

Equation (13.13) can also be derived on microscopic grounds by assuming a correlated random walk, i.e. by a random walk in which the jump directions in any two consecutive intervals are correlated; it may also be obtained from a dichotomous model in which particles switch between two different states, and also from a random walk with a continuous distribution function of pausing times (Masoliver 1992). The correlated random walk was introduced by Fürth in 1917, to model diffusion in biological and physical problems. The same technique was developed in 1921 by G. I. Taylor to analyse turbulent diffusion; in 1953 it was popularized by the classical work of Goldstein (1951).

13.2.1 Correlated Random Walk

Assume that at the initial time $t = 0$, a set of particles are present at $x = 0$. At time $t = t_0$, half of the particles jump a distance d to the right and half to the left. From now on, at each interval t_0, every particle jumps a distance d, with a probability p of jumping in the same direction as the previous jump and a probability $q = 1 - p$ of jumping in the opposite direction. Note that in a normal random walk, the probability of jumping to the right or to the left is the same, i.e. $p = 1/2$, so that there is no correlation between the speed direction at successive jumps. We now show that this correlation leads to the telegrapher equation. Assume that $\gamma(n, \nu)$ is the fraction of particles that at time $t = nt_0$ are at position $x = \nu d$. We denote by $\alpha(n, \nu)$ and $\beta(n, \nu)$ the fraction of particles which are reaching position νd from the left and from the right, respectively. As a consequence, one has

$$\gamma(n, \nu) = \alpha(n, \nu) + \beta(n, \nu). \tag{13.14}$$

Since the particles which at time $(n + 1)t_0$ occupy the position νd were at a previous time at $(\nu - 1)d$ or $(\nu + 1)d$, it is easy to check that

$$\begin{aligned}
\alpha(n+1, \nu) &= p\alpha(n, \nu - 1) + q\beta(n, \nu - 1) \\
&= p\gamma(n, \nu - 1) - c\beta(n, \nu - 1), && (13.15a) \\
\beta(n+1, \nu) &= p\beta(n, \nu + 1) + q\alpha(n, \nu + 1) \\
&= p\gamma(n, \nu + 1) - c\alpha(n, \nu + 1), && (13.15b)
\end{aligned}$$

with $c = p - q$ the correlation between two successive jumps. Conversely, the particles which at $(n - 1)t_0$ were at νd, will arrive at $t = nt_0$ either at $\nu + 1$ or $\nu - 1$, so that

$$\gamma(n, \nu - 1) = \alpha(n, \nu + 1) + \beta(n, \nu - 1). \tag{13.16}$$

From (13.14–13.16) it follows that

$$\gamma(n + 1, \nu) = p[\gamma(n, \nu - 1) + \gamma(n, \nu + 1)] - c\gamma(n - 1, \nu). \tag{13.17}$$

This result shows that the fraction of particles which at time $(n + 1)t_0$ are at place νd depends not only on the distribution of particles at the previous time nt_0, as in the usual Markovian random walk, but also on the distribution at $(n - 1)t_0$.

To transform (13.17) into a differential equation, we write $t_0 \to \Delta t$, $d \to \Delta x$, $\Delta x = v\Delta t$ (with v the flight speed of the particle during the jump), $c = 1 - (\Delta t/\tau)$, for $\Delta t < \tau$ and $c = 0$ for $\Delta t > \tau$, and $p = \frac{1}{2}(1 + c) = 1 - (2\tau)^{-1}\Delta t$. This expression for c follows from considering that within the short-time limit, the correlation between the speeds at two successive jumps tends to 1, and that for $\Delta t > \tau$ the correlation is lost; the quantity τ is a constant giving information about the loss of correlation with increasing time. If $w(t, x)$ is the probability density of the distribution of particles, the previous identifications allow to rewrite (13.17) as

$$w(t+\Delta t,x)=[1-(2\tau)^{-1}\Delta t][w(t,x-\Delta x)+w(t,x+\Delta x)]$$
$$\times(1-\tau^{-1}\Delta t)w(t-\Delta t,x). \tag{13.18}$$

Expanding this expression up to second order in Δt and setting finally $\Delta t=\tau$ yields

$$\tau\frac{\partial^2 w}{\partial t^2}+\frac{\partial w}{\partial t}=\tau v^2\frac{\partial^2 w}{\partial x^2}, \tag{13.19}$$

which is a telegrapher's equation with relaxation time τ and diffusion coefficient τv^2. Here there is no drift term because we have assumed that there is no external force causing a systematic motion of the particles in a given direction.

It is also interesting to expand (13.18) at higher order instead of limiting it to the second order. Taking into account that $w(t+\Delta t)=\exp[\Delta t(\partial_t)]$ with $\partial_t=\partial/\partial t$, and analogously for $w=(x+\Delta x)$, it results that

$$2[\cosh(\tau\partial_r)-1]w+\frac{\tau}{\Delta t}[\cosh(d\partial_x)-\exp(-\tau\partial_r)]w=2[\cosh(d\partial_x)-1]w, \tag{13.20}$$

where $\cosh(a)$ and $\exp(-a)$ stand for the corresponding Taylor expansions of these functions in powers of a. One may also write (13.20) in the form

$$\sum_i a_i\frac{\partial^i w}{\partial t^i}=\sum_j b_j\frac{\partial^{2j} w}{\partial t^{2j}}, \tag{13.21}$$

where the explicit expressions for the coefficients a_i and b_j can be directly calculated from (13.20) (Problem 13.5). Expression (13.21) is different from the usual Kramers–Moyal expansion, where only the first-order time derivative is kept on the left-hand side, while an infinite expansion in spatial derivatives appears in the right-hand side. Here, space and time are kept on equal footing, a necessary requisite to capture the effects of memory. As shown by Rosenau (1993), the spectrum of the telegrapher equation reproduces satisfactorily the spectrum of the original discrete process of the correlated random walk for all wavelengths. This is remarkable because in general the short-wavelength limit of a continuum model differs widely from the corresponding discrete microscopic model. Indeed, the well known Fokker–Planck equation, which is a good description of a completely uncorrelated random walk for long times, differs very much from it in the short-wavelength regime. The reason for the much more satisfactory behaviour of the telegrapher equation is that it preserves the characteristic speed of the walker, d/t_0, in contrast with the Fokker–Planck equation, where this information is lost.

13.2.2 H–Theorem for Telegrapher Type Equation

A natural question, from the thermodynamic point of view, is whether an H-theorem is satisfied for kinetic equations of the telegrapher type (Camacho and Jou 1992). Consider, for instance, an equation of the form

$$\tau\frac{\partial^2 f}{\partial t^2}+\frac{\partial f}{\partial t}=\nabla\cdot D_0\left[k_{\mathrm{B}}T\nabla f+(\nabla U_{\mathrm{ext}})f\right]. \tag{13.22}$$

This relation generalises the Smoluchowski equation describing the dispersion of non-interacting Brownian particles under an external potential density $U_{\mathrm{ext}}(\boldsymbol{x})$. Here, $f(\boldsymbol{x},t)$ is the probability distribution function of the particles, D_0 the inverse of the friction coefficient and τ a relaxation time. By analogy with kinetic theory, we define the entropy S by

$$S=-k_{\mathrm{B}}\int f(\boldsymbol{x},t)[\ln f(\boldsymbol{x},t)-1]\mathrm{d}\boldsymbol{x}. \tag{13.23}$$

Since (13.22) is valid in a system at constant temperature T, it is more convenient to use the free energy $\Phi=U-TS$, with $U=\int f(\boldsymbol{x},t)u(\boldsymbol{x})\mathrm{d}\boldsymbol{x}$ rather than the S function itself. The evolution of Φ is given by

$$\frac{\mathrm{d}\Phi}{\mathrm{d}t}=\int\frac{\partial f}{\partial t}\left(k_{\mathrm{B}}T\ln f+u(\boldsymbol{x})\right)\mathrm{d}\boldsymbol{x}. \tag{13.24}$$

Substituting $\partial f/\partial t$ drawn from (13.22) in (13.24), one obtains

$$\frac{\mathrm{d}\Phi}{\mathrm{d}t}=-\tau\int\frac{\partial^2 f}{\partial t^2}\left[k_{\mathrm{B}}T\ln f+u(\boldsymbol{x})\right]\mathrm{d}\boldsymbol{x}-D_0\int\frac{1}{f}\left[k_{\mathrm{B}}T\nabla f+(\nabla u(\boldsymbol{x}))\right]^2\mathrm{d}\boldsymbol{x}, \tag{13.25}$$

as is easily seen by integration by parts and assuming that the flux vanishes at the boundaries. The second term in the right-hand side of (13.25) is negative, because the friction coefficient is positive, but the first one has no definite sign. When the relaxation time τ is zero, (13.22) reduces to the Smoluchowski equation and $\mathrm{d}\Phi/\mathrm{d}t$ is definite negative, implying an irreversible behaviour. However, $\mathrm{d}\Phi/\mathrm{d}t$ is not always negative when τ is different from zero, so that it may be claimed that generally the H-theorem is not satisfied.

By analogy with the macroscopic formulation of extended irreversible thermodynamics, we introduce with Camacho and Jou (1992) a generalised entropy S which depends not only on f but also on the probability flux $\boldsymbol{j}$, defined by way of the usual conservation equation

$$\frac{\partial f}{\partial t}+\nabla\cdot\boldsymbol{j}=0. \tag{13.26}$$

The generalised entropy S will now take, instead of (13.23), the form

$$S=-k_{\mathrm{B}}\int\mathrm{d}x[f\ln f+\alpha(f)\boldsymbol{j}^2], \tag{13.27}$$

where $\alpha(f)$ is an undefined coefficient depending on f which will be identified below. The evolution equation for the generalised free energy Φ obtained by using this generalised entropy S is now given by

$$\frac{\mathrm{d}\Phi}{\mathrm{d}t} = \int \left\{ \frac{\partial f}{\partial t} \left[U_{\text{ext}}(x) + k_{\text{B}}T \ln f\right] + k_{\text{B}}T\alpha' j^2(\partial f/\partial t) + 2k_{\text{B}}T\alpha \boldsymbol{j} \cdot \frac{\partial \boldsymbol{j}}{\partial t} \right\} \mathrm{d}\boldsymbol{x}, \tag{13.28}$$

where α' stands for $\mathrm{d}\alpha(f)/\mathrm{d}f$. After integration by parts one obtains

$$\frac{\mathrm{d}\Phi}{\mathrm{d}t} = \int \left\{\boldsymbol{j} \cdot \left[\nabla(U_{\text{ext}}(\boldsymbol{x}) + k_{\text{B}}T \ln f + k_{\text{B}}T\alpha' j^2) + 2k_{\text{B}}T\alpha(\partial \boldsymbol{j}/\partial t)\right]\right\} \mathrm{d}\boldsymbol{x}. \tag{13.29}$$

To preserve the negative character of $\mathrm{d}\Phi/\mathrm{d}t$, it is observed that $\boldsymbol{j}$ cannot be independent of the term inside the brackets; the simplest relation for $\boldsymbol{j}$ is then

$$\boldsymbol{j} = -D\left[\nabla(U_{\text{ext}}(\boldsymbol{x}) + k_{\text{B}}T \ln f + k_{\text{B}}T\alpha' j^2\right] + 2k_{\text{B}}T\alpha(\partial \boldsymbol{j}/\partial t), \tag{13.30}$$

D being a scalar function of $\boldsymbol{x}$ and t. Introducing (13.30) into (13.29) and assuming that the term in j^2 may be neglected in comparison to $\partial \boldsymbol{j}/\partial t$, one recovers (13.22) provided the coefficient α is identified as $\alpha = \tau(2k_{\text{B}}TD_0 f)^{-1}$. This result is important as it shows that it is possible to formulate an H-theorem for the kinetic telegrapher equation at the condition of generalising in a suitable way the Boltzmann expression for the entropy. A formulation of the H-theorem for a generalised master equation involving relaxation terms was also proposed by Vlad and Ross (1993).

Applications of the telegrapher equation in stochastic problems are numerous; let us mention diffusion of light in turbid media, scattering and absorption of laser radiation from biological tissues, heat transport, etc. For example, a telegrapher equation was used by Schweizer (1985) to describe the behaviour of photons in stellar atmospheres. The double-peak structure resulting from the response of (13.13) to a delta-function source may explain that the temporal luminosity profiles observed in many X-ray bursters are composed of a precursor peak and a main diffusion peak.

13.3 Non-Fickian Diffusion in Polymers

Departures from Fick's law are observed in diffusion processes, particularly those involving polymers (Hopfenberg and Stannett 1973; Frisch 1980). Diffusion plays a rate-controlling role in many industrial and biological processes. In particular, it is of interest in dry-spinning of fibres in coating of substrates via deposition and subsequent drying of polymer solutions, and in the design of drug-delivery systems. Long relaxation times have also a great influence on diffusive processes in glasses.

Let us turn our attention to some phenomenological observations. The most common experiments where non-Fickian effects are perceptible are sorption, desorption and permeation of a small solvent in a film or membrane of glassy polymer. The initial concentration of the permeant is suddenly increased (sorption) or decreased (desorption) around the sample, or at one side of it (permeation). The experimental quantities of interest are the mass uptake $m(t)$ per unit surface as a function of time, in sorption and desorption experiments, or the volume throughput $V(t)$ per unit area of membrane, in permeation.

The mass uptake $m(t)$ is defined as the mass of solvent absorbed by the film per unit area, i.e.

$$m(t) = M \int_0^l \mathrm{d}x\, [c(x,t) - c_0], \tag{13.31}$$

where M is the molar mass of the solvent and $c(x,t)$ its concentration, in moles per unit volume, across the film, of thickness l. In permeation, the volume throughput per unit area is

$$Q(t) = \int_0^t \mathrm{d}t' J(t'), \tag{13.32}$$

with J the volume flux of the solvent. Both $m(t)$ and $V(t)$ have been widely studied in the context of the classical diffusion theory (Crank 1975). Specially interesting for our discussion are the short-time limit behaviour of $m(t)$ and the long-time behaviour of $V(t)$, which in the classical Fickian theory are respectively given by (Crank 1975)

$$\frac{m(t)}{m(\infty)} = \left(\frac{16Dt}{\pi l^2}\right)^{1/2}, \tag{13.33}$$

$$V(t) \approx \frac{D(c_1 - c_0)}{l}\left(t - \frac{l^2}{6D}\right) \text{ for } t \to \infty, \tag{13.34}$$

with c_1 and c_0 the concentrations of the solvent on each side of the membrane. It follows that $m(t)/m(\infty)$ behaves as $t^{1/2}$ at short times and that the time lag in permeation, i.e. the time at which $V(t)$ vanishes, behaves as l^2 and is given by $t^* = l^2/(6D)$. It must be kept in mind that these expressions refer to differential sorption and permeation, i.e. they correspond to small changes in concentration, in order to avoid non-linearities arising from the sensitive dependence of D on c.

Expressions (13.33–13.34) are usually satisfied far from the glass transition temperature. Close to the transition, and below it, non-Fickian features appear and manifest themselves through several phenomena: case-II and super-case-II diffusion, which are discussed below, two-stage sorption, sigmoidal sorption, and pseudo-Fickian behaviour.

The physical cause responsible for these peculiar behaviours is usually interpreted as the coupling of viscous stresses and diffusion. During diffusion of small molecules in a polymer solution, this coupling, resulting from the swelling due to the solvent, produces a relative motion between neighbouring chains of the polymer, whose mutual friction will emerge in a viscous stress. Since this stress is coupled to diffusion, it is natural to take it into account in the same way as in Chap. 2 viscous pressure was coupled with heat conduction. Paralleling the developments of Chap. 2, we simply rewrite (2.70–2.72) with the heat flux replaced by the diffusion flux.

The resulting equations are

$$\tau_1 \dot{\boldsymbol{J}} = -(\boldsymbol{J} + \rho D \nabla c) + \beta'' \tilde{D} T \nabla \cdot \overset{0}{\mathbf{P}}{}^v + \beta' \tilde{D} T \nabla p^v, \tag{13.35}$$

$$\tau_0 \dot{p}^v = -(p^v + \zeta \nabla \cdot \boldsymbol{v}) + \beta' T \zeta \nabla \cdot \boldsymbol{J}, \tag{13.36}$$

and

$$\tau_2 (\overset{0}{\mathbf{P}}{}^v)^{\cdot} = -(\overset{0}{\mathbf{P}}{}^v + 2\eta \overset{0}{\mathbf{V}}) + 2\beta' T \eta (\overset{0}{\nabla \boldsymbol{J}})^s, \tag{13.37}$$

where β' and β'' arise from the coupling of diffusion and viscous effects in the expression of the entropy flux, which, in absence of thermal effects, is given by

$$\boldsymbol{J}^s = -\mu T^{-1} \boldsymbol{J} + \beta'' \overset{0}{\mathbf{P}}{}^v \cdot \boldsymbol{J} + \beta' p^v \boldsymbol{J}. \tag{13.38}$$

The last two terms on the right-hand side of (13.38) are non-classical and analogous to those introduced in (2.48); the quantity $\tilde{D}$ in (13.35) stands for $\tilde{D} = \rho D (\partial \mu / \partial c)^{-1}$. For simplicity, and in accordance with the literature, we restrict ourselves to the one-dimensional problem, with only c, J_x, and P_{xx}^v as variables, and ignore the bulk effects ($p^v = 0$); moreover, we assume that $\tau_0 = \tau_2$, $\beta' = \beta'' = \beta$, and that the velocity gradients vanish. After these simplifications, (13.35–13.37) reduce to

$$\tau_1 \dot{J}_x + J_x = -\rho D \frac{\partial c}{\partial x} + \beta \tilde{D} T \frac{\partial P_{xx}^v}{\partial x}, \tag{13.39}$$

$$\tau_2 \dot{P}_{xx}^v + P_{xx}^v = T \beta \eta_l \frac{\partial J_x}{\partial x}, \tag{13.40}$$

with $\eta_l = \frac{4}{3}\eta + \zeta$ the longitudinal viscosity.

It is observed that when the solvent molecules penetrate into the polymer, a sharp advancing boundary is produced between the inner glassy region and the outer swollen gel. The boundary moves with a constant velocity in case-II diffusion, or it accelerates in super-case-II diffusion. The short-time expression for the mass uptake may be expressed generally as $m(t)/m(\infty) \sim t^n$, with $n = 1$ for case-II, $n > 1$ for super-case-II, and $n = \frac{1}{2}$ for the usual Fickian diffusion (Fig. 13.1). Although a well-defined boundary could also appear in classical Fick diffusion with a sufficiently steep variation of the diffusion coefficient with the concentration, such a boundary would advance as $t^{1/(2+n)}$ (if D depends on c as c^n) instead of t. Case-II diffusion has been observed in solutions of methanol in polymethyl methacrylate (PMMA) in the range $0 - 15$°C, in solutions of alkanes in polystyrene in the range $25 - 50$°C, in solutions of benzene in epoxy resins. Super-case-II diffusion has been observed for ethanol, propanol and butanol in thin films of PMMA (Thomas and Windle 1982; Durning and Tabor 1986).

Case-II diffusion can be simply described by means of a Maxwell–Cattaneo equation as obtained from (13.39) with $\beta = 0$. This has been done by Neogi (1983) in the context of non-equilibrium thermodynamics with internal variables. The fractional mass uptake in this model for times longer than l^2/D is given by

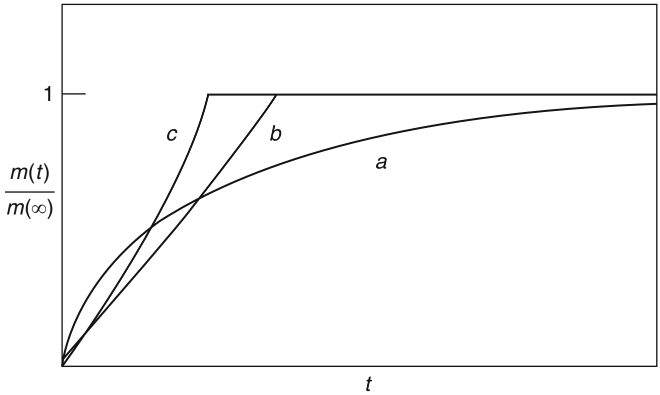


Fig. 13.1 Fractional mass uptake $m(t)/m(\infty)$ as a function of time t for Fickian diffusion (**a**), case-II diffusion (**b**), and super-case-II diffusion (**c**)

Table 13.1 Speeds of fronts in case-II diffusion (Hopfenger et al. 1969; Neogi 1969; Thomas and Windle 1982; Durning and Tabor 1986)

System	Speed (ms^{-1})	$T(°C)$
n-pentane in biaxially oriented polystyrene	1.4×10^{-6}	30
	1.3×10^{-6}	35
n-pentane in cast annealed polystyrene	0.8×10^{-6}	30
	0.7×10^{-6}	35
Benzene in epoxy resins	5.9×10^{-8}	70
Methanol in PMMA	1.0×10^{-9}	24
	1.0×10^{-7}	62

$$\frac{m(t)}{m(\infty)} = \frac{2}{l}\sqrt{\frac{D}{\tau}}t, \qquad t < \frac{l}{2}\sqrt{\frac{\tau}{D}},$$

$$\frac{m(t)}{m(\infty)} = 1, \qquad t > \frac{l}{2}\sqrt{\frac{\tau}{D}}. \tag{13.41}$$

This corresponds to two fronts of solvent advancing from the left and from the right towards the centre of the membrane with speed $(D/\tau)^{1/2}$, which is the speed predicted by the Maxwell–Cattaneo equation. Each front must travel a distance $l/2$ before arriving at the centre. When the fronts collide, they may occasionally clash and give rise to oscillations which die away rapidly. Some characteristic speeds of the fronts in case-II diffusion are given in Table 13.1.

In super-case-II, the front accelerates. This is observed in very thin membranes of the order of 1 mm thickness. The acceleration of the front has been explained by the fact that the differential swelling stress increases when the residual thickness of the core is reduced. Super-case-II diffusion cannot be interpreted from the simple

Maxwell–Cattaneo model, because Maxwell–Cattaneo's equation does not include the coupling between stress and diffusion described by the last term on the right of (13.39).

The set of equations (13.39–13.40) is richer than Maxwell–Cattaneo's law. To show this by means of a simple example, we neglect τ_1 in the evolution equation (13.39) of the diffusion flux and keep the relaxation effects only for the viscous pressure. Under this assumption, (13.39) may be written as

$$J_x = -\tilde{D}\frac{\partial}{\partial x}\left(\mu - T\beta P^v_{xx}\right). \tag{13.42}$$

It is worth comparing this equation with the basic idea underlying the Thomas–Windle theory (1982), one of the most successful models of super-case-II diffusion. These authors assume that the stress P^v_{xx} affects the chemical potential in the same way as an 'osmotic' pressure; in other words, the diffusion originates in the gradient of a non-equilibrium chemical potential given by

$$\mu_i(T, p + P^v_{xx}, c_i) = \mu_{i,\mathrm{eq}}(T, p, c_i) + \int_p^{p+P^v_{xx}} \frac{\partial \mu_i}{\partial p'}\mathrm{d}p' = \mu_{i,\mathrm{eq}}(T, p, c_i) + v_i P^v_{xx}, \tag{13.43}$$

with v_i the partial volume of species i per unit mass. Comparison of (13.42) and (13.43) yields $-T\beta = v_1$, with v_1 the partial volume per unit mass of the solvent.

To close the set of equations, a supplementary relation between P^v_{xx} and J_x is needed. This relation is provided by (13.40), written in the form

$$\tau_2 \dot{P}^v_{xx} + P^v_{xx} = \eta_l v_1 \frac{\partial J_x}{\partial x}. \tag{13.44}$$

In their theory, Thomas and Windle take $\tau_2 = 0$, but this is not consistent because it yields zero transport when η_l is very high, in contrast with experimental observations. To circumvent this difficulty, Durning and Tabor (1986) used (13.44) with τ_2 different from zero. Combining (13.42) and (13.43), they obtain for the diffusion flux

$$J_x = -\rho D\frac{\partial c}{\partial x} - D''\frac{\partial}{\partial x}\int_{-\infty}^{t} \mathrm{d}t' \exp\left[-(t-t')/\tau_2\right]\frac{\partial c}{\partial t'}, \tag{13.45}$$

after using the mass balance $\partial c/\partial t = -\partial J_x/\partial x$ and identifying D'' as $D'' = v_1^2 \tilde{D}\rho\eta_l\tau_2$. Durning and Tabor analysed the consequences of (13.45) in classical and oscillatory sorption. In the context of glassy diffusion, when suitable functions for $D(c)$ and $\eta_l(c)$ are used, relation (13.45) predicts a good agreement with experimental results. All these examples show clearly that EIT provides a useful thermodynamic framework for non-Fickian diffusion.

13.4 Hyperbolic Reaction–Diffusion Systems

Up to now, we have considered that the only process influencing concentration changes is mass transport, eventually coupled with viscous shearing. In some systems, concentration changes may also be due to chemical reactions. Assume, for instance, that a function $F(c)$, generally non-linear, describes the change of particles concentration c per unit time and volume due to chemical reactions. The balance equation is

$$\frac{\partial c}{\partial t} + \nabla \cdot \boldsymbol{J} = F(c), \tag{13.46}$$

where $\boldsymbol{J}$ is the flux of particles, usually given by Fick's law $\boldsymbol{J} = -\rho D \nabla c$. Here, instead, we assume that $\boldsymbol{J}$ satisfies a relaxation equation of the Maxwell–Cattaneo type (13.9). By combining (13.46) and (13.9), one obtains in the one-dimensional case the following non-linear hyperbolic reaction–diffusion equation (HRD) commonly called reaction-telegrapher equation

$$\tau \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + F(c) + \tau \frac{\partial F}{\partial t}. \tag{13.47}$$

The presence of the relaxation time τ does not only influence diffusion (first term on the left-hand side) but also the chemical reaction (two last terms on the right-hand side), in such a way that not only $F(c)$ but also its time derivative has an influence on the evolution of concentration distribution.

Many practical applications of HRD equations can be found in natural systems (Fort and Méndez 2001; Méndez and Fort 1999, 2009). For instance, in the spreading of epidemics, τ is related to the incubation time, which may be comparable or even longer than the time corresponding to the diffusive propagation of the corresponding micro-organisms between neighbouring people. A further example is the propagation of forest fires: τ is the mean ignition time, i.e. the average time needed to set fire from a burning tree to a green tree (Fedotov 1998). Another illustration is found in human migrations, where τ is the time scale between two successive migrations; experimental values obtained from archaeological data for the spread of the Neolithic transition in Europe indicate that $\tau = 25$ years (Méndez and Fort 1999). Hyperbolic Lotka–Volterra equations (e.g. Lebon et al. 2008) are used to describe the interaction between farmers and hunter-gatherers in the expansion of agricultural communities; in this case, τ s the mean generation time and its value is 12.5 years (Cavalli-Sforza 1988). A further example of relaxation effects is the self-inductance of the axon membrane, which contributes with a finite relaxation time to the propagation of action potential in nerves. HRD equations may also be derived from kinetic theory arguments (Méndez and Fort 1999). Thermodynamic properties derived from the kinetic model indicate that the entropy is a function of the concentration and the flux of particles.

Mathematically, HRD equation (13.47) has two homogeneous solutions which are obtained by setting $F(c) = 0$. The resulting solutions are connected by a heteroclinic orbit in the phase space which represents the irreversible process joining two equilibrium states. When reactive processes are coupled to diffusion and both occur on the same time scale, the dynamics of the system is described by a wave front. The speed v of the wave front in the long-time limit is found to be constant, unlike parabolic reaction–diffusion equations, where the speed of the wave front is unbounded. In hyperbolic reaction–diffusion processes, the speed has always upper and lower bounds (Fedotov 1998; Méndez and Fort 1999, 2009)

$$v_L \le v \le (D/\tau)^{1/2}. \tag{13.48}$$

Here we show, by means of a simple argument, how to determine the upper bound (Méndez and Compte 1998). Take a piecewise linear reaction term of the form

$$F(c) = \Omega[-c + H(c - c^*)], \tag{13.49}$$

with Ω the inverse of a reaction time, c^* a given value of the concentration, defining the model and H the Heaviside step function. Shape-preserving wave fronts correspond to similarity solutions of the form $c(x,t) = c(x - vt)$, with v the front speed. Assuming that $c > c^*$ for $x - vt > 0$ and $c < c^*$ for $x - vt < 0$, one may replace $H(c - c^*)$ by $H(x - vt)$, whose Fourier transform is

$$\hat{H}(k,t) = \frac{\exp[-\mathrm{i}kvt]}{\mathrm{i}k}. \tag{13.50}$$

The Fourier transform of (13.47) is then given by

$$\begin{aligned}\tau\frac{\partial^2 \hat{c}(k,t)}{\partial t^2} + (1 + \Omega\tau)\frac{\partial \hat{c}(k,t)}{\partial t} &= -Dk^2\hat{c}(k,t) - \Omega\hat{c}(k,t)\\ &\quad + \Omega\left(\frac{1}{\mathrm{i}k} - \tau v\right)\exp[\mathrm{i}kvt]. \end{aligned}\tag{13.51}$$

In terms of the dimensionless quantities $k^* = k\sqrt{D/\Omega}$, $x^* = x\sqrt{\Omega/D}$, $a = \Omega\tau$ and $v^* = v/\sqrt{\Omega D}$, the solution for the density profile may be finally expressed, after some lengthy calculations, as (Méndez and Compte 1998; Méndez et al. 2009)

$$\begin{aligned}c(x^*) = \frac{1}{2} + H(x^*)&\left[\frac{1}{2} + \left(-\frac{1}{2} + \frac{v^*(1-a)}{2\sqrt{v^{*2}(1-a)^2 + 4}}\right)\exp(m_- x^*)\right]\\ + H(-x^*)&\left[-\frac{1}{2} + \left(\frac{1}{2} + \frac{v^*(1-a)}{2\sqrt{v^{*2}(1-a)^2 + 4}}\right)\exp(m_+ x^*)\right], \end{aligned}\tag{13.52}$$

where

$$m_\pm = \frac{-v^*(1+a) \pm \sqrt{v^{*2}(1-a)^2 + 4}}{2(1 - av^{*2})}. \tag{13.53}$$

The conditions that c must tend to 1 for positive high values of x^* and to zero for large (but negative) values of x^* require, respectively, that $m_- < 0$ and $m_+ > 0$. These restrictions are only fulfilled when $|v^*| \leq 1/\sqrt{a}$, which in terms of the wave speed yields $v \leq \sqrt{D/\tau}$, as given by (13.48). This upper limit for the speed of the front diverges in the parabolic case, when τ vanishes. The upper bound coincides with that obtained for the telegrapher equation in the high frequency limit. Different techniques like linearization around the equilibrium solutions, variational methods, asymptotic analysis and numerical simulations have been used to determine these bounds in more general situations (Méndez and Compte 1998; Méndez and Fort 1999, 2009).

13.5 Thermo-diffusion in Binary Mixtures

In this section, we relax the hypothesis of uniform temperature and focus on the problem of coupling of heat and mass transfer in a binary mixture of Eulerian fluids with respective mass densities ρ_1, ρ_2 and velocities $\boldsymbol{v}_1$, $\boldsymbol{v}_2$. As in the previous sections, the analysis is restricted to a linear approach in the dissipative fluxes. Extensions to more complex situations, as multi-component viscous mixtures, polymeric solutions, and non-linearities will not raise major difficulties.

The space $\mathcal{V}$ of state variables could be selected as $\rho_1, \rho_2, \boldsymbol{v}_1, \boldsymbol{v}_2, u, \boldsymbol{q}$, but a better selection, for practical reasons is

$$\mathcal{V} : \rho,\ c_1,\ u,\ \boldsymbol{v},\ \boldsymbol{q},\ \boldsymbol{J}, \tag{13.54}$$

with $\rho = \rho_1 + \rho_2$ the total mass density, $c_1 = \rho_1/\rho$ the mass fraction of component 1, u the specific internal energy, $\boldsymbol{v} = (\rho_1\boldsymbol{v}_1 + \rho_2\boldsymbol{v}_2)/\rho$ the barycentric velocity, $\boldsymbol{q}$ the heat flux vector, and $\boldsymbol{J} = \boldsymbol{J}_1(= -\boldsymbol{J}_2)$ the mass flux of component 1. In absence of chemical reactions and viscous effects, the variables ρ, c_1, $\boldsymbol{v}$, and u obey the classical balance equations

$$\dot{\rho} = -\rho\nabla\cdot\boldsymbol{v}, \tag{13.55a}$$

$$\rho\dot{c}_1 = -\nabla\cdot\boldsymbol{J}, \tag{13.55b}$$

$$\rho\dot{\boldsymbol{v}} = -\nabla p, \tag{13.55c}$$

$$\rho\dot{u} = -\nabla\cdot\boldsymbol{q} + p\nabla\cdot\boldsymbol{v}. \tag{13.55d}$$

To determine the evolution equations of the flux variables $\boldsymbol{q}$ and $\boldsymbol{J}$, let us start from the generalized Gibbs' relation

$$\dot{s} = T^{-1}\dot{u} - T^{-1}p\,(1/\rho)^{\cdot} - T^{-1}\mu\dot{c} + \frac{\partial s}{\partial \boldsymbol{J}}\cdot\dot{\boldsymbol{J}} + \frac{\partial s}{\partial \boldsymbol{q}}\cdot\dot{\boldsymbol{q}}, \tag{13.56}$$

wherein c, $\boldsymbol{J}$ and μ stand for c_1, $\boldsymbol{J}_1$ and $\mu_1 - \mu_2$ respectively. Let us in addition assume that $\partial s/\partial \boldsymbol{J}$ and $\partial s/\partial \boldsymbol{q}$ are given by the following linear constitutive equations

$$\frac{\partial s}{\partial \boldsymbol{J}} = -\frac{1}{\rho}(\alpha \boldsymbol{J} + \gamma \boldsymbol{q}), \tag{13.57a}$$

$$\frac{\partial s}{\partial \boldsymbol{q}} = -\frac{1}{\rho}(\beta \boldsymbol{q} + \delta \boldsymbol{J}), \tag{13.57b}$$

with $\gamma = \delta$ as a consequence of the equality of the mixed derivatives of s with respect to $\boldsymbol{q}$ and $\boldsymbol{J}$. A more general description including non-linear contributions may be found in Lebon et al. (2003). The phenomenological coefficients α, β, γ and δ may depend on ρ, c and u (or T) but not on the fluxes. Moreover, concavity of entropy s implies that

$$\alpha > 0, \quad \beta > 0, \quad \alpha\beta - \gamma^2 > 0. \tag{13.58}$$

After substitution of the balance equations (13.55) in Gibbs' relation (13.56), one is led to

$$\boldsymbol{J}^s = \frac{1}{T}(\boldsymbol{q} - \mu \boldsymbol{J}), \tag{13.59}$$

$$\sigma^s = -\boldsymbol{q} \cdot \left[-\nabla T^{-1} + \beta \dot{\boldsymbol{q}} + \gamma \dot{\boldsymbol{J}}\right] - \boldsymbol{J} \cdot \left[\nabla(\mu T^{-1}) + \alpha \dot{\boldsymbol{J}} + \gamma \dot{\boldsymbol{q}}\right] \tag{13.60}$$

Expression (13.59) of the entropy flux is the same as that obtained in Chap. 1 in the framework of Classical Irreversible Thermodynamics; the simplest way to guarantee the positiveness of the rate of entropy production (13.60) is to assume that

$$\beta \dot{\boldsymbol{q}} + \gamma \dot{\boldsymbol{J}} - \nabla T^{-1} = -L\boldsymbol{q} - M\boldsymbol{J}, \tag{13.61}$$

$$\alpha \dot{\boldsymbol{J}} + \gamma \dot{\boldsymbol{q}} + \nabla(\mu T^{-1}) = -R\boldsymbol{q} - N\boldsymbol{J}, \tag{13.62}$$

with L, M, N and R allowed to depend on ρ, T and c. After substitution of the evolution equations (13.61) and (13.62) in expression (13.60), it is found that

$$\sigma^s = Lq^2 + NJ^2 + (M + R)\boldsymbol{q} \cdot \boldsymbol{J}, \tag{13.63}$$

from which follows that

$$L > 0, \quad N > 0, \quad LN > \frac{1}{4}(M + R)^2. \tag{13.64}$$

In the Box 13.2, the evolution equations (13.61–13.62) are solved with respect to $\dot{\boldsymbol{q}}$ and $\dot{\boldsymbol{J}}$ respectively. It is shown that these results are closer to Onsager original formulation than these of the classical theory of irreversible thermodynamics (De Groot and Mazur 1962).

Box 13.2 Other expressions for the evolution equations of the fluxes
Solving (13.61) and (13.62) in terms of $\dot{\boldsymbol{J}}$ and $\dot{\boldsymbol{q}}$ and setting $\alpha\beta - \gamma^2 = \Delta > 0$, one obtains after elementary arithmetics

$$\Delta \begin{pmatrix} \dot{\boldsymbol{J}} \\ \dot{\boldsymbol{q}} \end{pmatrix} = \begin{pmatrix} \beta\gamma \\ -\gamma\alpha \end{pmatrix} \begin{pmatrix} \nabla(\mu T^{-1}) \\ \nabla T^{-1} \end{pmatrix} - \begin{pmatrix} N\beta - M\gamma R\beta - L\gamma \\ M\alpha - N\gamma L\alpha - R\gamma \end{pmatrix} \begin{pmatrix} \boldsymbol{J} \\ \boldsymbol{q} \end{pmatrix} \quad (13.2.1)$$

Expressing $\boldsymbol{J}$ and $\boldsymbol{q}$ in terms of the derivatives $\partial s/\partial \boldsymbol{J}$ and $\partial s/\partial \boldsymbol{q}$, it is found in virtue of (13.57) that

$$\begin{pmatrix} \boldsymbol{J} \\ \boldsymbol{q} \end{pmatrix} = \frac{\rho}{\Delta} \begin{pmatrix} -\beta & \gamma \\ \gamma & -\alpha \end{pmatrix} \begin{pmatrix} \partial s/\partial \boldsymbol{J} \\ \partial s/\partial \boldsymbol{q} \end{pmatrix}. \quad (13.2.2)$$

Moreover, recalling that $\mu T^{-1} = -\partial s/\partial c$, $T^{-1} = \partial s/\partial u$, relation (13.2.1) can be cast in the form

$$\begin{pmatrix} \dot{\boldsymbol{J}} \\ \dot{\boldsymbol{q}} \end{pmatrix} = \frac{1}{\Delta} \begin{pmatrix} \beta\gamma \\ -\gamma\alpha \end{pmatrix} \nabla \begin{pmatrix} \partial s/\partial c \\ \partial s/\partial u \end{pmatrix}$$
$$- \frac{\rho}{\Delta^2} \begin{pmatrix} -N\beta^2 - L\gamma^2 + \beta\gamma(R+M) & -M\gamma^2 - R\alpha\beta + \gamma(\alpha L + \beta N \\ -R\gamma^2 - M\alpha\beta + \gamma(L\alpha + M\beta) & -N\gamma^2 - L\alpha^2 + \alpha\gamma(R+M) \end{pmatrix}$$
$$\begin{pmatrix} \partial s/\partial \boldsymbol{J} \\ \partial s/\partial \boldsymbol{q} \end{pmatrix}. \quad (13.2.3)$$

This expression is interesting as it is reminiscent of the flux–force relation introduced by Onsager in his original papers of 1931. It is indeed confirmed by (13.2.3) that the thermodynamic fluxes in Onsager's acception, i.e. the time derivatives of the state variables $\boldsymbol{J}$ and $\boldsymbol{q}$ are linearly related to the thermodynamic fluxes defined, by Onsager, as the derivatives of entropy with respect to the same variables. According to Onsager, the matrix of the phenomenological coefficients relating these fluxes and forces are symmetric, from which follows $M = R$. It is worth stressing that the arguments leading to this symmetry relation parallels faithfully Onsager's original demonstration and that, in that respect, it can be claimed that EIT is closer to Onsager's approach than Classical Irreversible Thermodynamics, wherein the definition of fluxes and forces is different from that proposed by Onsager's.

In absence of coupling term in Gibbs' relation (13.56), i.e. for $\gamma = 0$, the evolution equations take the simplified form

$$\begin{pmatrix} \dot{\boldsymbol{J}} \\ \dot{\boldsymbol{q}} \end{pmatrix} = \begin{pmatrix} \frac{1}{\alpha} & 0 \\ 0 & \frac{1}{\beta} \end{pmatrix} \begin{pmatrix} \nabla(\frac{\partial s}{\partial c}) \\ \nabla(\frac{\partial s}{\partial u}) \end{pmatrix} + \rho \begin{pmatrix} \frac{1}{\alpha\tau_J} & \frac{R}{\alpha\beta} \\ \frac{M}{\alpha\beta} & \frac{1}{\beta\tau_q} \end{pmatrix} \begin{pmatrix} \frac{\partial s}{\partial \boldsymbol{J}} \\ \frac{\partial s}{\partial \boldsymbol{q}} \end{pmatrix}, \quad (13.2.4)$$

with $\tau_J = \alpha/N$ and $\tau_q = \beta/L$ designating the positive relaxation times. If we represent by $\mathcal{F}$ and $\mathcal{C}$ the state spaces of fluxes $(\boldsymbol{J}, \boldsymbol{q})$ and of classical variables (c, u) respectively, we are in position to write the evolution equations (13.2.4) in the more compact form

$$\dot{\boldsymbol{\mathcal{F}}} = \mathbf{L} \cdot \nabla \left(\frac{\partial s}{\partial \mathcal{C}} \right) + \mathbf{M} \cdot \frac{\partial s}{\partial \boldsymbol{\mathcal{F}}}. \qquad (13.2.5)$$

The factors **L** and **M** represent respectively a skew-symmetric and a symmetric matrix of the phenomenological coefficients. It is important to note that the time evolution of the flux variables can be expressed in terms of one single thermodynamic potential, here the specific entropy s. A similar conclusion was reached in the GENERIC formulation of non-equilibrium thermodynamics (see Sect. 1.5).

Let us close this section with some considerations about steady flows. Solving the set (13.61) and (13.62) with respect to $\boldsymbol{J}$ and $\boldsymbol{q}$ yields the linear Soret and Dufour laws

$$\boldsymbol{J} = -L_{JJ} \nabla(\mu T^{-1}) - L_{Jq} \nabla T^{-1}, \qquad (13.65)$$

$$\boldsymbol{q} = -L_{qq} \nabla T^{-1} - L_{qJ} \nabla(\mu T^{-1}), \qquad (13.66)$$

wherein the transport coefficients L_{JJ}, L_{Jq}, L_{qq} and L_{qJ} are defined as follows:

$$L_{JJ} = \frac{L}{\Delta'}, \; L_{Jq} = \frac{R}{\Delta'}, \; L_{qq} = \frac{N}{\Delta'}, \; L_{qJ} = \frac{M}{\Delta'}, \qquad (13.67)$$

with Δ' given by $\Delta' = NL - MR \geq 0$. In virtue of Onsager's reciprocal relation $M = R$, it is found that $L_{Jq} = L_{qJ}$ expressing the equality between the Soret and the Dufour coefficients.

13.6 Suspensions of Solid Particles in Fluids

In some regards, suspensions can be considered as molecular mixtures in which the solute molecules are replaced by solid particles of supra-molecular size. Thus, the description of suspensions is often an extension of the corresponding one for molecular mixtures. In particular significant progresses have been achieved in the recent years to develop a description containing the Fick, Soret and Dufour laws as limiting cases. This was accomplished for instance within the internal variables approach (Maugin 1999; Lhuillier 2000). Here a different approach based on EIT is proposed: the drift flux of particles is upgraded to the status of state variable and the corresponding evolution equation is established. Its final form is rather complex and its physical meaning is clarified by addressing to the two-fluid model of suspensions (Nigmatulin 1990).

13.6.1 Suspensions Versus Molecular Diffusion

Suspensions of particles in fluids behave in some aspects like a binary mixture of solute molecules in a solvent. However, the particle size is much larger than the molecular size and this has two main consequences. First, the volume of a particle is a well-defined quantity while the volume of a molecule is not. The description of suspensions will involve not only the particle mass fraction $c(= \mathrm{d}M_\mathrm{p}/\mathrm{d}M)$, but also their volume fraction $\phi_\mathrm{p}(= \mathrm{d}V_\mathrm{p}/\mathrm{d}V)$. These two quantities are related by

$$\rho c = \phi_\mathrm{p}\rho_\mathrm{p}, \tag{13.68}$$

where $\rho(= \mathrm{d}M/\mathrm{d}V)$ is the total mass per unit volume of the suspension, also given by

$$\rho = \phi_\mathrm{p}\rho_\mathrm{p} + (1 - \phi_\mathrm{p})\rho_\mathrm{f}, \tag{13.69}$$

$\rho_\mathrm{f}\,(= \mathrm{d}M_\mathrm{f}/\mathrm{d}V_\mathrm{f})$ is the mass per unit volume of pure fluid and $\rho_\mathrm{p}\,\left(= \mathrm{d}M_\mathrm{p}/\mathrm{d}V_\mathrm{p}\right)$ is the mass per unit volume of the material from which the particles are made. The second main difference between suspensions and molecular mixture is the large inertia of a particle and the relative ease with which the average particle velocity $\boldsymbol{v}_\mathrm{p}$ be different from the average fluid velocity $\boldsymbol{v}_\mathrm{f}$, hence the importance of the particle diffusion flux

$$\boldsymbol{J} = \rho c(\boldsymbol{v}_\mathrm{p} - \boldsymbol{v}) = \rho c(1 - c)(\boldsymbol{v}_\mathrm{p} - \boldsymbol{v}_\mathrm{f}). \tag{13.70}$$

Moreover, to describe the suspension, one will use not only the well-known mass-weighted $\boldsymbol{v}$ velocity but also the volume-weighted velocity $\boldsymbol{u}$ defined respectively as

$$\boldsymbol{v} = c\boldsymbol{v}_\mathrm{p} + (1 - c)\boldsymbol{v}_\mathrm{f}, \tag{13.71}$$

$$\boldsymbol{u} = \phi_\mathrm{p}\boldsymbol{v}_\mathrm{p} + (1 - \phi_\mathrm{p})\boldsymbol{v}_\mathrm{f}. \tag{13.72}$$

It is not difficult to convince oneself of the relations

$$\phi_\mathrm{p} = c + \rho c\,(1 - c)\left(\frac{1}{\rho_\mathrm{p}} - \frac{1}{\rho_\mathrm{f}}\right), \tag{13.73}$$

$$\boldsymbol{u} = \boldsymbol{v} + \left(\frac{1}{\rho_\mathrm{p}} - \frac{1}{\rho_\mathrm{f}}\right)\boldsymbol{J}, \tag{13.74}$$

showing that ϕ_p and $\boldsymbol{u}$ are generally different from c and $\boldsymbol{v}$, respectively, except for the special case of matched densities between the fluid and the particles. We will consider an isotropic suspension of spherical and rigid particles moving in a Newtonian fluid.

13.6.2 EIT Description of Suspensions

Suspensions of rigid and spherical particles behave like a Newtonian fluid and the viscous pressure does not display any non-standard feature. Moreover, the scale of thermal effects is of the order of 10^4 smaller than that of the diffusion and this justifies that heat flux will not be considered as an independent variable, and the temperature T will denote the local equilibrium temperature. The only new relevant variable is therefore the particle drift flux $\boldsymbol{J}$, and the generalized Gibbs' equation can be cast in the form

$$T\mathrm{d}s = \mathrm{d}u + p\mathrm{d}\rho^{-1} - \mu\mathrm{d}c - \alpha\boldsymbol{J}\cdot\mathrm{d}\boldsymbol{J}, \tag{13.75}$$

wherein $\mu = \mu_{\mathrm{p}} - \mu_{\mathrm{f}}$ is the relative chemical potential and $\alpha(\rho, T, c)$ a positive coefficient in order to satisfy the local equilibrium stability requirement. As a consequence of (13.75), the generalised pressure and chemical potential are defined as

$$p^* = p_{\mathrm{eq}} - \frac{1}{2}\frac{\partial\alpha}{\partial(1/\rho)}\boldsymbol{J}^2, \tag{13.76}$$

$$\mu^* = \mu_{\mathrm{eq}} + \frac{1}{2}\frac{\partial\alpha}{\partial c}\boldsymbol{J}^2. \tag{13.77}$$

In the above results and throughout this section, the subscript eq will be attached to local equilibrium quantities depending on u (or T), ρ, and c but not on $\boldsymbol{J}$.

The total density, mass fraction, momentum and internal energy balance laws are written in the usual form,

$$\dot{\rho} = -\rho\nabla\cdot\boldsymbol{v}, \tag{13.78}$$

$$\rho\dot{c} = -\nabla\cdot\boldsymbol{J}, \tag{13.79}$$

$$\rho\dot{\boldsymbol{v}} = -\nabla\cdot\boldsymbol{\Pi}, \tag{13.80}$$

$$\rho\dot{u} = -\nabla\cdot\boldsymbol{q} - \prod : \nabla\boldsymbol{v}, \tag{13.81}$$

where $\prod$ stands for the symmetric pressure tensor. Combining the above equations for the standard state variables together with the extended Gibbs relation (13.75), one obtains the balance of entropy in the usual form

$$\rho\dot{s} + \nabla\cdot\boldsymbol{J}^s = \sigma^s \geq 0, \tag{13.82}$$

with the rate of dissipated energy $T\sigma^s$ given by

$$T\sigma^s = \nabla\cdot(T\boldsymbol{J}^s + \mu\boldsymbol{J} - \boldsymbol{q}) - \boldsymbol{J}^s\cdot\nabla T - (\boldsymbol{\Pi} - p\mathbf{U}) : \nabla\boldsymbol{v} - \boldsymbol{J}\cdot\left(\nabla\mu + \rho\alpha\dot{\boldsymbol{J}}\right) \geq 0. \tag{13.83}$$

To obtain a more pertinent expression for the entropy production rate, and to deduce the restrictions placed by the second law $\sigma^s \geq 0$, one needs assumptions concerning the way the relative motion enters into the undetermined fluxes $\prod$ and $\boldsymbol{q}$. Taking into account their well-known expressions for molecular mixtures and suspensions (Lhuillier 1995), together with simple symmetry and dimensional considerations, one is led to propose:

$$\prod = \boldsymbol{\tau} + p\mathbf{U} + \gamma \boldsymbol{J}\boldsymbol{J}, \tag{13.84}$$

The constitutive equation for $\boldsymbol{q}$ will be derived at the end of this sub-section. Concerning the entropy flux, we suggest expressing it in the general form

$$\boldsymbol{J}^s = \frac{1}{T}\left[(\boldsymbol{q} - \mu\boldsymbol{J}) - \delta\boldsymbol{\tau}\cdot\boldsymbol{J} - \kappa\boldsymbol{\tau}^{\mathrm{d}}\cdot\boldsymbol{J}\right], \tag{13.85}$$

where $\boldsymbol{\tau}$ and $\boldsymbol{\tau}^{\mathrm{d}}$ are two viscous pressure tensors. The global convective motion of the mixture is influenced by $\boldsymbol{\tau}$ while the relative motion will be seen to be influenced by both $\boldsymbol{\tau}$ and $\boldsymbol{\tau}^{\mathrm{d}}$. Expression (13.84) of the total pressure tensor is a generalization of the classical mechanical pressure tensor given by the two first terms of the right-hand side. Relation (13.85) of the entropy flux contains the classical contribution (the two terms between parentheses) and extra terms arising from the coupling of the fluxes and the pressure tensors, typical of the EIT formalism. A large indeterminacy is left in the above two expressions, through three arbitrary scalars, γ, δ and κ which may depend on the specific volume, the temperature and the particle mass fraction. With (13.84) and (13.85) taken for granted, the entropy production rate finally appears in the standard form of a sum of products of fluxes and thermodynamic forces:

$$\begin{aligned}T\sigma^s = &-\boldsymbol{\tau} : \nabla(\boldsymbol{v} + \delta\boldsymbol{J}) - \boldsymbol{\tau}^{\mathrm{d}} : \nabla(\delta\boldsymbol{J}) - \boldsymbol{J}\cdot\Big[\nabla\mu^* + \rho\alpha\dot{\boldsymbol{J}} + \delta\nabla\cdot\boldsymbol{\tau} \\ &+\kappa\nabla\cdot\boldsymbol{\tau}^{\mathrm{d}} + \gamma\boldsymbol{J}\cdot\nabla\boldsymbol{v} + \tfrac{1}{2}\alpha_v(\nabla\cdot\boldsymbol{v})\boldsymbol{J}\Big] - \boldsymbol{J}^s\cdot\nabla T \geq 0,\end{aligned} \tag{13.86}$$

where α_v stands for $\partial(\alpha)/\partial(1/\rho)$. The viscous dissipation involves the gradients of the two velocities $v + \delta\boldsymbol{J}$ and $\kappa\boldsymbol{J}$, suggesting to write for τ and τ^{d}:

$$\boldsymbol{\tau} = -\eta_1\left[\nabla(v + \delta\boldsymbol{J})\right]^{\mathrm{sym}}, \tag{13.87}$$

$$\boldsymbol{\tau}^{\mathrm{d}} = -\eta_2[\nabla(\kappa\boldsymbol{J})], \tag{13.88}$$

wherein η_1 and η_2 are viscosity coefficients. It is important to realize that, in contrast with pure Newtonian fluids, $\boldsymbol{\tau}$ in (13.87) is no longer given by Newton's law $\boldsymbol{\tau} = -\eta\nabla\boldsymbol{v}$. By writing (13.87–13.88) we have omitted the coupling between $\boldsymbol{\tau}$ (respectively $\boldsymbol{\tau}^{\mathrm{d}}$) and $\nabla(\kappa\boldsymbol{J})$ (respectively $\nabla(\boldsymbol{v} + \delta\boldsymbol{J})$).

From expression (13.86) of the rate of dissipated energy, one is led to write the entropy flux and the general evolution equations for the particles diffusion flux respectively as

$$\boldsymbol{J}^s = -\frac{\lambda}{T}\nabla T - \omega_1 \boldsymbol{J}, \tag{13.89}$$

$$\rho\alpha\dot{\boldsymbol{J}} + \frac{1}{2}\alpha_v(\nabla\cdot\boldsymbol{v})\boldsymbol{J} + \gamma(\boldsymbol{J}\cdot\nabla)\boldsymbol{v} + \delta\nabla\cdot\boldsymbol{\tau} + \kappa\nabla\cdot\boldsymbol{\tau}^{\mathrm{d}} + \nabla\mu = -\omega_2\nabla T - \xi\boldsymbol{J}, \tag{13.90}$$

λ, ω_1, ω_2 and ξ are phenomenological coefficients whose physical meaning will become clear in the foregoing. In virtue of Onsager–Casimir's reciprocal relations, one has $\omega_1 = -\omega_2 \equiv \omega$ with a sign minus because of the opposite parities of $\boldsymbol{J}^s$ and $\dot{\boldsymbol{J}}$ with respect to time reversal. Concerning the coefficient α, it is interesting to express it in terms of the relaxation time τ_m of the diffusion flux through

$$\frac{\rho\alpha}{\xi} = \tau_m. \tag{13.91}$$

Expression (13.90) is the main result of the analysis, as it provides the lacking evolution equation of the extra flux variable. After substitution of (13.89) and (13.90) in expression (13.86) of the rate of dissipated energy, it is found that

$$T\sigma^s = \eta_1\boldsymbol{\tau} : \boldsymbol{\tau} + \eta_2\boldsymbol{\tau}^{\mathrm{d}} : \boldsymbol{\tau}^{\mathrm{d}} + \xi\boldsymbol{J}\cdot\boldsymbol{J} + \frac{\lambda}{T}\nabla T\cdot\nabla T \geq 0. \tag{13.92}$$

It follows that the four dissipative coefficients η_1, η_2, ξ and λ are positive but no restriction is placed on the sign of ω. Besides ξ and ω, the evolution equation (13.90) of $\boldsymbol{J}$ depends on four arbitrary parameters: α which was introduced in Gibb's equation (13.75) and the three parameters γ, δ and κ appearing in (13.84) and (13.85). In case all coefficients except ξ vanish, the evolution equation (13.90) boils down to

$$\boldsymbol{J} = -\frac{1}{\xi}\nabla\mu - \frac{\omega}{\xi}\nabla T. \tag{13.93}$$

Comparing the above relations with Soret's law it is directly seen that $1/\xi$ can be identified as the coefficient of diffusion and ω/ξ as the coefficient of thermal diffusion. For isothermal processes one recovers the Fick law $\boldsymbol{J} = -\rho D\nabla c$ with the diffusion coefficient $\rho D = (\partial\mu/\partial c)_T/\xi$. A further comparison of both expressions (13.85) and (13.89) of $\boldsymbol{J}^s$ leads to the missing constitutive equation for the heat flux vector $\boldsymbol{q}$, namely

$$\boldsymbol{q} = -\lambda\nabla T + (\mu - \omega_1 T)\boldsymbol{J} + (\delta\boldsymbol{\tau} + \kappa\boldsymbol{\tau}^{\mathrm{d}})\cdot\boldsymbol{J}. \tag{13.94}$$

In absence of matter motion ($\boldsymbol{J} = 0$), one finds back Fourier's law from which is inferred that λ can be identified with the heat conductivity.

To summarize, the basic relations of the model are the five evolution equations (13.78–13.81) and (13.90) coupled with the constitutive relations (13.84), (13.94), (13.87), (13.88) for $\prod$, $\boldsymbol{q}$, $\boldsymbol{\tau}$ and $\boldsymbol{\tau}^{\mathrm{d}}$ respectively. To complete the description, one needs to formulate the remaining unknown quantities α, γ, κ and δ in terms of the state variables, this will be achieved in the next sub-section by comparing with other models.

13.6.3 Comparison with Other Models

A few models exist in the literature which end with an expression for the time-evolution of the relative particle flux $\boldsymbol{J}$. As will be seen, they are all particular cases of the general result (13.90).

13.6.3.1 Internal Variables Theory

The internal variables approach has been used to study non-Fickian diffusion in suspensions (e.g. Lhuillier 1995).The new state variable is the relative velocity $\boldsymbol{v}_{\mathrm{p}} - \boldsymbol{v}_{\mathrm{f}}$ and the starting point is the following expression for the specific free energy

$$\phi(\rho, T, c, v_p - v_f) = \phi_{\mathrm{eq}}(\rho, T, c) + \Delta\phi, \tag{13.95}$$

where $\Delta\phi = \frac{1}{2}c(1-c)(\boldsymbol{v}_p - \boldsymbol{v}_f)^2$ is that part of the free energy that depends only on the internal variable. The expressions of the momentum and entropy fluxes were found to be

$$\boldsymbol{\Pi} = p\mathbf{U} + (\boldsymbol{v}_{\mathrm{p}} - \boldsymbol{v}_{\mathrm{f}})\boldsymbol{J} + \boldsymbol{\tau}, \tag{13.96}$$

$$\boldsymbol{J}^s = \frac{1}{T}\left[\boldsymbol{q} - \mu\boldsymbol{J} - (\boldsymbol{u} - \boldsymbol{v})\cdot\boldsymbol{\tau} - (\boldsymbol{v}_{\mathrm{p}} - \boldsymbol{v}_{\mathrm{f}})\cdot\boldsymbol{\tau}^{\mathrm{d}}\right], \tag{13.97}$$

where $\boldsymbol{u}$ is the average velocity defined in (13.72). The $(\boldsymbol{u} - \boldsymbol{v})\cdot\boldsymbol{\tau}$ contribution to $\boldsymbol{J}^s$ is necessary because it is wanted that the viscous dissipation involves the gradient of $\boldsymbol{u}$ (and not the gradient of $\boldsymbol{v}$), a result well-known in the theoretical modelling of suspensions (Brenner 1970). Comparing the above expressions with (13.84), (13.85) and the Gibbs equation (13.75) written in terms of the free energy ϕ, it is not difficult to check that the internal variable approach leads to the particular values

$$\rho\alpha = \gamma = \kappa = \frac{1}{\rho c(1-c)}, \quad \delta = \frac{1}{\rho_{\mathrm{p}}} - \frac{1}{\rho_{\mathrm{f}}}. \tag{13.98}$$

Introducing these values in (13.96), one obtains the evolution equation for $\boldsymbol{J}$ as it would be derived from the evolution equation obtained for $\boldsymbol{v}_{\mathrm{p}} - \boldsymbol{v}_{\mathrm{f}}$ within the internal variables model. Remember also that the above results correspond to a rather special assumption concerning $\Delta\phi$, and it would be interesting to know what happens in a more general case.

To shed further light on the model described by the evolution relation (13.90), we address to the well-known two-fluid model of suspensions.

13.6.3.2 The Two-Fluid Model

Although the view point of the two-fluid model is rather different than the EIT model, we find it interesting to confront both approaches. Besides the conservation of the overall momentum, the two-fluid model of suspensions introduces the momentum balance for the particulate phase, i.e. the average equation of motion for the particles. This couple of equations is written as (e.g. Nigmatulin 1990; Lhuillier 1995)

$$\rho\dot{\boldsymbol{v}} = -\nabla p - \nabla\cdot\boldsymbol{\tau}, \tag{13.99}$$

$$\rho c\frac{\mathrm{d}_\mathrm{p}\boldsymbol{v}_\mathrm{p}}{\mathrm{d}t} = -\phi(\nabla p + \nabla\cdot\boldsymbol{\tau}) + \boldsymbol{F}^\mathrm{d} - \nabla\cdot\boldsymbol{\tau}^\mathrm{d} + \boldsymbol{F}. \tag{13.100}$$

In the momentum balance (13.100), there appears the particle acceleration $\mathrm{d}_\mathrm{p}\boldsymbol{v}_\mathrm{p}/\mathrm{d}t = (\partial/\partial t + \boldsymbol{v}_\mathrm{p}\cdot\nabla)\boldsymbol{v}_\mathrm{p}$. The forces exerted by the fluid on the particles have three different origins: (i) a generalized Archimedes force proportional to the particles volume fraction, and depending on the pressure p and the suspension viscous stress τ, (ii) a dissipative force and stress written as $\boldsymbol{F}^\mathrm{d} - \nabla\cdot\boldsymbol{\tau}^\mathrm{d}$, and (iii) a non-dissipative force $\boldsymbol{F}$.

From the definition $\boldsymbol{J} = \rho c(\boldsymbol{v}_\mathrm{p} - \boldsymbol{v})$, we derive the following identity

$$\frac{\partial\boldsymbol{J}}{\partial t} + \nabla\cdot(\boldsymbol{v}_\mathrm{p}\boldsymbol{J}) + (\boldsymbol{J}\cdot\nabla)\boldsymbol{v} \equiv \rho c\left(\frac{d_\mathrm{p}\boldsymbol{v}_\mathrm{p}}{\mathrm{d}t} - \dot{\boldsymbol{v}}\right). \tag{13.101}$$

Making use of the two-fluid momentum equations (13.99) and (13.100), one transforms this identity into an evolution equation for $\boldsymbol{J}$ given by

$$\begin{aligned}\dot{\boldsymbol{J}} + (\nabla\cdot\boldsymbol{v})\boldsymbol{J} + (\boldsymbol{J}\cdot\nabla)\boldsymbol{v} + \nabla\cdot\left(\frac{\boldsymbol{J}\boldsymbol{J}}{\rho c}\right) - c\nabla\cdot\left(\frac{\boldsymbol{J}\boldsymbol{J}}{\rho c(1-c)}\right)\\ + (\phi_\mathrm{p} - c)(\nabla p + \nabla\cdot\boldsymbol{\tau}) - \boldsymbol{F} - \boldsymbol{F}^\mathrm{d} + \nabla\cdot\boldsymbol{\tau}^\mathrm{d} = 0\end{aligned} \tag{13.102}$$

A mere comparison with the EIT result (13.90) reveals that $\boldsymbol{\tau}$ and $\boldsymbol{\tau}^\mathrm{d}$ correspond to the previously defined tensors (hence the same notation), that the friction force is

$$\boldsymbol{F}^\mathrm{d} = -\frac{\boldsymbol{J}}{\tau_\mathrm{m}}, \tag{13.103}$$

and, finally, that the non-dissipative fluid-particles force $\boldsymbol{F}$ can be written as

$$\boldsymbol{F} = -\rho c(1-c)\left[\nabla\mu + \omega\nabla T - \left(\frac{1}{\rho_\mathrm{p}} - \frac{1}{\rho_\mathrm{f}}\right)\nabla p\right]. \tag{13.104}$$

The difference between (13.102) and evolution equation (13.90) is the absence of terms in $\nabla\cdot\boldsymbol{J}\boldsymbol{J}$. This is so because we have neglected terms of third order in $(\boldsymbol{J}\boldsymbol{J})\cdot\boldsymbol{J}$ in the constitutive equation (13.85) of the entropy flux. Let us further comment on expression (13.104) of $\boldsymbol{F}$. From the classical Gibbs energy per unit mass $g = u - Ts + p/\rho$ and its differential form $\mathrm{d}g = (1/\rho)\mathrm{d}p - s\mathrm{d}T + \mu\mathrm{d}c$, one obtains

$$\nabla\mu + \omega\nabla T - \left(\frac{1}{\rho_\mathrm{p}} - \frac{1}{\rho_\mathrm{f}}\right)\nabla p$$
$$= \frac{\partial\mu}{\partial c}\nabla c + \left(\omega - \frac{\partial s}{\partial c}\right)\nabla T + \left(\frac{\partial(1/\rho)}{\partial c} - \frac{1}{\rho_\mathrm{p}} + \frac{1}{\rho_\mathrm{f}}\right)\nabla p. \tag{13.105}$$

Since $1/\rho = c/\rho_p + (1-c)/\rho_f$, the ∇p contribution to the osmotic force $\boldsymbol{F}$ vanishes if ρ_p and ρ_f do not depend on c, which is the usual case actually. With regard to the ∇T contribution, it will give rise to a thermal force driving the particles towards hotter or colder regions depending on the sign of $\omega - \partial s/\partial c$, which is usually small. Concerning the ∇c contribution to the osmotic force, it always drives the particles towards regions with a lower particle concentration because $(\partial\mu/\partial c)_{p,T} > 0$ is a condition of thermodynamic stability. In short, the non-dissipative force $\boldsymbol{F}$ includes an important concentration-diffusion force, a rather small thermo-diffusion force, and a negligibly small baro-diffusion force. Note that EIT and the two-fluid model are complementary. From one side, the two-fluid model has benefited from the expressions (13.103) and (13.104) provided by EIT. Conversely, the two-fluid model is essential in interpreting the evolution equation (13.90) of EIT in terms of the simpler momentum equations (13.99) and (13.100).

The most important EIT contribution is embodied in the evolution equations (13.90) for the diffusion flux $\boldsymbol{J}$. This expression, when coupled to the classical balance laws of total mass, particle mass fraction, momentum and energy, determine the time evolution of the selected state variables. To our knowledge, it is the first time that a systematic thermodynamic analysis of matter transport in disperse media is proposed. The several undetermined transport coefficients appearing in (13.90) are identified by comparing with the theory of internal variables and Classical Irreversible Thermodynamics. We were able to express all the parameters in terms of well-known quantities, like heat conductivity, diffusion and thermo-diffusion coefficients, and relaxation times. A new expression of the non-dissipative part of the force exerted by the fluid on the particles has been derived. Nevertheless, it should be realized that the above model is a rather simplified version. Indeed, the suspension particles are supposed to be rigid without deformations, third and higher order contributions in the fluxes have been omitted, and the heat flux $\boldsymbol{q}$ is not considered as an independent variable, but is given by (13.94). Recently, Lebon et al. (2007) have proposed a more complete analysis incorporating $\boldsymbol{q}$ as independent variable.

13.7 Microstructure in Rapid Solidification of Binary Alloys

The microstructure of solid systems, as for instance binary alloys, depends on the solidification velocity. Recent advanced technologies in rapid solidification of metallic systems have allowed to investigate undercooling far below the equilibrium solidification temperature. Under this condition, the classical theories, based on local equilibrium, lead to several contradictions with experiments. To mention some of them (Galenko 2004): (i) when the interface velocity V increases, the solute boundary layer near the interface shrinks below physically acceptable values, (ii) the so-called solute partition function $k(V)$ (defined below) is found to depart radically from experimental data, and (iii) the models of dendritic solidification predict a smooth growth of the solidification velocity with increase of undercooling instead of the abrupt change observed in alloys.

These contradictions can be avoided by taking explicitly into account relaxation effects of the diffusion flux. These effects become particularly relevant in rapid solidification processes of metallic liquids when the interface velocity V is or the order or even higher that the diffusion speed $V_D = (D/\tau)^{1/2}$ in the bulk liquid.

The set of governing equations are the usual balance laws of concentration and temperature, namely

$$\tau\frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = D\nabla^2 c, \tag{13.106}$$

$$\frac{\partial T}{\partial t} = \chi\nabla^2 T, \tag{13.107}$$

wherein the relaxation time of the heat flux has been assumed to be negligible, and c is the mass concentration of the dilute component. Moreover, in rapid solidification, one has to add the specific relations (e.g. Galenko 2004)

$$-a_L\nabla T_L + a_S\nabla T_S = T_Q V, \tag{13.108}$$

$$-D_L\nabla c_L = -(c_L - c_S)V + \tau\frac{\partial}{\partial t}\left[(c_L - c_S)V\right], \tag{13.109}$$

$$T_I = T_M + \Omega(V)c_L + d(\alpha)k(V) - V/\mu(\alpha), \tag{13.110}$$

$$c_S = k(V)c_L, \tag{13.111}$$

in these equations, V is the solidification velocity in the direction normal to the interface, T_Q is the adiabatic solidification temperature, defined by $T_Q = Q/c_p$ with Q the latent heat of solidification and c_p the specific heat at constant pressure, T_M is the equilibrium solidification temperature, indexes L and S stand for the liquid and solid phases respectively, and $T_I = T_L = T_S$ is the interface temperature, $d(\alpha)$ and $\mu(\alpha)$ are the anisotropic capillary and anisotropic kinetic coefficients defined by

$$d(\alpha) = d_0(1 + \varepsilon_c\cos 4\alpha), \quad \mu(\alpha) = \mu_0(1 - \varepsilon_k\cos 4\alpha), \tag{13.112}$$

with d_0 the capillary length, μ_0 the averaged kinetic coefficient of growth, ε_c and ε_k are the strengths of crystalline anisotropy, and α the angle between the normal to the interface and the direction of growth. The function $k(V)$ represents the non-equilibrium solute partition coefficient

$$k(V) = \frac{(1 - V^2/V_D^2)k_e + V/V_{DI}}{(1 - V^2/V_D^2)[1 - (1 - k_e)C_L] + V/V_{DI}} \quad \text{for } V < V_D, \tag{13.113a}$$

$$k(V) = 1 \text{ for } V > V_D, \tag{13.113b}$$

where k_e is the coefficient for equilibrium solute partitioning, and V_{DI} the diffusion speed at the interface; finally, the function $\Omega(V)$ is the slope of the liquidus line in the kinetic phase diagram, given by

$$\Omega(V) = \frac{\Omega_e}{1 - k_e}\left\{[1 - k(V)]\left[1 - \ln\frac{k(V)}{k_e}\right] + [1 - k(V)]\left[\ln\frac{k(V)}{k_e} + [1 - k(V)]\frac{V}{V_D}\right]\right\}, \tag{13.114}$$

where Ω_e is the liquidus line slope in the equilibrium phase diagram of a binary system.

The system of equations (13.106–13.114) has been solved for planar and non-planar rapidly moving interfaces by Galenko (2004). The results indicate that an interface moving with velocity V equal or higher than the diffusion speed V_D is not able to modify the concentration, and the solidification proceeds without any solute redistribution ahead of the interface.

Equations (13.106–13.114) have also been used (Galenko and Danilov 2000; Galenko 2004) to investigate morphological transitions during rapid solidification of alloys. The changing of the interface morphology with the interface velocity is important, for instance, for single-phase solidification, i.e. when the liquid transforms into solid without precipitation of additional phases. Figure 13.2 shows schematically the solid–liquid interface morphologies for different values of the interface velocity V. At small velocities, the initially smooth interface remains planar up to a critical velocity V_C, defined by a criterion of constitutional undercooling (Kurz and Fisher 1992). Beyond V_C, the smooth interface becomes unstable and the interface exhibits a steady cellular morphology. By further increasing the velocity, this morphology becomes unstable and dendritic patterns develop, when the thickness of the solute diffusion layer ahead of the interface is large enough to produce secondary branches due to morphological instability of the cellular interfaces, as

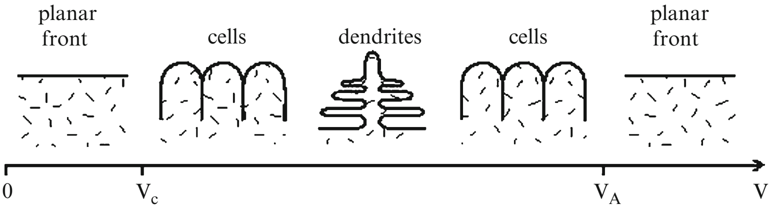


Fig. 13.2 Morphological diagram for solidification of binary systems (reprinted with permission from Galenko P, Danilov DA (2004) Phys Rev E 69:051608)

shown in Fig. 13.3a. At higher interface velocity, dendritic patterns degenerate into the form of rapidly moving cells, when the solute diffusion layer ahead of the interface becomes thinner (Fig. 13.3b). For velocities larger than a critical value V_A, the interface becomes planar again, and this morphology remains absolutely stable. Figure 13.3c shows the degeneration of cellular arrays into a plane interface. This happens when the width of the diffusional layer becomes shorter than the radius of the tip of the dendrites or cells. Figure 13.3c and d represent planar interfaces, but under two different situations. Figure 13.3c corresponds to a speed higher than V_A but lower than the solute diffusion speed V_D. In this case, the solidification proceeds by chemical partition mechanism, meaning that the chemical composition of the solid phase is different from that of the liquid phase, the relation between both is given by the partition coefficient. In contrast, Fig. 13.3d corresponds to a propagation speed V higher than V_D; in this case the progression is so fast that there is no time left for solute diffusion ahead of the interface, and solidification with the initial composition of the liquid occurs.

The transition from diffusion-limited to diffusionless growth of crystals shown in Fig. 13.3c–d can be quantitatively described from expression (13.113) of the solute partitioning coefficient. Figure 13.4 shows that the predictions of Eq. (13.113) are in good agreement with experimental data on non-equilibrium solute partition in solidification of Si–As alloys. Note the abrupt transition from diffusion-limited to diffusionless growth of crystals at $V = V_D$.

Concerning non-isothermal crystal growth, a first explanation of the transitions was proposed by Kurz and Fisher (1992) using classical models of dendritic growth, but these models predict a smooth transition, in contradiction with experiments, which show a rather sharp change in the behaviour of dendrite velocity and dendrite tip radius (Herlach et al. 1997). The occurrence of this sharp break at $V = V_D$ is reflected from the model described by Eqs. (13.106–13.114). The solution of these equations (Galenko and Danilov 1999) predicts that the transition from diffusion-limited to diffusionless growth happens at $V = V_D$, and that is characterized by an abrupt change of the slope of the dendrite tip velocity versus undercooling (see Fig. 13.5) The same property is observed with the dendrite tip radius (Galenko and Danilov 1999).

13.8 Problems

13.1. *Molecular diffusion*: Examine the problem of molecular diffusion in a binary mixture of viscous fluids described by Newton's law $\mathbf{P} = -2\eta\nabla\boldsymbol{v}$ in the framework of EIT. Compare with the results of Sect. 13.1.

13.2. *Anomalous diffusion*: In usual diffusion, the second moments of the displacement in the long-time limit behave as $\langle(\Delta x)^2\rangle \approx t$. In several situations, one finds instead $\langle(\Delta x)^2\rangle \approx t^{2/\delta}$. If $\delta < 2$ this behaviour is called super-diffusive and if $\delta > 2$ it is called sub-diffusive (Bouchaud JP, Georges A (1990) Phys Rep 195:127; Sahimi M (1993) Rev Mod Phys 65:1393). Anomalous

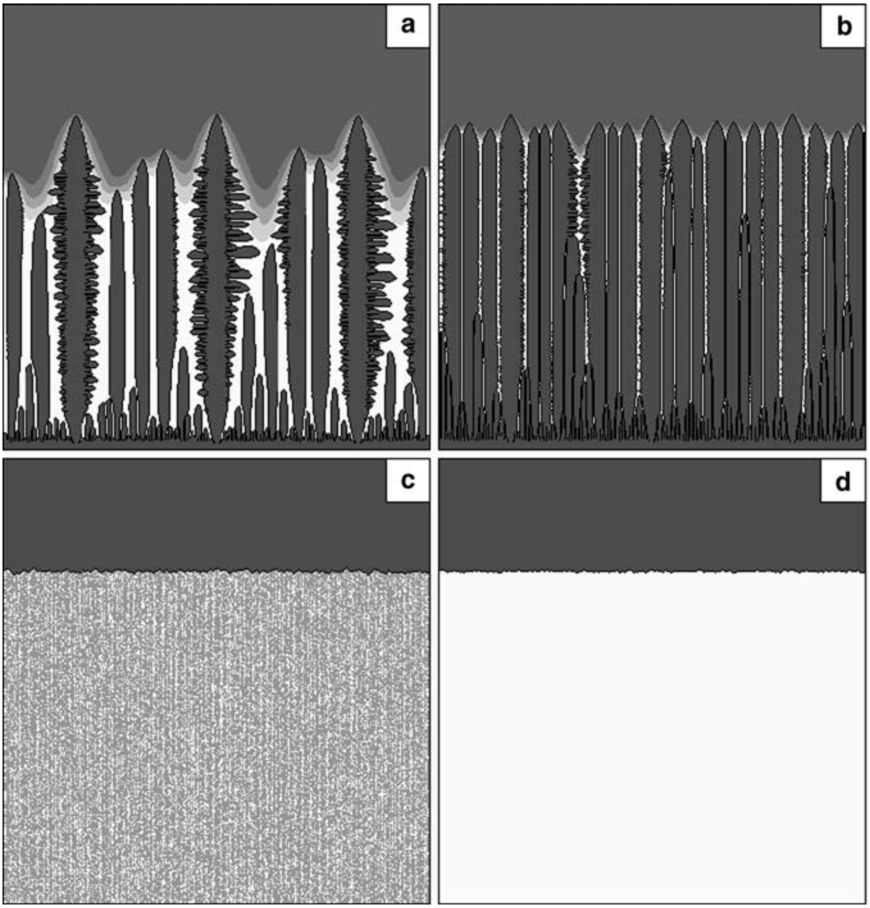


Fig. 13.3 Isothermal 2D solidification of Cu–30 at.% Ni alloy (reprinted with permission from Galenko P, Krivilyov MV (2000) Model Simul Mater Sci Eng 8:81): (**a**) dendritic patterns, (**b**) dense cellular structure, (**c**) almost chemically partitionless solidification at $V_A < V < V_D$ (grey colour in solid indicates a concentration C_s different from the initial one C_0), (**d**) diffusionless solidification at $V > V_D$

diffusion, may arise if the stochastic motions are characterized either by a wide distribution of waiting times, or of jumping lengths, in contrast to the usual Brownian motion, which is characterized by a very narrow distribution of waiting times and jumping lengths. (a) Show that a behaviour $\langle(\Delta x)^2\rangle \approx t^3$ may arise if one assumes an equation of the form $\partial c/\partial t = D(x,t)\partial^2 c/\partial x^2$ with $D(x,t) \approx x^a t^b$ and $3a + 2b = 4$. (b) Generalise this result for $\langle(\Delta x)^2\rangle \approx t^{2/\delta}$.

13.3. Another way to describe anomalous diffusion is to start from an equation of the form $\partial c/\partial t = D\partial^2 c^{q-1}/\partial x^2$. (a) Show that the solution of this equation with an initial delta condition has the form $c(x,t) = t^{-1/q} f(\xi)$ with

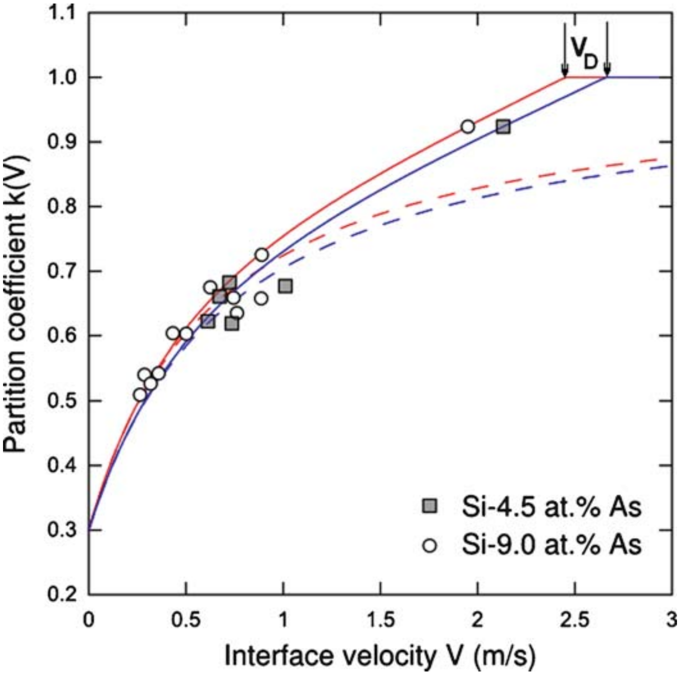


Fig. 13.4 Solute partition coefficient $k(V)$ versus interface velocity V for experimental data on solidification of Si–As alloys Arrows indicate the values of the solute diffusion velocities $V = V_D$ for both alloys. The dashed lines show the predictions by the model of Aziz and Kaplan (1988) based on local equilibrium hypothesis with $V_D \to \infty$ in Eq. (13.113). The solid lines correspond to the complete Eq. (13.113) (reprinted with permission from Galenko P (2007) Phys Rev E 76:031606)

$\xi = t^{-1/q}x$ and thus yields $\langle \Delta x^2 \rangle \approx t^{2/(q-1)}$. (b) Show that for $q = 2$, $f(\xi) = K \exp[-\xi^2/4D]$, that for $q > 2$, $f(\xi) = B(A^2 - \xi^2)^{1/(q-2)}$, and for $q < 2$, $f(\xi) = B(A^2 + \xi^2)^{-1/(2-q)}$ with A and B constants which depend on the value of q.

13.4. *Two-layer model and the telegrapher equation*: The so-called two-layer model consists of a system whose particles jump at random between two states, 1 and 2, having associated velocities $v_1 = v$ and $v_2 = -v$ respectively along the x axis. Assume that the rate R of particle exchange between the two states per unit time and length is proportional to the difference of the probability densities P_1 and P_2, i.e. $R = r(P_1 - P_2)$. Show that the evolution equations for the total probability density $P = P_1 + P_2$ and for the probability flux $J = (P_1 - P_2)v$ are respectively

$$\frac{\partial P}{\partial t} + \frac{\partial J}{\partial x} = 0,$$
$$\tau \frac{\partial J}{\partial t} + J = -D \frac{\partial P}{\partial x},$$

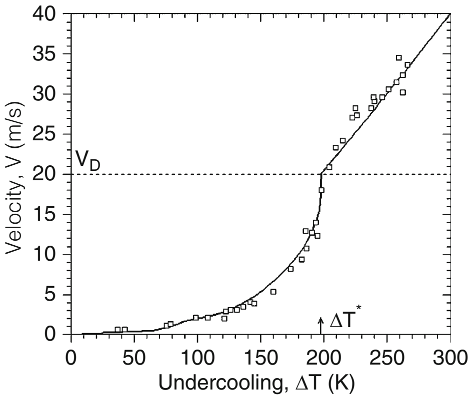


Fig. 13.5 Dendrite tip velocity versus undercooling in Cu–30 at.% Ni alloy (*solid curve*). Experimental data (*open squares*) are taken from Herlach et al. (1999) (reprinted with permission from Galenko P, Danilov DA (1997) Phys Lett A 235:271)

with $\tau = 1/(2r)$ and $D = v^2\tau$ (see Van den Broeck C (1990) Physica A 168:677; Camacho J, Zakari M (1994) Phys Rev E 50:4233).

13.5. Derive (13.21) from (13.20) and obtain the explicit expressions for the coefficients appearing in (13.21), which are $a_i\,(i \text{ odd}) = (i!)^{-1}(\Delta t)^{i+1}$, $a_i\,(i \text{ even}) = (i!)^{-1}(\Delta t)^i(2\tau - \Delta t)$, $b_i = [(2j)!]^{-1}(\Delta x)^{2j}(2\tau - \Delta t)$.

13.6. *Fast solidification fronts*: In fast solidification of alloys the relaxational aspects of diffusion must be taken into account when the velocity v of the front separating the solid and liquid phases is comparable or higher than the diffusion speed $v_D = (D/\tau_D)^{1/2}$, where D is the diffusion coefficient and τ_D the relaxation time of the diffusion flux (Galenko, Danilov (2000a, b)). As an illustration of he influence of the finite value of v_D (in contrast with the classical parabolic situation where $\tau_D = 0$ v_D diverges), consider $k(v)$, the partition coefficient of the solute, defined by the ratio of concentrations of solute in the solid and the liquid phases, given by (13.113). Estimate the difference between the equilibrium partition coefficient k_e and $k(v)$ in a 3% Ag–Cu alloy and a 10% Ni–Fe alloy where

Alloy	k_e	v_D (m s^{-1})	v_{DI} (m s^{-1})
Ag–Cu	0.44	10	10
Ni–Fe	0.21	37	25

for wavefronts at $v = 5\,\text{m s}^{-1}$ and $v = 15\,\text{m s}^{-1}$ (the velocity v of the wavefront depends on the degree of undercooling with respect to the melting point).

13.7. Assume the hyperbolic reaction–diffusion equation (13.47), with a source term given by $F(c) = \Omega f(c)$, where Ω is the inverse of a reaction time. Use the dimensionless variables proposed in Sect. 13.5, namely, $t^* = \Omega t$, $x^* = x(\Omega/D)^{1/2}$ and $a = \Omega\tau$, and consider $\partial f/\partial t = f'(c)\partial c/\partial t$ with

$f'(c) = \partial f/\partial t$. Assume a concave positive reaction term with $f(c = 0) = f(c = 1) = 0$ and a traveling wavefront $c(x - vt)$, with v the speed of the front. (a) Show that the front will satisfy

$$(1 - av^2)\frac{\partial^2 c}{\partial z^2} + v\left[1 - af'(c)\right]\frac{\partial c}{\partial z} + f(c) = 0,$$

with $z = x - vt$. (b) Linearize this equation around $c = 0$ and assume solutions of the form $c \cong \exp(\lambda z)$. Show that the positiveness of n requires that

$$v \geq v_L = \frac{2\sqrt{f'(0)}}{1 + af'(0)}.$$

(c) Obtain this lower bound for the logistic source term $f(c) = c(1 - c)$ (Méndez, Fort, Farjas (1999)).

13.8. *Suspensions*: Repeat the analysis of the suspensions model presented in Sect. 13.6.2 by introducing the heat flux $\boldsymbol{q}$ among the set of independent variables (Lebon G et al. 2009).

Chapter 14
Electrical Systems and Micro-devices Modelization

This chapter is devoted to the analysis of electrical phenomena. After establishing the generalised equations for electrical transport, we analyse in the first section the second moments of the current fluctuations in non-equilibrium steady states, and discuss the crossed terms which link fluxes and forces. In the second section, we revisit Onsager's reciprocal relations and observe that the formalism of extended irreversible thermodynamics (EIT) is closer to Onsager's original treatment than classical irreversible thermodynamics (CIT), as already mentioned in Box 13.2.

In the next sections, we discuss two topics of practical interest: charge transport in submicronic electronic devices and dielectrical relaxation in fluids. Recent descriptions of charge transport in submicronic electronic devices have opened a promising field of application for EIT. Indeed, although the carrier transport can be described by means of the Boltzmann equation, to solve it is a very difficult task and, furthermore, it contains more information than needed in practical applications. Therefore, it is common in practice to consider a reduced number of moments, which are directly related with density, charge flux, internal energy, energy flux and so on, and which are measurable and controllable variables. This kind of approach is referred to as a hydrodynamical model and EIT is very helpful in determining which truncations of the hierarchy of the evolution equations for the moments are compatible with thermodynamics. Such a modelization is of considerable interest in practical applications as it allows obtaining the temperature and velocity profiles in microelectronic devices in very short times, say a few seconds in comparison with several hours or even weeks required by Monte-Carlo simulations. Finally, we briefly discuss another problem of practical interest in materials sciences: dielectric relaxation in liquids in the range of high frequencies. From a theoretical point of view, this analysis is illuminating as it serves to illustrate the relations between EIT and the thermodynamics with internal variables.

14.1 Electrical Systems: Evolution Equations

We consider here electric conduction in a rigid metallic sample. We assume that the electric current is due to the motion of electrons with respect to the lattice. The independent variables for this problem in CIT are the internal energy per unit mass

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_14,

u and the charge per unit mass, z_e; in EIT, the electric current $\boldsymbol{i}$ is selected as an additional independent variable. For the system under study, the balance equations of charge and internal energy read

$$\rho \dot{z}_e = -\nabla \cdot \boldsymbol{i}, \tag{14.1a}$$

$$\rho \dot{u} = -\nabla \cdot \boldsymbol{q} + \boldsymbol{i} \cdot \boldsymbol{E}, \tag{14.1b}$$

respectively, with $\boldsymbol{E}$ the electric field and $\boldsymbol{i} \cdot \boldsymbol{E}$ the Joule heating term. In order to find the evolution equation for $\boldsymbol{i}$ we proceed by analogy with Sect. 13.1.

Ignoring heat transport for the moment, the generalised Gibbs equation takes the form (Jou et al. 1982)

$$\mathrm{d}s = T^{-1}\mathrm{d}u - T^{-1}\mu_e \mathrm{d}z_e - \alpha \boldsymbol{i} \cdot \mathrm{d}\boldsymbol{i}, \tag{14.2}$$

with μ_e being the chemical potential of electrons and α a phenomenological coefficient independent of $\boldsymbol{i}$. Equation (14.2) leads, by following the same procedure as in Sect. 13.1, to the evolution equation for $\boldsymbol{i}$:

$$\tau_e \frac{\mathrm{d}\boldsymbol{i}}{\mathrm{d}t} = -(\boldsymbol{i} - \sigma_e \boldsymbol{E}'), \tag{14.3}$$

where $\boldsymbol{E}' = \boldsymbol{E} - T\nabla(T^{-1}\mu_e)$, τ_e is the relaxation time, and σ_e the electrical conductivity, provided that α in (14.2) is identified as $\alpha = \tau_e(\rho\sigma_e T)^{-1}$. The generalised entropy is now given by

$$\rho s = \rho s_{\mathrm{eq}} - \frac{\tau_e}{2\sigma_e T} \boldsymbol{i} \cdot \boldsymbol{i}. \tag{14.4}$$

Equation (14.3) generalises the usual Ohm law $\boldsymbol{i} = \sigma_e \boldsymbol{E}$ and is often used in plasma physics and in the analysis of high-frequency currents (Krall and Trivelpiece 1973) but without any reference to its thermodynamic context. Expression (14.3) has also been obtained in the kinetic theory in the linearized relaxation-time approximation.

Relation (14.3) can similarly be derived from the simplest model of ionic conduction in a dilute solution. Consider a system with a number density n of ions of charge q, mass m and apparent radius r moving in a fluid of viscosity η; the current density is then given by $\boldsymbol{i} = nq\boldsymbol{v}$, $\boldsymbol{v}$ being the drift velocity of ions. By supposing that the number of ions is much smaller than the number of neutral solvent particles, the barycentric velocity of the system is practically zero. Assuming that the resistive force is given by Stokes' law $F = 6\pi\eta r v$ with η the dynamic viscosity, one recovers (14.3), with

$$\sigma_e = nq^2(6\pi\eta r)^{-1} \text{ and } \tau_e = m(6\pi\eta r)^{-1}.$$

When these results are introduced in expression (14.4), one obtains

$$\rho s = \rho s_{\mathrm{eq}} - \tfrac{1}{2} n m v^2 T^{-1}, \tag{14.5}$$

which indicates that the effect of the current is to reduce the equilibrium entropy by an amount equal to the kinetic energy of ions divided by the absolute temperature.

If instead of particles with the same radius, they have different radii distributed according to a law $f(r)$, then the current density takes the form

$$\boldsymbol{i}(t) = \int_0^\infty \mathrm{d}r f(r) q \boldsymbol{v}(r,t), \tag{14.6}$$

with q the charge of each particle and $\boldsymbol{v}$ the drift velocity of particles of radius r. After sudden suppression of the electrical field $\boldsymbol{E}$, the current $\boldsymbol{i}$ will decay due to the viscosity of the solvent. According to the Stokes law, the decrease of $\boldsymbol{i}$ is given by

$$\boldsymbol{i}(t) = \int_0^\infty \mathrm{d}r f(r) q \boldsymbol{v}_{ss}(r) \exp[-t/\tau(r)], \tag{14.7}$$

where $\boldsymbol{v}_{ss} = q\boldsymbol{E}(6\pi\eta r)^{-1}$ is the steady-state drift velocity and $\tau(r)$ is the relaxation time of the particles, given by $\tau(r) = m(r)(6\pi\eta r)^{-1} \approx r^2$. Writing $\boldsymbol{v}_{ss}$ in terms of the steady state flux $\boldsymbol{i}(0) = \sigma_e \boldsymbol{E}$, relation (14.7) becomes

$$\boldsymbol{i}(t) = \boldsymbol{i}(0) \int_0^\infty \mathrm{d}r f(r) q^2 (6\pi\eta r \sigma_e)^{-1} \exp[-t/\tau(r)]. \tag{14.8}$$

Before proceeding further, we recall some mathematical results. Let us define a function of time $\chi(t)$ by

$$\chi(t) = \int_0^\infty \mathrm{d}x g(x) \exp[-t/\tau(x)],$$

with $\tau(x) = \tau_0 x^s$ and $g(x) \approx x^m \exp(-cx)$, where s, m and c are numerical constants. Application of the saddle-point method shows that at sufficiently long times, $\chi(t)$ behaves as

$$\chi(t) \approx \exp[-(t/\tau_0)^{1/(1+s)}]. \tag{14.9}$$

Transposing this result to (14.8) with $\tau(r) \approx r^2$ and $f(r)$ given by $f(r) \approx r^m \exp(-cr)$, it is found that $\boldsymbol{i}(t)$ decays as

$$\boldsymbol{i}(t) = \boldsymbol{i}(0) \exp[-(t/\tau)^{1/3}]. \tag{14.10}$$

The interesting result is that $\boldsymbol{i}(t)$ does not decay as a single exponential, but rather as a stretched exponential owing to the presence of the exponent $1/(1+s)$. Such a form of decay is known under the name of the Kohlrausch or Williams–Watts law. This behaviour is not unusual in physics; it generally arises in phenomena described by a hierarchy of variables with relaxation times obeying a scaling law (Schlesinger 1988; Jou and Camacho 1990). The above example was treated to make explicit that EIT is not restricted to simple exponentials, but that it can also cope with more general situations. The corresponding generalised entropy is now given by

$$s = s_{\mathrm{eq}} - \frac{1}{2T}\int_0^\infty \mathrm{d}r f(r) \frac{\tau(r)}{\sigma_e(r)} q\boldsymbol{v}(r) \cdot q\boldsymbol{v}(r). \tag{14.11}$$

Another interesting consequence of expression (14.3) can be drawn from the following example. Consider the alternating electric field $E = E_0 \cos(\omega t)$ acting on the system. The electric current solution of (14.3) has the form

$$i = i_1 \cos \omega t + i_2 \sin \omega t, \tag{14.12}$$

with $i_1 = \sigma_e(1+\omega^2\tau^2)^{-1}E_0$ and $i_2 = \sigma_e\omega\tau_e(1+\omega^2\tau^2)^{-1}E_0$. In CIT the entropy production is given by $\sigma^s_{\mathrm{CIT}} = T^{-1}\boldsymbol{i} \cdot \boldsymbol{E}$, and in our example by

$$\sigma^s_{\mathrm{CIT}} = \frac{\sigma_e}{T} \frac{\cos^2 \omega t + \omega\tau_e \cos\omega t \sin\omega t}{1+\omega^2\tau_e^2} E_0^2. \tag{14.13}$$

The denominator is always positive but not necessarily the numerator. At low frequencies, the first term in the numerator overcomes the second one and the classical entropy production is positive, but at high frequencies the second term dominates, and σ^s_{CIT} becomes negative in each cycle in a given time interval. Note that the average of (14.13) over a cycle is positive. Thus, at sufficiently high frequencies, the classical expression for the second law is instantaneously violated, but not on the average. In contrast, the entropy production as obtained from EIT is always positive, since its expression is

$$\sigma^s_{EIT} = (T\sigma_e)^{-1} i^2,$$

which is unconditionally positive.

The second moments of the fluctuations of the electric current density $\boldsymbol{i}$ are easily derived from the Gibbs' equation (14.2). Its second differential, at constant electron density, is

$$\delta^2 s = -\left(\frac{1}{c_v T^2} + \frac{1}{2}\frac{\partial^2\alpha}{\partial u^2} i_0^2\right)(\delta u)^2 - \alpha\delta\boldsymbol{i} \cdot \delta\boldsymbol{i} - 2\frac{\partial\alpha}{\partial u}\boldsymbol{i}_0 \cdot \delta u \delta\boldsymbol{i}, \tag{14.14}$$

where c_v is the specific heat capacity at constant volume, $\boldsymbol{i}_0$ the mean electric current, and α stands for $\tau_e v (T\sigma_e)^{-1}$. Introduction of (14.14) into the Einstein formula (5.5) for the probability of fluctuations yields the second moments of the fluctuations in presence of a mean electric current $\boldsymbol{i}_0$:

$$\langle \delta i_x \delta i_x \rangle = \frac{k_{\mathrm{B}} T \sigma_e}{\tau_e v}\left[1 + \frac{c_v T^2}{\alpha}\left(\frac{\partial\alpha}{\partial u}\right)^2 i_0^2\right]. \tag{14.15}$$

In (14.15) it is assumed that $\boldsymbol{i}_0$ is directed along the x axis. In equilibrium, $\boldsymbol{i}_0 = 0$ and one obtains

$$\langle \delta i_x \delta i_x \rangle = \frac{k_\mathrm{B} T \sigma_e}{\tau_e v}, \tag{14.16}$$

which is the Green–Kubo expression for the electrical conductivity in the case of an exponential decay of the fluctuations of the current. This result is analogous to expressions (5.19) for the fluctuations of the heat flux and the viscous pressure. Equation (14.16) is also related to the well-known Nyquist formula for current fluctuations, as it gives the fluctuations in terms of the electrical resistance.

Relation (14.16) allows one to express σ_e in terms of τ_e. Indeed, the microscopic operator for the density current is $\boldsymbol{i} = \int e\boldsymbol{C} f \,\mathrm{d}\boldsymbol{C}$ with $\boldsymbol{C}$ being the peculiar velocity and e the electron charge, from which follows that the second moments of $\boldsymbol{i}$ are, both in classical and in Fermi–Dirac statistics, $\langle \delta i_x \delta i_x \rangle = ne^2 k_\mathrm{B} T (m\,v)^{-1}$. One thus recovers the well-known Drude relation, $\sigma_e = (ne^2/m)\tau_e$, from which follow that $\alpha = (Tn^2e^2)^{-1}$. When this result is introduced into relation (14.15), together with the expressions $\mathrm{d}u = c_v \mathrm{d}T$ and $\boldsymbol{i}_0 = \sigma_e \boldsymbol{E}$, one finds that

$$\langle \delta i_x \delta i_x \rangle = \frac{k_\mathrm{B} T \sigma_e}{\tau_e v} \left[1 + \frac{Te^2}{m^2 c} \left(\frac{E\tau}{T} \right)^2 \right]. \tag{14.17}$$

The non-equilibrium correction can be evaluated by recalling that the heat capacity per unit mass for an electron gas in Fermi–Dirac statistics is $c = \pi^2 k_\mathrm{B}^2 T (2m\varepsilon_\mathrm{F})^{-1}$, with ε_F the Fermi energy. Defining a mean free path ℓ as $\ell = \tau_e v_\mathrm{F}$, with v_F the Fermi velocity $v_\mathrm{F} = (2\varepsilon_\mathrm{F}/m)^{1/2}$, one may write (14.17) as

$$\langle \delta i_x \delta i_x \rangle = \frac{k_\mathrm{B} T \sigma_e}{\tau_e v} \left[1 + \pi^{-2} \left(\frac{eE\ell}{k_\mathrm{B} T} \right)^2 \right]. \tag{14.18}$$

This expression is comparable to the result obtained from the kinetic theory of gases (Tremblay and Vidal 1982), which predicts a coefficient 0.156 instead of $\pi^{-2} (= 0.101)$ in front of the non-equilibrium corrections.

The generalised Gibbs equation (14.2) has also been used to analyse the statistics of open and closed pores in simple models of biological membranes; this is an interesting topic in biophysics (de Felice 1981; Jou et al. 1986) and is explicitly treated in this last reference (see Problem 14.1). Furthermore, more elaborated versions of EIT including higher-order fluxes have been applied to transport problems in semiconductors, as shown in Sect. 14.3

14.2 Cross Terms in Constitutive Equations: Onsager's Relations

Amongst the most important features of classical non-equilibrium thermodynamics are the Onsager reciprocal relations; as repeatedly recalled, they cannot be obtained from purely macroscopic arguments alone, but only with the help of supplementary hypotheses, such as the time-reversal symmetry of equilibrium correlation functions and linear regression of fluctuations. It is natural to ask whether the formalism of EIT is able to shed a new light on Onsager's relations. As expected, it turns out that Onsager's results remain outside the scope of macroscopic thermodynamics but, notwithstanding this observation, the EIT formulation is closer to the original Onsager derivation than that of classical non-equilibrium thermodynamics (Llebot et al. 1983).

Consider a rigid and isotropic body, crossed by a heat flux $\boldsymbol{q}$ and an electric flux $\boldsymbol{i}$. The generalised Gibbs equation has the form

$$\begin{aligned} \mathrm{d}s = T^{-1}\mathrm{d}u - \mu_e T^{-1}\mathrm{d}z_e - (\rho T)^{-1}(\alpha_{11}\boldsymbol{q} + \alpha_{12}\boldsymbol{i}) \cdot \mathrm{d}\boldsymbol{q} \\ -(\rho T)^{-1}(\alpha_{21}\boldsymbol{q} + \alpha_{22}\boldsymbol{i}) \cdot \mathrm{d}\boldsymbol{i}\,. \end{aligned} \tag{14.19}$$

In virtue of the balance equations (14.1a and b) for u and z_e, one obtains for the entropy balance

$$\begin{aligned} \rho\frac{\mathrm{d}s}{\mathrm{d}t} + \nabla\cdot\left(\frac{1}{T}\boldsymbol{q} - \frac{\mu_e}{T}\boldsymbol{i}\right) = \boldsymbol{q}\cdot\left(\nabla T^{-1} - \frac{\alpha_{11}}{T}\frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} - \frac{\alpha_{21}}{T}\frac{\mathrm{d}\boldsymbol{i}}{\mathrm{d}t}\right) \\ +\boldsymbol{i}\cdot\left(\frac{\boldsymbol{E}}{T} - \nabla\frac{\mu_e}{T} - \frac{\alpha_{12}}{T}\frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} - \frac{\alpha_{22}}{T}\frac{\mathrm{d}\boldsymbol{i}}{\mathrm{d}t}\right), \end{aligned} \tag{14.20}$$

from which follow immediately the expressions of the entropy flux $\boldsymbol{J}^s$ and the entropy production σ^s. The entropy production, given by the right-hand side of (14.20), has still the structure of a bilinear form. To obtain the simplest evolution equations for $\boldsymbol{q}$ and $\boldsymbol{i}$ compatible with a definite positive entropy production, one assumes linear relations between the thermodynamic forces and the fluxes $\boldsymbol{q}$ and $\boldsymbol{i}$. This results in

$$\nabla T^{-1} - \frac{\alpha_{11}}{T}\frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} - \frac{\alpha_{21}}{T}\frac{\mathrm{d}\boldsymbol{i}}{\mathrm{d}t} = \mu'_{11}\boldsymbol{q} + \mu'_{12}\boldsymbol{i}\,, \tag{14.21a}$$

$$\frac{\boldsymbol{E}}{T} - \nabla\frac{\mu_e}{T} - \frac{\alpha_{12}}{T}\frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} - \frac{\alpha_{22}}{T}\frac{\mathrm{d}\boldsymbol{i}}{\mathrm{d}t} = \mu'_{21}\boldsymbol{q} + \mu'_{22}\boldsymbol{i}\,, \tag{14.21b}$$

with $\mu'_{11} \geq 0$, $\mu'_{22} \geq 0$, and $\mu'_{11}\mu'_{22} \geq \frac{1}{4}(\mu'_{12}+\mu'_{21})^2$, as a consequence of $\sigma^s > 0$.

To show that the matrix of the coefficients $\boldsymbol{\mu}'$ is symmetric, we start from Onsager's original result (Sect. 5.6) stating that if the evolution equations are given by $\mathrm{d}\boldsymbol{\beta}/\mathrm{d}t = \mathbf{L}\cdot(\partial S/\partial\boldsymbol{\beta})$, then $\mathbf{L}$ is a symmetric matrix. Let us assume that ∇T^{-1} and $\boldsymbol{E}T^{-1} - \nabla(\mu_e T^{-1})$ vanish in (14.21), so that they refer to fluctuations near an equilibrium state. Then, (14.21) can be presented in the form

$$\begin{pmatrix} \mathrm{d}\boldsymbol{q}/\mathrm{d}t \\ \mathrm{d}\boldsymbol{i}/\mathrm{d}t \end{pmatrix} = T(\boldsymbol{\alpha}^T)^{-1}\cdot\boldsymbol{\mu}'\cdot\begin{pmatrix} \boldsymbol{q} \\ \boldsymbol{i} \end{pmatrix}. \tag{14.22a}$$

This expression may be rewritten in terms of the derivatives of the generalised entropy (14.19) with respect to $\boldsymbol{q}$ and $\boldsymbol{i}$ as

$$\begin{pmatrix} \mathrm{d}\boldsymbol{q}/\mathrm{d}t \\ \mathrm{d}\boldsymbol{i}/\mathrm{d}t \end{pmatrix} = \rho T^2 \left[(\boldsymbol{\alpha}^T)^{-1} \cdot \boldsymbol{\mu}' \cdot \boldsymbol{\alpha}^{-1} \right] \begin{pmatrix} \partial S/\partial \boldsymbol{q} \\ \partial S/\partial \boldsymbol{i} \end{pmatrix}. \tag{14.22b}$$

According to Onsager's results, the matrix $\mathbf{L} = (\boldsymbol{\alpha}^T)^{-1} \cdot \boldsymbol{\mu}' \cdot \boldsymbol{\alpha}^{-1}$ is symmetric. Since $\boldsymbol{\alpha}$ is symmetric, because it is the matrix of the second derivatives of S, it follows that $\boldsymbol{\mu}' = \boldsymbol{\alpha} \cdot \mathbf{L} \cdot \boldsymbol{\alpha}$ is itself symmetric. In contrast, the matrix $\boldsymbol{\tau}$ of the relaxation times, given by $\boldsymbol{\tau} = (T\boldsymbol{\mu}')^{-1} \cdot \boldsymbol{\alpha}$ is generally not symmetric.

In non-equilibrium steady states, (14.21) may be compared with the usual phenomenological equations (De Groot and Mazur 1962) expressing the coupling between thermal and electrical effects and given by

$$\nabla T^{-1} = \frac{1}{\lambda T^2} \boldsymbol{q} - \frac{\Pi + \mu_e}{\lambda T^2} \boldsymbol{i}, \tag{14.23a}$$

$$\boldsymbol{E} - \nabla \mu_e = \frac{\varepsilon}{\lambda} \boldsymbol{q} - \left(\varepsilon \frac{\Pi + \mu_e}{\lambda} - r \right) \boldsymbol{i}, \tag{14.23b}$$

where λ is the thermal conductivity at zero electric current, ε the differential thermoelectric power or Seebeck coefficient, Π the Peltier coefficient, and r the isothermal electrical resistivity. By comparison of (14.21) and (14.23), one is led to the identifications

$$\mu'_{11} = (\lambda T^2)^{-1}, \mu'_{21} = (\varepsilon T - \mu_e)(\lambda T^2)^{-1},$$
$$\mu'_{12} = (\Pi + \mu_e)(\lambda T^2)^{-1}, \mu'_{22} = rT^{-1} + (\mu_e - T)(\Pi + \mu_e)(\lambda T^2)^{-1}.$$

From the symmetry of $\boldsymbol{\mu}'$ it follows that $-(\Pi + \mu_e) = \varepsilon T - \mu_e$, so that

$$\varepsilon T = -\Pi, \tag{14.24}$$

which is the well-known second Thomson relation.

It is interesting to emphasize that the argument leading to the symmetry of the phenomenological matrix $\boldsymbol{\mu}'$ is parallel to that presented by Onsager himself, who postulated that thermodynamic fluxes are time derivatives of state variables, whilst the forces are derivatives of the entropy with respect to state variables. Since in EIT the quantities $\boldsymbol{q}$ and $\boldsymbol{i}$ are basic state variables, it is clear that (14.22) relates the time derivatives of the basic variables with $\partial S/\partial \boldsymbol{q}$ and $\partial S/\partial \boldsymbol{i}$, just like in the Onsager original derivation, where the time derivatives of the basic variables (here, the thermodynamic fluxes) are linearly related to the derivatives of the entropy with respect to these variables (the thermodynamic forces). In CIT, the transposition of Onsager's arguments from the microscopic to the macroscopic level raises some difficulties, since the heat flux and the pressure tensor cannot be directly identified as time derivatives of state variables.

14.3 Hydrodynamical Models of Transport in Semiconductors and Plasmas

Electrical transport can be described by means of a Boltzmann equation for the charge carriers. However, to solve directly this equation is mathematically a very hard task. A possible simplification consists in restricting to a few practically relevant lowest-order moments of the distribution function. This kind of approach is called the hydrodynamical approach (Hänsch 1991).

14.3.1 Transport in Semiconductors

One challenge in the analysis of transport phenomena is the study of charge transport in submicronic semiconductor devices, which is essential for the optimization of their functioning and design.

The evolution equations for the moments are directly obtained from the Boltzmann equation. In the case of electrons in the conduction band of the semiconductor, it takes the form

$$\frac{\partial f}{\partial t} + \boldsymbol{v}(\boldsymbol{k}) \cdot \nabla f - e\boldsymbol{E} \cdot \nabla_k f = Q, \tag{14.25}$$

with $f(\boldsymbol{x}, \boldsymbol{k}, t)$ being the distribution function and $\boldsymbol{k}$ the electron momentum, comprised in the first Brillouin zone, $\boldsymbol{v}(\boldsymbol{k}) = \nabla_k \varepsilon$ is the electron group velocity and Q the collision term. In the effective-mass approximation (Anile and Pennisi 1992; Anile and Muscato 1995; Anile et al. 2003, 2005), the energy $\varepsilon(k)$ is given by $\varepsilon(k) = \frac{1}{2}k^2/m^*$ and $\boldsymbol{v}(\boldsymbol{k}) = \boldsymbol{k}/m^*$, m^* being the effective electron mass (for instance, in silicon $m^* = 0.26 m_e$ with m_e being the electron mass). Multiplying (14.25) by several products of the components of $\boldsymbol{k}$, and integrating one obtains a hierarchy of equations for the different moments. Besides the mass conservation equation for the zeroth-order moment, one finds

$$\frac{\partial}{\partial t}(n v_i) + \frac{\partial \theta_{ij}}{\partial x_j} + \frac{neE_i}{m^*} = Q_i, \tag{14.26}$$

$$\frac{\partial \theta_{<ij>}}{\partial t} + \frac{\partial \theta_{<ij>r}}{\partial x_r} + \frac{2neE_{<i} v_{j>}}{m^*} = Q_{<ij>}, \tag{14.27}$$

in which θ_{ij}, Q_i and Q_{ij} stand for the moments of f and of Q with respect to $\boldsymbol{k}$, namely $\theta_{ij} = (1/m^{*2}) \int \mathrm{d}\boldsymbol{k}\, f\, k_i k_j$, $Q_i = (1/m^*) \int \mathrm{d}\boldsymbol{k}\, Q\, k_i$, $Q_{ij} = (1/m^*) \int \mathrm{d}\boldsymbol{k}\, Q\, k_i k_j$ and so on, and the symbol $\langle \cdots \rangle$ denotes the completely symmetric and traceless part of the corresponding tensor. Furthermore, one obtains for the energy $W = \int \mathrm{d}\boldsymbol{k}\, f(\boldsymbol{k}) \varepsilon(\boldsymbol{k})$ and the energy flux $\boldsymbol{S}_i = \int \mathrm{d}\boldsymbol{k}\, f(\boldsymbol{k}) \varepsilon(\boldsymbol{k}) \boldsymbol{v}(\boldsymbol{k})$ the following equations:

$$\frac{\partial W}{\partial t} + \frac{\partial S_i}{\partial x_i} + neE_i v_i = Q_w, \tag{14.28}$$

$$\frac{\partial S_i}{\partial t}+\frac{\partial S_{ij}}{\partial x_j}+e\left[E_j\theta_{ij}+(W/m^*)E_i\right]=Q_i', \tag{14.29}$$

wherein $Q_w=\int \mathrm{d}\boldsymbol{k}\,Q\varepsilon(\boldsymbol{k})$, $Q_i'=(1/m^*)\int \mathrm{d}\boldsymbol{k}\,Q\varepsilon(\boldsymbol{k})k_i$, and $S_{ij}=(1/m^{*2})\int d\boldsymbol{k}$ $f(\boldsymbol{k})\varepsilon(\boldsymbol{k})k_ik_j$. These equations are complemented by the Poisson equation which relates the electrical potential to the charge density.

Depending on the choice of variables and the level at which the hierarchy is truncated, one obtains different hydrodynamical models. A simple one is the so-called drift-diffusion model (Hänsch 1991), which includes the number density of electrons and holes among the set of independent variables, but not their energies W. A more sophisticated but popular model is the Blotekjaer (1970) and Baccarani and Wordemann's one (1985) usually denoted as BBW, wherein the energy of electrons and of holes are taken as independent variables, but not the heat flux, which is assumed to be given by the Fourier law.

These models present severe drawbacks; to optimize the description, a sound analysis of other possible truncations is highly desirable. Let us go back to the scheme (14.26–14.29), based on the variables n, v_i, W, S_i, and $\theta_{<ij>}$ (both for electrons and for holes); to close the problem one needs constitutive equations expressing S_{ij} and the collision terms Q_w and Q_i' in terms of the basic variables. Extended irreversible thermodynamics provides a way to determine which kind of truncations is compatible with thermodynamics. Application of EIT to the analysis of submicronic devices has been performed by Anile et al. (2003, 2005). We summarize here their main results concerning the closure problem, the modelling of the collision terms and the heat flux, but to avoid lengthy developments we will skip all the details.

We first introduce some definitions. We decompose the electron momentum $\boldsymbol{k}$ according to $\boldsymbol{k}=m^*(\boldsymbol{u}+\boldsymbol{c})$, with $\boldsymbol{u}$ being the average velocity and $\boldsymbol{c}$ the peculiar electron velocity, while $\hat{\theta}_{ijr}$ represents the moments of the distribution function with respect to $\boldsymbol{c}$. The part of S_{ij} independent of $\boldsymbol{u}$ is $\hat{\theta}_{ijrr}$ and the part of the energy flux S_i independent of $\boldsymbol{u}$ is the heat flux q_i. By applying the methods of EIT, the following closure relations have been obtained (Anile and Pennisi 1992; Anile and Muscato 1995; Anile et al. 2003, 2005):

$$\begin{aligned}\hat{\theta}_{<ijk>}&=\frac{1}{5}\left(q_i\delta_{jk}+q_j\delta_{ki}+q_k\delta_{ij}\right)+\frac{2m^*}{15nk_\mathrm{B}T}\left(q_i\hat{\theta}_{jk}+q_j\hat{\theta}_{ki}+q_k\hat{\theta}_{ij}\right)\\&\quad-\frac{2m^*}{15nk_\mathrm{B}T}q_l\left(\hat{\theta}_{<li>}\delta_{jk}+\hat{\theta}_{<lj>}\delta_{ki}+\hat{\theta}_{<lk>}\delta_{ij}\right),\end{aligned} \tag{14.30a}$$

$$\begin{aligned}\hat{\theta}_{ijrr}&=\left[\frac{5n}{2m^*}(k_\mathrm{B}T)^2+\left(\sigma-\frac{2}{5nk_\mathrm{B}T}\right)\boldsymbol{q}\cdot\boldsymbol{q}\right]\delta_{ij}+2\sigma q_iq_j\\&\quad+\frac{7k_\mathrm{B}T}{2}\hat{\theta}_{<ij>}+\frac{m^*}{n}\hat{\theta}_{<il>}\hat{\theta}_{<jl>}.\end{aligned} \tag{14.30b}$$

Here, a definite value of the unknown parameter σ is provided by the maximum-entropy approach, or alternatively it may be determined by comparison with Monte

Carlo computer simulations or by experiments. The best value for σ is -0.1321, up to values of E of the order of 10^5 V/cm.

The constitutive equations for the collision terms will be obtained from the Baccarani–Wordeman model, and take the form

$$Q_i = -\frac{nv_i}{\tau_p},\ Q_i' = -\frac{S_i}{\tau_q},\ Q_w = -\frac{W - W_0}{\tau_w},\ Q_{<ij>} = -\frac{\theta_{<ij>}}{\tau_s}, \tag{14.31}$$

where τ_p, τ_q, τ_w and τ_s are the corresponding relaxation times. It turns out that if τ_p and τ_q are independent of the fluxes (what is assumed by Baccarani and Wordeman), Onsager's relations are only satisfied when the two relaxation times are equal. However, Monte Carlo simulations show that this assumption is only valid at high energy, and that it is strongly violated at low energy. In order to recover the Onsager relations at high and low energies, Anile et al. (2003) redefine τ_p and τ_q as

$$\frac{1}{\tau_p} = a + b\frac{S}{J},\quad \frac{1}{\tau_q} = a' + b'\frac{S}{J}, \tag{14.32}$$

with S and J the magnitude of the energy flux $\boldsymbol{S}$ and the electric flux $\boldsymbol{J}$ respectively. The Onsager relations are then satisfied if $a' + \frac{5}{2}b'k_{\mathrm{B}}T = \frac{5}{2}k_{\mathrm{B}}T\left(a + \frac{7}{2}bk_{\mathrm{B}}T\right)$.

Finally, in contrast with most theories, where the Fourier law is assumed a priori, Anile et al. (2003) derive from the evolution equation (14.29) the following constitutive equation for the heat flux in the steady state:

$$\frac{q_i}{\tau_q} = -\frac{5nk_B^2T}{2m^*}\frac{\partial T}{\partial x_i} + \frac{5}{2}k_{\mathrm{B}}TJ_i\left(\frac{1}{\tau_p} - \frac{1}{\tau_q}\right). \tag{14.33a}$$

Instead, in the BBW model, the heat flux is modellized as

$$\frac{q_i}{\tau_q} = -\left(\frac{5}{2} + c\right)\frac{nk_{\mathrm{B}}^2T}{m^*}\frac{\partial T}{\partial x_i}, \tag{14.33b}$$

where c is a constant parameter whose value is obtained through comparison with experimental data. The second term in the right-hand side of (14.33a) plays a great role in semiconductor devices, as it accounts for the strong decrease of the effective thermal conductivity.

A way to check the quality of the truncation is to compare the predictions of the hydrodynamic models with Monte Carlo simulations when applied to a typical device such as a $n^+ - n - n^+$ ballistic diode (Fig. 14.1).

Assume that this diode consists of a 0.1 µm n^+ region, a 0.4 µm n region, and another 0.1 µm n^+ region, at 300 K and with a doping density $n = 5 \times 10^{23}\,\mathrm{m}^{-3}$ in the channel and $n^+ = 10^{26}\,\mathrm{m}^{-3}$ in the 0.1 µm regions. The results of Monte Carlo simulations are generally used as a benchmark to check the results provided by hydrodynamic descriptions. In particular, for silicon at room temperature (and considering only intra-valley scattering with acoustic phonons and inelastic

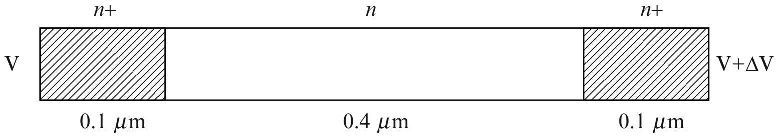


Fig. 14.1 A n^+–n–n^+ silicon diode. The doping density in the region n^+ is higher than in the region n

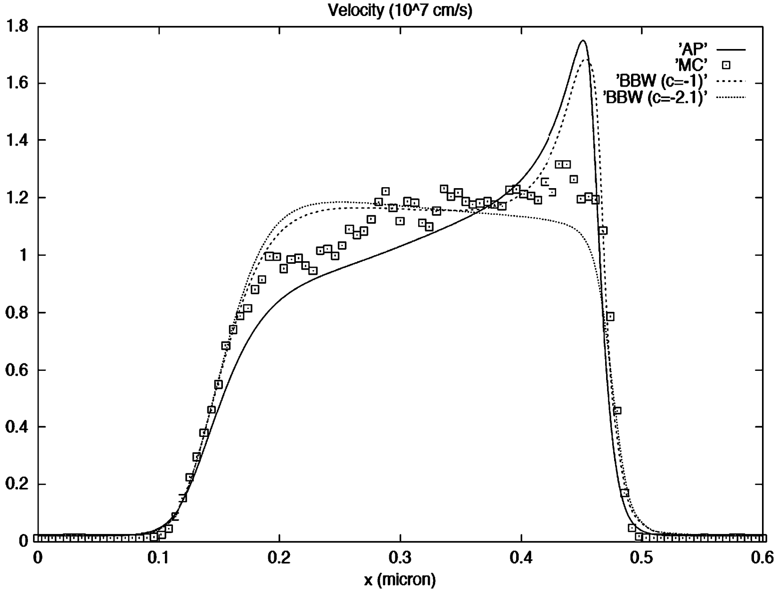


Fig. 14.2 Electron velocity profiles in the $n^+ - n - n^+$ silicon diode obtained, respectively, by Monte Carlo simulations (*squares*), the hydrodynamical model of Anile and Pennisi (AP), and the BBW model with $c = -1$ (*dashed line*) and $c = -2.1$ (*dotted line*) (reprinted from Romano V, Russo G (2000) Math Models Methods Appl Sci 10:1099)

intervalley scattering with optical phonons), Anile et al. (2003) find $\tau_w = 3.82\,\text{ps}$, $a = 42.8\,(\text{ps})^{-1}$, $b = 1.07\,(\text{eV ps})^{-1}$, $a' = 4.322\,(\text{ps})^{-1}$, and $b' = 0.0045\,\text{eV}(\text{ps})^{-1}$ (ps stands for picosecond). With these values, the hydrodynamic model provides results which are in good agreement with Monte Carlo simulations as reflected by Fig. 14.2. Nevertheless, it is worth stressing that, compared to the Monte Carlo simulation, the hydrodynamic models are much more economical with regard to the computing time consumption. To obtain one point in the Monte Carlo simulation, it takes several hours, in comparison with the few minutes necessary to get the whole curve for the profile in the hydrodynamical model.

Another important topic in microelectronic devices of nanometric size is the contribution of ballistic electrons to charge transport, because the size of the device becomes comparable to the mean-free path. The ballistic transport of electrons and holes was observed in GaAs in 1985, and since that time, many efforts have been displayed to take advantage of these characteristics to increase the speed and improve the efficiency of the devices.

The presence of ballistic electrons gives rise to several peaks in the velocity distribution function, and as a consequence a high number of moments are required instead of only a few ones as in systems close to equilibrium. Therefore, the technique developed in Sect. 4.7 based on an infinite number of moments could be useful to study charge transport in a way similar to that followed in Chap. 10 to describe ballistic heat transport. In the above models, it has been assumed that the lattice is a thermal bath at constant temperature. However, when the devices are increasingly miniaturized up to dimensions of the order of the phonon mean-free path, phonon–phonon scattering becomes rare and, therefore, inefficient to establish thermal equilibrium in the lattice. Then the heat delivered by the fast electrons of the conduction band, accelerated by the high electric fields, cannot be removed fast enough and local overheating may occur, which is on of the common causes of device damage. Muscato and Di Stefano (2008) have considered the non-equilibrium hot electrons besides optical and acoustic phonons, and have obtained the corresponding temperature and velocity profiles. Other progresses in this field have been performed with non-parabolic bands and taking into account quantum corrections (Junk and Romano 2005; Romano 2007).

14.3.2 Transport in Plasmas

Hydrodynamical models are not exclusive of semiconductors: they were already used by Bloch in 1933 for the description of electron gases and have been often exploited since that time (Barton 1979; Dempsey and Halperin 1992). As an illustration of the importance of going beyond local-equilibrium hydrodynamics (Tokatly and Pankratov 1999, 2000), we present here the derivation of the frequency dispersion relation for plasma waves.

In the local-equilibrium version, one takes the electron density n, the velocity $\mathbf{v}$, the pressure p (or the temperature T), and the electrostatic potential φ as independent variables. The corresponding set of evolution equations are the continuity equation, and Euler and Poisson equations. They result in a dispersion relation for plasma longitudinal waves of the form

$$\omega^2(k) = \omega_p^2 + v_0^2 k^2, \tag{14.34}$$

with k being the wavevector and ω_p the plasma frequency. For degenerate Fermi gases with Fermi velocity v_F, it turns out that v_0 is given by $v_0^2 = \frac{1}{3}v_\mathrm{F}^2$ instead of the experimental result $v_0^2 = \frac{3}{5}v_\mathrm{F}^2$. The reason of this discrepancy is that electron gases are often found in the collisionless (Vlasov) regime, with very long relaxation times, which classical hydrodynamics does not include in its description. It turns out that introduction of $\mathbf{P}^v$ as a further independent variable is sufficient to yield the correct plasma dispersion relation up to the order in k^4. Here, we will restrict our attention to the order k^2 as in (14.34).

We follow here the presentation of Tokatly and Pankratov (1999, 2000). The evolution equations for n, $\boldsymbol{v}$, p and $\mathbf{P}^v$ are

$$\frac{\mathrm{d}n}{\mathrm{d}t} + n\nabla\cdot\boldsymbol{v} = 0, \tag{14.35}$$

$$mn\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} + \nabla p + \nabla\cdot\mathbf{P}^v - en\nabla\varphi = 0, \tag{14.36}$$

$$\frac{\mathrm{d}p}{\mathrm{d}t} + \frac{5}{3}p\nabla\cdot\boldsymbol{v} + \frac{2}{3}\mathbf{P}^v : \nabla\boldsymbol{v} = 0, \tag{14.37}$$

$$\frac{\mathrm{d}\mathbf{P}^v}{\mathrm{d}t} + \mathbf{P}^v(\nabla\cdot\boldsymbol{v}) + \mathbf{P}^v\cdot\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^T\cdot P^v - \frac{2}{3}\mathbf{P}^v : \nabla\boldsymbol{v}$$
$$+p\left[\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^T - \frac{2}{3}(\nabla\cdot\boldsymbol{v})\mathrm{U}\right] = 0. \tag{14.38}$$

Note that (14.37) is the energy balance equation and that in (14.38) the right-hand side, which we usually take of the form $-(1/\tau_2)\mathbf{P}^v$, is assumed to vanish since we are considering the collisionless regime, for which the relaxation time τ_2 is very long.

The linearized equations for perturbations δn, $\delta\boldsymbol{v}$, δp, $\delta\mathbf{P}^v$, and $\delta\varphi$ are

$$\frac{\partial\delta n}{\partial t} + n_0\nabla\cdot\delta\boldsymbol{v} = 0, \tag{14.39}$$

$$mn_0\frac{\partial\delta\boldsymbol{v}}{\partial t} + \nabla\delta p + \nabla\cdot\delta\mathbf{P}^v - en_0\nabla\delta\varphi = 0, \tag{14.40}$$

$$\frac{\partial\delta p}{\partial t} + \frac{5}{3}p_0\nabla\cdot\delta\boldsymbol{v} = 0, \tag{14.41}$$

$$\frac{\partial\delta\mathbf{P}^v}{\partial t} + p_0\left[(\nabla\delta\boldsymbol{v}) + \nabla\delta\boldsymbol{v})^T - \frac{2}{3}\mathrm{U}(\nabla\cdot\delta\boldsymbol{v})\right] = 0, \tag{14.42}$$

$$\nabla^2\delta\varphi = 4\pi e\delta n. \tag{14.43}$$

To obtain the dispersion relation, we assume plane-wave solutions where $\boldsymbol{v}$ and $\mathbf{P}^v$ have only one non-vanishing component, v_x and P^v_{xx} respectively. Differentiation of (14.41) with respect to x yields

$$-\frac{\partial^2\delta n}{\partial t^2} + \frac{1}{m}\frac{\partial^2\delta p}{\partial x^2} + \frac{1}{m}\frac{\partial^2\delta P^v_{xx}}{\partial x^2} - \frac{en_0}{m}\frac{\partial^2\varphi}{\partial x^2} = 0. \tag{14.44}$$

From (14.33), (14.41), and (14.42) it is inferred that

$$\delta p = \frac{5}{3}\frac{p_0}{n_0}\delta n, \ \delta P^v_{xx} = \frac{4}{3}\frac{p_0}{n_0}\delta n. \tag{14.45}$$

Introduction of (14.45) into (14.44) together with (14.43) gives an expression like (14.34) with

$$v_0^2 = \frac{5p_0}{3mn_0} + \frac{4p_0}{3mn_0} = \frac{3p_0}{mn_0}. \tag{14.46}$$

The first contribution arises from δp, which is the only contribution appearing in the local-equilibrium theory, whereas the second one comes from the addition of $\mathbf{P}^v$ as independent variable. For a Fermi degenerate gas, $p_0 = \frac{1}{5}mn_0v_F^2$ and the result (14.46) is the correct one, in good agreement with experiments. A more general presentation of the hydrodynamics of Fermi liquids, would include a hierarchy of higher-order fluxes as that presented in Sect. 4.7.

14.4 Dielectric Relaxation of Polar Liquids

Up to now we have dealt with charge transport from one place to another. Dielectric relaxation, instead, is a local effect in the sense that electric charges move inside globally neutral particles (usually macromolecules) which remain themselves at rest. The electric polarization $\boldsymbol{P}$ of such molecules relaxes to its final equilibrium value, which depends on the electric field $\boldsymbol{E}$ applied to the system. The simplest model to describe this relaxation is Debye's model, according to which (De Groot and Mazur 1962)

$$\tau_1 \frac{\mathrm{d}\boldsymbol{P}}{\mathrm{d}t} + \boldsymbol{P} = \chi_0 \boldsymbol{E}, \tag{14.47}$$

where χ_0 is the electric susceptibility and τ_1 the relaxation time. This equation gives a satisfactory description of low-frequency phenomena, but it is insufficient at high frequencies, and a generalisation is therefore required.

A possible way to describe dielectric relaxation in polarizable media is to introduce one or several polarization vectors as internal independent variables (see for instance Ciancio et al. 1990; Ciancio and Verhas 1991; Conforto and Giambò 1996). In the classical description, the state variables are the density of internal energy ρu and the density of polarization charges ρ_p (defined as minus the divergence of the polarization vector $\boldsymbol{P}$), whose time evolutions are given by the energy and charge balance laws

$$\rho \dot{u} = \boldsymbol{E} \cdot \boldsymbol{J}_p, \quad \dot{\rho}_p = -\nabla \cdot \boldsymbol{J}_p, \tag{14.48}$$

where $\boldsymbol{J}_p = \mathrm{d}\boldsymbol{P}/\mathrm{d}t$ is the polarization current. In the classical approach, $\boldsymbol{J}_p$ is given by the constitutive law (14.47) instead of being considered as an independent variable.

The first step beyond the classical approach would be to include $\boldsymbol{J}_p$ as an additional independent variable, as was done, for instance, with the heat flux in Sect. 2.3. However, experimental observations on ultrafast dielectric response of dense polar liquids require a higher level of precision so that, here, we will take not only $\boldsymbol{J}_p$ but also its 'flux' $\Lambda = \mathrm{d}^2\boldsymbol{P}/\mathrm{d}t^2$ as additional independent variables. It must be stressed that the meaning of the 'fluxes' $\boldsymbol{J}_p$ and Λ is conceptually different from that of the fluxes of heat or mass diffusion introduced earlier. Indeed, the latter refer to displacements of particles (or quasiparticles) in space, while the former are taken at a given point of space and describe the variation of a given quantity, respectively $\boldsymbol{P}$ and its time derivative, in the course of time. Although in EIT the transport fluxes receive special attention, purely relaxational 'fluxes' may also be incorporated in the formalism, and the experience gained in the analysis of the former may be applied to the latter. This assertion will be illustrated by the foregoing considerations.

It could be asked why 'fluxes' of higher orders, like $\mathrm{d}^n\boldsymbol{P}/\mathrm{d}t^n$, are not introduced by analogy with the continued-fraction description of Sect. 4.7: the equivalent of (4.110) would correspond in this case to the Mori formalism (1965). However, as seen in Sect. 9.3, one obtains generally very reasonable results by taking only the heat flux and the flux of the heat flux as variables. By analogy, and because of the satisfactory agreement with the experimental results in the ultrafast dielectric response, we limit here the hierarchy of variables to the second order in time derivatives.

The generalised Gibbs equation corresponding to the extended description incorporating the four variables u, ρ_p, $\boldsymbol{J}_p$, and Λ is (del Castillo and Dàvalos-Orozco 1990 del Castillo et al. 1997; del Castillo and Rodríguez 1989)

$$\rho\dot{s} = T^{-1}\rho\dot{u} + T^{-1}\varphi\dot{\rho}_p + (\alpha_1\boldsymbol{J}_p + \alpha_2\Lambda)\cdot\dot{\boldsymbol{J}}_p + (\alpha_3\boldsymbol{J}_p + \alpha_4\Lambda)\cdot\dot{\Lambda}, \quad (14.49)$$

where $\alpha_2 = \alpha_3$ by the integrability condition, and φ is the electric potential, related to the electrical field $\boldsymbol{E}$ by $\boldsymbol{E} = -\nabla\varphi$. Classical irreversible thermodynamics corresponds to the particular situation where all the coefficients $\alpha_i\,(i = 1, 2, 3)$ vanish.

We take for the entropy flux $\boldsymbol{J}^s$ the expression

$$\boldsymbol{J}^s = (\varphi/T)\boldsymbol{J}_p, \quad (14.50)$$

which is the flux of internal electric energy divided by the absolute temperature. Note that this 'flux' does not represent a transport of entropy from one place to another, but the 'flux' of entropy between different internal states of the molecules of the system. By combining (14.48–14.50), it is easy to check that the entropy production is given by

$$\sigma^s = \left[\frac{1}{T}(\boldsymbol{E} - \boldsymbol{E}_0) + \alpha_1\frac{\mathrm{d}\boldsymbol{J}_p}{\mathrm{d}t} + \alpha_3\frac{\mathrm{d}\Lambda}{\mathrm{d}t}\right]\cdot\boldsymbol{J}_p + \left[\alpha_2\frac{\mathrm{d}\boldsymbol{J}_p}{\mathrm{d}t} + \alpha_4\frac{\mathrm{d}\Lambda}{\mathrm{d}t}\right]\cdot\Lambda, \quad (14.51)$$

where $\boldsymbol{E}_0$ is the value of $\boldsymbol{E}$ at equilibrium ($\boldsymbol{E} = -\nabla\varphi$). In the linear approximation, one may formulate the evolution equations for the fast variables $\boldsymbol{J}_p$ and Λ as follows

$$\frac{1}{T}(\boldsymbol{E} - \boldsymbol{E}_0) + \alpha_1\frac{\mathrm{d}\boldsymbol{J}_p}{\mathrm{d}t} + \alpha_3\frac{\mathrm{d}\Lambda}{\mathrm{d}t} = \mu_1\boldsymbol{J}_p + \mu_3\Lambda, \quad (14.52\mathrm{a})$$

$$\alpha_2\frac{\mathrm{d}\boldsymbol{J}_p}{\mathrm{d}t} + \alpha_4\frac{\mathrm{d}\Lambda}{\mathrm{d}t} = \mu_3\boldsymbol{J}_p + \mu_2\Lambda, \quad (14.52\mathrm{b})$$

where Onsager's reciprocal relations, expressed by the presence of the same coefficient μ_3 in both equations, are taken for granted. The above equations may be written in terms of $\boldsymbol{P}$ and Λ in the form

$$-\tau_2 \frac{\mathrm{d}^2 \boldsymbol{P}}{\mathrm{d}t^2} + \tau_1 \delta \left(1 + \lambda_2 \frac{\mathrm{d}}{\mathrm{d}t}\right) \Lambda - (\boldsymbol{P} - \chi_0 \boldsymbol{E}) = 0, \tag{14.53}$$

$$\left(1 + \lambda_3 \frac{\mathrm{d}}{\mathrm{d}t}\right) \Lambda + \frac{1}{\delta} \left(1 + \lambda_4 \frac{\mathrm{d}}{\mathrm{d}t}\right) \frac{\mathrm{d}\boldsymbol{P}}{\mathrm{d}t} = 0, \tag{14.54}$$

with the following identifications: $\tau_2 = -T\chi_0\alpha_1$, $\tau_1 = \frac{1}{4}\mu_3^2 T\chi_0/\mu_2$, $\delta = 2\mu_2/\mu_3$, $\lambda_2 = \lambda_4 = -2\alpha_3/\mu_3$, and $\lambda_3 = -\alpha_4/\mu_2$.

If the relaxation times λ_2, λ_3, and λ_4 are small, (14.54) reduces to

$$\frac{\mathrm{d}\Lambda}{\mathrm{d}t} = -\frac{\mu_3}{2\mu_2} \frac{\mathrm{d}\boldsymbol{P}}{\mathrm{d}t} \tag{14.55}$$

and (14.53) takes the form

$$\tau_2 \frac{\mathrm{d}^2 \boldsymbol{P}}{\mathrm{d}t^2} + \tau_1 \frac{\mathrm{d}\boldsymbol{P}}{\mathrm{d}t} + (\boldsymbol{P} - \chi_0 \boldsymbol{E}) = 0, \tag{14.56}$$

which is a first generalisation of the Debye equation (14.47) for $\boldsymbol{P}$.

Relevant experimental information can be obtained from the autocorrelation function for the polarization vector $\boldsymbol{P}$, given by

$$\phi_a(t) = \frac{\langle \delta P_a(t) \delta P_a(0) \rangle}{\langle \delta P_a(0) \delta P_a(0) \rangle}, \tag{14.57}$$

where $a = x$ or z (x is the transverse mode and z the longitudinal mode, when $\boldsymbol{E}$ is assumed to be directed along the z axis). Indeed, the dielectric susceptibility $\chi(\omega)$ and the complex dielectric constant $\varepsilon(\omega)$ are given by the relations

$$\frac{\chi(\omega) - \chi_\infty}{\chi(0) - \chi_\infty} = \frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon(0) - \varepsilon_\infty} \frac{\varepsilon(0)}{\varepsilon(\omega)} = \mathcal{L}(-\dot{\phi}_z) \text{ (longitudinal mode)} \tag{14.58}$$

$$\frac{\chi(\omega) - \chi_\infty}{\chi(0) - \chi_\infty} = \frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon(0) - \varepsilon_\infty} = \mathcal{L}(-\dot{\phi}_x) \text{ (transverse mode)}$$

where $\mathcal{L}(\cdots)$ denotes the Laplace–Fourier transform, while index ∞ corresponds to the limit of infinite frequency. From the Laplace–Fourier transforms of (14.53–14.54), namely

$$\begin{aligned} -(1 + \tau_2^2\omega^2)\boldsymbol{P} + \tau_1\delta(1 + \mathrm{i}\lambda_2\omega)\Lambda &= -\chi_0\boldsymbol{E}, \\ \delta^{-1}(1 + \mathrm{i}\lambda_4\omega)\mathrm{i}\omega\boldsymbol{P} + (1 + \mathrm{i}\lambda_3\omega)\Lambda &= 0, \end{aligned} \tag{14.59}$$

it follows that the Laplace–Fourier transform of (14.57) has the form

$$\phi_a(\omega) = \frac{1}{-\mathrm{i}\omega - \frac{M_0}{-\mathrm{i}\omega + \frac{M_0+\gamma_2}{-\mathrm{i}\omega - \frac{\gamma_3}{M_0}}}}, \tag{14.60}$$

with $M_0 = -\gamma_3/\gamma_1$, $\gamma_1 = (\lambda_1 + 2\lambda_2\tau_1)(\lambda_1\lambda_3 + \lambda_2^2\tau_1)^{-1}$;

$$\gamma_2 = (\lambda_3 + \tau_1)(\lambda_1\lambda_3 + \lambda_2^2\tau_1)^{-1}; \text{ and } \gamma_3 = (\lambda_1\lambda_3 + \lambda_2^2\tau_1)^{-1}.$$

If λ_2=0, this expression reduces to the classical model of Kivelson and Keyes (1972) The parameter λ_2 (or μ_3) represents the coupling between two dynamical effects described by $\boldsymbol{J}_p$ and Λ, as exhibited by (14.52). Del Castillo et al. (1997) have compared (14.60) with the experimental data on the transverse mode of chloroform in the Cole–Cole diagram, representing the imaginary versus the real part of the complex dielectric constant $\varepsilon(\omega)$. They find that for chloroform at 295 K ($\varepsilon(0) = 4.71$, $\varepsilon_\infty = 2.13$), the choice $\tau_2 = 6.33 \times 10^{-12}$ s, $\tau_1 = 0.38 \times 10^{-12}$ s, $\lambda_3 = 0.33 \times 10^{-12}$ s and $\lambda_2 = 0.012 \times 10^{-12}$ s yields a much better agreement for the high-frequency knob of the Cole–Cole plot than the model corresponding to $\lambda_2 = 0$.

Note that the coupling expressed by λ_2 is analogous to that between the flux of the heat flux **Q** and the heat flux $\boldsymbol{q}$ in equations (9.25–9.26). This exhibits the importance of the cross-coupling effects which are easily taken into account in a macroscopic formalism but which are more difficult to implement in a microscopic approach. It can therefore be stated that it is the same general unifying scheme which is applicable to the descriptions of non-classical heat transport and ultrafast dielectric relaxation.

14.5 Problems

14.1. *Channels in a membrane*: Assume that there are N channels per unit area in a membrane, and that each of them may be either open or closed. Across the membrane there exists a perpendicular electric field $\boldsymbol{E}$, and each channel has an electric dipolar moment $\boldsymbol{p}$ and an electric conductance ξ. Consider the following two simple models: (1) the energy of the open state is $H_{\text{open}} = -pE$ and the energy of the closed state is $H_{\text{closed}} = 0$; (2) $H_{\text{open}} = 0$, $H_{\text{closed}} = -pE$.

(a) Show that the characteristic curves $I - E$ at constant temperature, I being the electric current per unit area of the membrane, are

$$I = \xi E N \frac{\exp[pE/(k_{\mathrm{B}}T)]}{1 + \exp[pE/(k_{\mathrm{B}}T)]} (\text{case } 1),$$

$$I = \frac{\xi E N}{1 + \exp[pE/(k_{\mathrm{B}}T)]} (\text{case } 2).$$

(b) Assume that the contribution of the fluxes to the free energy of the pores is given by

$$g = g_{\mathrm{eq}}(N_{\mathrm{open}}, T, E) + aN_{\mathrm{open}} J_{\mathrm{o}}^2,$$

with J_{o} being the electric current through an open channel and $a = \tau v/(\sigma A^2) = \tau/(\xi l)$, v the volume of a pore, τ the relaxational time of the current in a pore, A and l the cross-sectional area and the length of the pore, and σ the conductivity of the pore, which is linked to the conductance ξ by $\xi = \sigma(A/l)$. Show that the previous expressions are modified to

$$I = \xi E N \frac{\exp\{(k_{\mathrm{B}}T)^{-1}[pE - (a\xi^2/2)E^2]\}}{1 + \exp\{(k_{\mathrm{B}}T)^{-1}[pE - (a\xi^2/2)E^2]\}} (\text{case } 1),$$
$$I = \frac{\xi E N}{1 + \exp\{(k_{\mathrm{B}}T)^{-1}[pE - (a\xi^2/2)E^2]\}} (\text{case } 2).$$

(*Hint*: determine the chemical potential of the open and closed pores, use $\mu_{\mathrm{open}} = \mu_{\mathrm{closed}}$ in equilibrium and remember that in the absence of fluxes $\mu_i(T, E, N_i) = g_i(T, E) + k_{\mathrm{B}}T \ln(N_i/N)$ both for open and closed pores. (See Jou D et al. (1986) J Chem Phys 85:5314.))

14.2. Assume that the generalised entropy $s(u, n, \boldsymbol{i})$ describing electric conduction includes fourth-order terms in the fluxes, instead of being limited to second-order terms as in (14.4); i.e. assume that

$$s(u, n, \boldsymbol{i}) = s_{\mathrm{eq}}(u, n) - \alpha i^2 - \beta i^4,$$

with u being the internal energy, n the number of electrons per unit volume, and $\boldsymbol{i}$ the electric current density. The coefficients α and β are related to the second-order and fourth-order moments of the fluctuations around equilibrium by

$$\langle(\delta i)^2\rangle = \frac{k_{\mathrm{B}}}{2\alpha},$$
$$\langle(\delta i)^2\rangle = \frac{3k_{\mathrm{B}}^2}{4\alpha^2} - \frac{3\beta k_{\mathrm{B}}^3}{2\alpha^4}.$$

(a) Show that for $\boldsymbol{i} = \int e\boldsymbol{v} f(\boldsymbol{v}) \mathrm{d}\boldsymbol{v}$ and for Maxwell–Boltzmann statistics one has $\alpha = k_{\mathrm{B}}(2e^2n^2k_{\mathrm{B}}T)^{-1}$ and $\beta = k_{\mathrm{B}}m(8e^4n^4k_{\mathrm{B}}^2T^2)^{-1}$ with e and m being the charge and mass of the electron. (b) Find out the value of i for which $(\partial^2 s/\partial i^2)_{u,n}$ vanishes. At this value, the second moments of the fluctuations would diverge and the role of the so-called hot electrons would become relevant.

14.3. *Non-equilibrium Einstein relation*: Around equilibrium, the classical Einstein relation between the diffusion coefficient D and the mobility ν eads as $qD/\nu = k_{\mathrm{B}}T$. When the electric field becomes important, some corrections appear, so that $qD/\nu = k_{\mathrm{B}}T(1 + aE^2 + \cdots)$ (see, for instance, Uribe FJ, Mason EA (1989) Chem Phys 133:335 and Vasconcellos AR et al. (1995) Physica A 221:495). Starting from the general expression for the Einstein relation $qD/\nu = n(\partial\mu/\partial n)_{T,V}$, with μ the chemical potential of the carriers and n the carrier density, and the expression for non-equilibrium chemical potential $\mu = \mu_{\mathrm{eq}} + \{\partial[\tau V/(2\sigma)]/\partial n\}J^2$, show that $qD/\nu \approx k_{\mathrm{B}}T[1 + \tau^2q^2(mk_{\mathrm{B}}T)^{-1}E^2]$. (*Hint*: use the Drude formula for the electrical conductivity σ_e.)

14.4. Consider a one-dimensional circuit with electrical resistance R and inductance L. The expression relating the intensity I of the electrical current to the electromotive force ξ is the relaxational equation

$$\xi = IR + L\frac{\mathrm{d}I}{\mathrm{d}t},$$

with relaxation time $\tau_e = L/R$. The intensity I is related to the flux of electric current i as $I = iA$, with A the cross-section of the conductor. The magnetic energy stored in the inductor is given by $U_{\mathrm{m}} = \frac{1}{2}LI^2$. Consider the total internal energy $U_{\mathrm{tot}} = U + U_{\mathrm{m}}$, with U the internal energy of the material. Show that the Gibbs equation

$$\mathrm{d}S = T^{-1}\mathrm{d}U + T^{-1}p\,\mathrm{d}V$$

may be rewritten as

$$\mathrm{d}S = T^{-1}\mathrm{d}U + T^{-1}p\,\mathrm{d}V - \frac{\tau_e V}{\sigma_e T}i\,\mathrm{d}i,$$

which is a relation reminiscent of the Gibbs equation (14.2) proposed in EIT. (*Hint*: recall that $R = (\sigma_e A)^{-1}l$, with l the length of the circuit.)

14.5. *Ballistic devices*: Much interest is paid to ballistic electronic devices, i.e. devices shorter than the mean-free path, where electrons move without collisions (Beenaker (1997)). The electric current between two reservoirs in which there is a difference $\Delta\mu$ in electrochemical potential of electrons is given by

$$j = -ev\frac{\mathrm{d}n}{\mathrm{d}\mu}\Delta\mu.$$

At low temperature, only the carriers on the Fermi surface will move. (a) Show that in this case, $\mathrm{d}n/\mathrm{d}\mu = (\pi\hbar v)^{-1}$, with v the Fermi velocity. (b) Show that the conductance, defined as $G = j/\Delta V$, is $G = e^2(\pi\hbar)^{-1}$. If the transmission coefficient is $\mathcal{T}$ instead of 1 one has $G = e^2(\pi\hbar)^{-1}\mathcal{T}$, which is the

Landauer formula (see Godoy, García-Colín (1999), for a discussion of this equation in the context of persistent random walks introduced in Sect. 13.2.1).

14.6. (a) Derive (14.52), taking into account that $\boldsymbol{E}_0$ is defined as $\boldsymbol{E}_0 = -\nabla\varphi$. (b) Obtain (14.53–14.54) and, from them, (14.60).

Chapter 15
From Thermoelastic Solids to Rheological Materials

In the previous chapters, EIT was essentially used in the framework of fluids. Here, we show that it finds also a field of applications in solid mechanics. Some classes of solids, like elastic bodies, may sustain deformations without undergoing instantaneously a motion. This property is not shared by fluids which, according to Newton's law $\mathbf{P}^v = -2\eta\mathbf{V}$, are instantaneously set in motion after application of a force. Moreover, in Newton's law the viscosity η may depend on temperature and pressure, but not on the velocity gradient. It has been observed that there exists a wide class of materials, such as polymers, soap solutions, some honeys, asphalts, and physiological fluids, that fail to obey Newton's law: these materials are generally referred to as viscoelastic materials. They behave as fluids with a behaviour reminiscent of solids by exhibiting elastic effects. In ordinary fluids, the relaxation of the pressure tensor is very short, in elastic bodies it is infinite so that no relaxation is observed: viscoelastic materials are characterized by relaxation times between these two limits. Materials with the above property are also called non-Newtonian in the technical literature. The terms 'viscoelastic' and 'non-Newtonian' are used rather loosely. Here we shall reserve the term 'non-Newtonian' for any material described by a non-linear constitutive relation between the pressure tensor and the velocity gradient tensor, and by shear-rate dependent material coefficients. The term 'viscoelastic' will be used for systems exhibiting both viscous and elastic effects. Historically, the linear viscoelastic models were the first to be proposed. Although very simple, they have proved to be useful for describing a wide range of materials and for providing the first step towards more realistic descriptions.

In Sect. 15.1, we discuss thermo-elasticity as the simplest coupling between heating and deformation in a solid; the main contribution of EIT is that Fourier's law is substituted by Cataneo's. Most of the viscoelastic models like these of Maxwell, Kelvin–Voigt, Poynting–Thomson are built up of from purely mechanical considerations as assemblages of springs and dashpots. Their usual thermodynamic descriptions are inspired either by the classical irreversible thermodynamics (e.g. Meixner 1954; Kluitenberg 1984), Rational Thermodynamics (e.g. Rivlin and Ericksen 1955; Noll 1974; Coleman et al., 1966) or internal variables theories (Bataille and Kestin 1975; Maugin and Muschik 1994; Maugin 1999). In Sect. 15.2 is proposed a derivation based on EIT wherein the viscous pressure tensor is introduced as additional independent variable. In Sect. 15.3, a simplified version of the

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_15, © Springer Science+Business Media LLC 2010

complex problem of plasticity is developed. More generally, it may also be asked what are the consequences of introducing a whole spectrum of relaxation modes for the pressure tensor, instead of working with one single mode. This problem was partially solved by Rouse (1953) and Zimm (1956), whose molecular models are very useful for describing dilute polymer solutions. We explore in Sect. 15.4 to what extent the Rouse and Zimm models can be incorporated into EIT. Finally, EIT is applied to non-Newtonian fluids; two EIT models are analysed: the first one reproduces fairly well the dependence of the viscometric functions on the strain rate in simple steady shearing flows, the second one reproduces the well-known Giesekus model (1982).

15.1 Thermoelasticity

Consider a deformable material continuous medium. Under external mechanical forces and heating, its configuration changes from a reference one, generally taken as the initial position, characterized by a volume V_R, bounding surface Σ_R and mass density ρ_R, to a deformed state with volume V, surface Σ and volume density ρ (see Fig. 15.1). The position vector of a material point P in the reference and current configurations is denoted by $\boldsymbol{X}$ and $\boldsymbol{x}$ respectively, both quantities are related by $\boldsymbol{x} = \chi(\boldsymbol{X}, t)$ called the motion or the deformation of the material body. In the present section, we are concerned with large deformations and shall work in the material or Lagrangian representation, meaning that all physical quantities are expressed in terms of the material coordinates $\boldsymbol{X}$. It is common in solid mechanics to prefer to work with the stress tensor $\mathbf{T}$ rather than with the pressure tensor $\mathbf{P}$ ($= -\mathbf{T}$) of fluid mechanics.

We first define the space of state variables. According to the lines of thought of EIT, it is given by the union of the space $\mathcal{C}$ of classical variables, namely the mass density, the specific internal energy u (or the non-equilibrium temperature θ), the strain tensor (identified here as the Green strain tensor $\mathbf{E}$ defined below), and the space $\mathcal{J}$ of flux variables, here the heat flux vector $\boldsymbol{Q}$. The next step is the derivation of the corresponding evolution equations. In the Lagrangian description, the balance

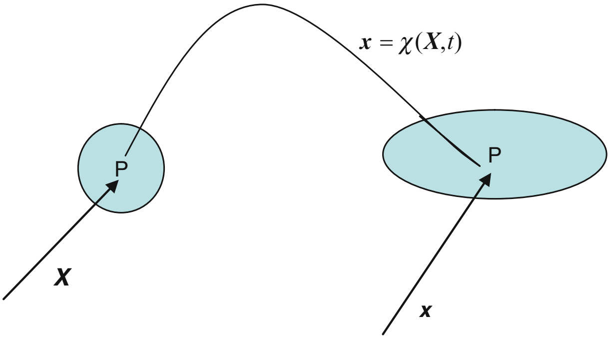


Fig. 15.1 Reference $(\boldsymbol{X})$ and actual $(\boldsymbol{x})$ configurations of a deformable material

of mass, momentum and internal energy are given by (e.g. Eringen 1980)

$$\dot{\rho}_R = 0, \tag{15.1}$$

$$\rho_R \ddot{\chi} = \nabla_X \cdot \tilde{\mathbf{T}} + \rho_R \boldsymbol{F}, \tag{15.2}$$

$$\rho_R \dot{u} = -\nabla_X \cdot \boldsymbol{Q} + \mathbf{T} : \dot{\mathbf{E}}, \tag{15.3}$$

where index X in ∇_X symbolizes the dependence on the $\boldsymbol{X}$-material configuration and a superimposed dot stands for the material time derivative: for instance, $\dot{\chi} = \partial \chi(\boldsymbol{X}, t)/\partial t$. The undefined quantities appearing in (15.2) and (15.3) are

- $\mathbf{F} = \nabla_X \chi(\boldsymbol{X}, t)$, the deformation gradient tensor.
- $\tilde{\mathbf{T}} = (\det \mathbf{F})\boldsymbol{\sigma} \cdot (\mathbf{F}^T)^{-1}$, the non-symmetric first Piola–Kirchhoff stress tensor with $\boldsymbol{\sigma}$ the symmetric Cauchy stress tensor.
- $\mathbf{T} = \mathbf{F}^{-1} \cdot \tilde{\mathbf{T}}$ the symmetric second Piola–Kirchhoff stress tensor.
- $\mathbf{E} = \frac{1}{2}(\mathbf{F}^T \cdot \mathbf{F} - \mathbf{U})$ the symmetric Green strain tensor.
- $\boldsymbol{Q} = (\det \mathbf{F})\mathbf{F}^{-1} \cdot \boldsymbol{q}$ the heat flux measured per unit area Σ_R with $\boldsymbol{q}$ the heat flux across the deformed surface Σ.

To obtain the missing evolution for the heat flux we shall invoke the second law. First, we introduce the constitutive relation which expresses the specific entropy s in terms of the basic state variables, i.e.

$$s = s(u, \mathbf{E}, \boldsymbol{Q}). \tag{15.4}$$

In differential form, one has

$$\mathrm{d}s = \theta^{-1}\mathrm{d}u + \frac{\partial s}{\partial \mathbf{E}} : \mathrm{d}\mathbf{E} + \frac{1}{\rho_R}\boldsymbol{\Lambda} \cdot \mathrm{d}\boldsymbol{Q}, \tag{15.5}$$

with $\boldsymbol{\Lambda} = \rho_R(\partial s/\partial \boldsymbol{Q})$. Our next task is to determine the restrictions placed by the second law of thermodynamics

$$\sigma^s = \rho_R \dot{s} + \nabla_X \cdot \boldsymbol{J}^s \geq 0. \tag{15.6}$$

Making use of Gibbs' relation (15.5) and the energy balance (15.3) in (15.6), one obtains

$$\sigma^s = \nabla_X \cdot \left(\boldsymbol{J}^s - \frac{\boldsymbol{Q}}{\theta}\right) + \boldsymbol{Q} \cdot \nabla_X \theta^{-1} + \left(\rho_R \frac{\partial s}{\partial \mathbf{E}} - \frac{\mathbf{T}}{\theta}\right) : \dot{\mathbf{E}} + \boldsymbol{\Lambda} \cdot \dot{\boldsymbol{Q}} \geq 0. \tag{15.7}$$

Since inequality (15.7) contains a divergence term,the positive definite property of σ^s implies the classical result

$$\boldsymbol{J}^s = \frac{1}{\theta}\boldsymbol{Q}. \tag{15.8}$$

A further examination of expression (15.7) shows that it is linear in $\dot{\mathbf{E}}$ but, since this time derivative is an arbitrary quantity, positiveness of (15.7) requires that

$$\mathbf{T} = -\rho_R \theta \frac{\partial s}{\partial \mathbf{E}}. \tag{15.9}$$

In its linear version, the constitutive equation (15.9) is given by the well known Neumann–Duhamel relation

$$\mathbf{T} = \boldsymbol{\mathcal{C}} : \mathbf{E} - \beta(\theta - \theta_r), \tag{15.10}$$

where $\boldsymbol{\mathcal{C}}$ is the fourth-order tensor of elastic moduli, β the second-order tensor of thermal moduli and θ_r a reference temperature. In virtue of the results (15.8) and (15.9), inequality (15.7) reads as

$$\sigma^s = \nabla_X \theta^{-1} \cdot \boldsymbol{Q} + \boldsymbol{\Lambda} \cdot \dot{\boldsymbol{Q}} \geq 0. \tag{15.11}$$

For simplicity, assume that Λ is a linear function of $\boldsymbol{Q}$,

$$\boldsymbol{\Lambda} = -\alpha(u, \mathbf{E}) \cdot \boldsymbol{Q}, \tag{15.12}$$

where $\alpha(u, \mathbf{E})$ is an arbitrary phenomenological second-order tensor depending generally on u and $\mathbf{E}$; it is a positive quantity to guarantee the stability of the equilibrium state. As a consequence, relation (15.11) will be given by

$$\sigma^s = \boldsymbol{Q} \cdot \left(\nabla_X \theta^{-1} - \alpha \cdot \dot{\boldsymbol{Q}} \right) \geq 0. \tag{15.13}$$

Expression (15.13) is interesting as it is bilinear in the thermodynamic flux $\boldsymbol{Q}$ and the corresponding thermodynamic force represented by the terms inside the parentheses. The simplest way to ensure that $\sigma^s \geq 0$ is to assume that there exists a linear relation between the conjugated force and the flux $\boldsymbol{Q}$, i.e.

$$\left(\nabla_X \theta^{-1} - \alpha \cdot \dot{\boldsymbol{Q}} \right) = \mathbf{L} \cdot \boldsymbol{Q}, \tag{15.14}$$

where $\mathbf{L}(u, \mathbf{E})$, a tensor of order two, represents a phenomenological coefficient generally function of u or the temperature θ and $\mathbf{E}$. After substitution of (15.14) in (15.13), one is led to

$$\sigma^s = \boldsymbol{Q} \cdot \mathbf{L} \cdot \boldsymbol{Q} \geq 0, \tag{15.15}$$

from which follows that $\mathbf{L}$ is a positive definite tensor, if in addition the Onsager reciprocity relations are taken for granted, $\mathbf{L}$ is also symmetric. The result (15.14) is the main contribution of EIT to the description of thermo-elasticity, by rewriting it under the form

$$\alpha \cdot \dot{\boldsymbol{Q}} = \nabla_X \theta^{-1} - \mathbf{L} \cdot \boldsymbol{Q}, \tag{15.16}$$

one obtains a Cattaneo-type equation which, for $\alpha = 0$, reduces to Fourier's law

$$\boldsymbol{Q} = -\boldsymbol{\lambda} \cdot \nabla_X \theta, \tag{15.17}$$

where $\lambda = \mathbf{L}^{-1}/\theta^2$ is the heat conductivity (symmetric) tensor which is not only function of the temperature field but also on the deformation state. In the case of isotropy, expression (15.17) simplifies as

$$\tau \dot{\boldsymbol{Q}} = -\lambda \nabla_X \theta - \boldsymbol{Q} \tag{15.18}$$

where $\tau = \alpha\lambda\theta^2$ designates a positive relaxation time and $\lambda = (L\theta^2)^{-1}$ the positive heat conductivity. Although the above analysis is strictly linear, there is no difficulty to generalize it to the non-linear regime. Instead of (15.14), we can write

$$\nabla_X \theta^{-1} - \alpha \cdot \dot{\boldsymbol{Q}} = \frac{\partial \Xi}{\partial \boldsymbol{Q}}, \tag{15.19}$$

where α is generally depending on the heat flux, the potential Ξ, usually called a dissipation potential, depends on the whole set of variables and satisfies the following three properties:

(i) $\Xi(\boldsymbol{Q} = 0) = 0$; (ii) Ξ reaches its minimum at $\boldsymbol{Q} = 0$; (iii) Ξ is convex in the neighbourhood of $\boldsymbol{Q} = 0$.

It follows from these properties that $\boldsymbol{Q} \cdot (\partial\Xi/\partial\boldsymbol{Q}) \geq 0$ and therefore the positiveness of σ^s is automatically satisfied. The right hand side of (15.14) corresponds to a particular choice of the dissipation potential, namely $\Xi = \frac{1}{2}\boldsymbol{Q} \cdot \mathbf{L} \cdot \boldsymbol{Q}$.

To summarize, the problem of thermo-elasticity is completely governed by the evolution equations (15.1–15.3) and (15.16) or (15.19), at the condition to be complemented by a constitutive equation expressing the internal energy u in terms of the basic variables.The only quantities that remain to be specified by constitutive relations are the heat conductivity tensor λ and the time-relaxation tensor α. From the above considerations, we can say that both are positive-definite tensors, whose explicit dependence with respect to the temperature and the strain tensor will be provided either by experimental measurements or microscopic theories. The physical situations in which the present extension of classical thermo-elasticity is expected to be pertinent occur when the relaxation time of the heat flux is not small or in phenomena involving short time scales. This is for instance the case within microsystems and nanostructures in the nano–pico–femto time scale, in fast thermal wave propagations as occurring in thermal shock and thermal resonance phenomena, in high-frequency processes which happen when an elastic solid is suddenly heated at one of its boundaries by means of a laser pulse, an electrical discharge or a fast exothermic chemical reaction.

15.2 Viscoelasticity

In the present section, it is shown that EIT accommodates the formulation of viscoelastic bodies as well. The following hypotheses are taken for granted: the material is isotropic, and temperature T_0 and mass density ρ_0 are supposed to be uniform so that heat and compressibility effects are omitted, and, in addition, we shall only be concerned with linear viscoelasticity. Generalization to non-linear anisotropic models submitted to thermal gradients, although it is not a trivial matter will not raise fundamental difficulties.

The choice of the state variables is inspired both by fluid mechanics and the theory of elasticity (Lebon et al. 2004): in the latter, the space of variables is essentially formed by the symmetric strain tensor. In fluid mechanics, the basic thermodynamic variables are the mass density, the internal energy and, within the standard point of view of EIT, the pressure or stress tensor playing the role of *flux* variable. Here, the space of state variables will therefore be selected as follows:

$$\mathcal{V} =: \mathbf{E}, u, \mathbf{T}^{(i)}, \tag{15.20}$$

with u and $\mathbf{E}$ designating, as usual, the internal energy per unit mass and the strain tensor, $\mathbf{T}^{(i)}$ is the inelastic stress tensor, defined as

$$\mathbf{T}^{(i)} = \mathbf{T} - \mathbf{T}^{(e)}, \tag{15.21}$$

where $\mathbf{T}$ is the total stress tensor and $\mathbf{T}^{(e)}$ its elastic part shown in the previous section to be given by

$$\mathbf{T}^{(e)} = -\rho_0 T_0 \frac{\partial s}{\partial \mathbf{E}}, \tag{15.22}$$

Assuming that $\partial s/\partial \mathbf{T}^{(i)}$ is a linear function of $\mathbf{T}^{(i)}$, Gibbs' relation will take the form

$$T_0 \mathrm{d}s = \mathrm{d}u - \mathbf{T}^{(e)} : \mathrm{d}\mathbf{E}/\rho_0 - \alpha \mathbf{T}^{(i)} : \mathrm{d}\mathbf{T}^{(i)}/\rho_0, \tag{15.23}$$

wherein α is a phenomenological coefficient not depending on $\mathbf{T}^{(i)}$. Stability of equilibrium which implies that $\partial^2 s/(\partial \mathbf{T}^{(i)} : \partial \mathbf{T}^{(i)}) < 0$ leads us to the conclusion that $\alpha > 0$. Time evolution of $\mathbf{E}$ and u is governed by the momentum and energy equations (15.3) and (15.4) respectively. Before formulating the missing evolution equation for $\mathbf{T}^{(i)}$, we shall preliminary derive the expression of the entropy production. Proceeding as in the previous section and making use of (15.22), it is easily checked that

$$T_0 \sigma^s = \mathbf{T}^{(i)} : (\dot{\mathbf{E}} - \alpha \mathbf{T}^{(i)}) \geq 0. \tag{15.24}$$

The simplest way to guarantee the positiveness of the dissipated energy $T_0 \sigma^s$ is to write

$$\dot{\mathbf{E}} - \alpha \dot{\mathbf{T}}^{(i)} = L \dot{\mathbf{T}}^{(i)}, \tag{15.25}$$

wherein L is a positive constant phenomenological coefficient. Here again, with analogy with the treatment of thermo-elasticity, we can easily generalize our results to non-linear situations by introducing the dissipation potential $\Xi(\mathbf{T}^{(i)})$ and by writing the right hand side of (15.25) $\partial \Xi/\partial \mathbf{T}^{(i)}$. Setting $\alpha/L = \tau$, $1/L = 2\eta$ in (15.25), one obtains the following linear time evolution equation

$$\tau \dot{\mathbf{T}}^{(i)} = 2\eta \dot{\mathbf{E}} - \mathbf{T}^{(i)}, \tag{15.26}$$

where τ is a positive relaxation times and η is a viscosity coefficient; the above relation is the corner-stones of our viscoelastic model. The corresponding dissipation energy is homogeneous of degree two in the components of the inelastic stress tensor:

$$T_0\sigma^s = (\mathbf{T}^{(i)} : \mathbf{T}^{(i)})(2\eta)^{-1} \geq 0, \tag{15.27}$$

from which follows that η is a positive quantity. In a linear theory, the elastic stress tensor $\mathbf{T}^{(e)}$ is a linear function of the deformation rate $\mathbf{E}$,

$$\mathbf{T}^{(e)} = 2G\mathbf{E}, \tag{15.28}$$

with G the Lamé coefficient of linear elasticity. After addition of (15.26), (15.28) and their time derivatives, one obtains the evolution equation for the total stress tensor $\mathbf{T} = \mathbf{T}^{(e)} + \mathbf{T}^{(i)}$, namely

$$\tau\dot{\mathbf{T}} + T = 2G(\tau_\varepsilon\dot{\mathbf{E}} + \mathbf{E}), \tag{15.29}$$

where the relaxation time τ_ε stands for $\tau_\varepsilon = \eta/G + \tau$. It is worth noticing that expression (15.29) is equivalent to the Poynting–Thomson or standard model of rheology and that such a model is directly amenable trough a thermodynamic description based on EIT.

The following particular cases area also of interest; by setting $\tau = 0$, relation (15.29) reduces to the Kelvin–Voigt body

$$\mathbf{T} = 2\eta\dot{\mathbf{E}} + 2G\mathbf{E}, \tag{15.30}$$

while by putting $G = 0$, one finds back Maxwell's equation

$$\tau\dot{\mathbf{T}} + \mathbf{T} = 2\eta\dot{\mathbf{E}}, \tag{15.31}$$

A combination of relation (15.26) and Newton's law of fluid mechanics will yield Jeffreys' model which is frequently used to model the earth crust. This is easily seen by decomposing the stress tensor into a viscous and a inelastic part in such a way that

$$\mathbf{T} = \mathbf{T}^{(v)} + \mathbf{T}^{(i)}, \tag{15.32}$$

where the viscous stress tensor is related to the elements of the strain tensor by the Newton's law

$$\mathbf{T}^{(v)} = 2\eta^s\dot{\mathbf{E}}, \tag{15.33}$$

where η^s designates the shear viscosity. Taking the time derivative of (15.33) combined to (15.25) results in

$$\dot{\mathbf{T}} + \tau^{-1}\mathbf{T} = 2\eta^s[\ddot{\mathbf{E}} + \left(\tau^J\right)^{-1}\dot{\mathbf{E}}], \tag{15.34}$$

the relaxation time τ^J being given by $\tau^J = \tau\eta^s/(\eta + \eta^s)$. The decomposition (15.32) is frequently used to describe dilute solutions of polymers, $\mathbf{T}^{(v)}$ represents then the contribution of the solvent, often a Newtonian fluid, and $\mathbf{T}^{(i)}$ is the mean stress tensor associated to the polymer molecules (see Sect. 15.4). Compared to expression (15.27), the dissipated energy will contain an additional term quadratic in the viscous stress tensor. The model proposed in this section is pertinent to describe materials and processes characterized by large values of the relaxation time of the inelastic stress tensor; such situations are expected to happen in superconductors, polymers, phase change in polymeric solutions and diffusion of polymers in solvents.

The aim of this section was to show that visco-elasticity is easily and naturally incorporated into an EIT description. It is worth to stress that EIT encompasses a larger class of materials than Maxwell's bodies as other materials, like these of Kelvin–Voigt, Poynting–Thomson and Jeffreys receive a direct interpretation. The various phenomenological material coefficients can be determined experimentally by measurements of wave velocity and attenuation coefficients (see Problems 15.12 and 15.13). Generalizations to plastic bodies and non-Newtonian fluids is treated in the next sections.

15.3 Plasticity

The models discussed so far are characterized by a time scale and do not place a limit to the values taken by the stress tensor. In plastic bodies, these two characteristics are lost so that the previous models are not directly applicable. The present approach deviates from the analyses developed earlier in this book by the fact that the dissipation function is homogeneous of degree one and that plasticity is independent of the time scale used to compute the rate of change. It must however be realized that this is a first partial attempt to provide an EIT description of plasticity and not an exhaustive theory.

Plasticity is a non-linear rate-independent process. The main property of plastic deformations is that, after unloading down at zero stress, there remains a residual deformation $\mathbf{E}^{(\mathrm{p})}$. In the theory of plasticity (e.g. Prager 1955; Ponter et al. 1974; Lambermont 1974; Perzyna 1974), it is therefore usual to split the strain tensor $\mathbf{E}$ into an elastic $\mathbf{E}^{(\mathrm{e})}$ and a plastic part $\mathbf{E}^{(\mathrm{p})}$ in such a way that $\mathbf{E} = \mathbf{E}^{(\mathrm{e})} + \mathbf{E}^{(\mathrm{p})}$. As in Sect. 15.2, we shall omit thermal and compressibility effects and consider for simplicity isotropic materials.

The space $\mathcal{V}$ of the basic state variables is selected as follows:

$$\mathcal{V} =: u, \mathbf{E}^{(\mathrm{e})}, \mathbf{T}^{(\mathrm{p})} \tag{15.35}$$

The choice of $\mathbf{E}^{(\mathrm{e})}$ as basic variable is motivated by the fact that we identify the strain variable by unloading and letting the body relax to equilibrium. By analogy with the viscous pressure tensor introduced in the EIT description of fluid mechanics, we select as extra variable the plastic stress $\mathbf{T}^{(\mathrm{p})}$ which is associated with the dissipated energy due to plastic deformations. From a microscopic point of view, the occurrence of $\mathbf{T}^{(\mathrm{p})}$ is a consequence of the forces acting on dislocation lines.

The specific entropy s is a function of the whole set of variables

$$s = s(u, \mathbf{E}^{(\mathrm{e})}, \mathbf{T}^{(\mathrm{p})}) \tag{15.36}$$

and the corresponding Gibbs equation is assumed to be given by

$$T_0 \mathrm{d}s = \mathrm{d}u - \frac{\mathbf{T}}{\rho_0} : \mathrm{d}\mathbf{E}^{(\mathrm{e})} - \frac{\mathbf{\Phi}^{(\mathrm{p})}}{\rho_0} : \mathrm{d}\mathbf{T}^{(\mathrm{p})}, \tag{15.37}$$

with

$$\mathbf{T} = -\rho_0 T_0 \frac{\partial s}{\partial \mathbf{E}^{(\mathrm{e})}}, \tag{15.38a}$$

$$\Phi^{(\mathrm{p})} = -\rho_0 T_0 \frac{\partial s}{\partial \mathbf{T}^{(\mathrm{p})}}. \tag{15.38b}$$

The equation of state (15.38a) is the usual definition of the total stress while the equation (15.38b) reflects the contribution of EIT. The set formed by the above equations of state and the momentum and energy balances allows in principle to determine $\mathbf{T}$, $\mathbf{\Phi}^{(\mathrm{p})}$, $\mathbf{E}^{(\mathrm{e})}$ and u, it remains to derive the two missing equations for the unknowns left, namely $\mathbf{E}^{(\mathrm{p})}$ and $\mathbf{T}^{(\mathrm{p})}$. Starting from expression (15.6) of the entropy production wherein $\boldsymbol{J}^s = 0$, it is found that

$$T_0 \sigma^s \equiv D(\dot{\mathbf{E}}^{(\mathrm{p})}, \dot{\mathbf{T}}^{(\mathrm{p})}) = \mathbf{T} : \dot{\mathbf{E}}^{(\mathrm{p})} - \mathbf{\Phi}^{(\mathrm{p})} : \dot{\mathbf{T}}^{(\mathrm{p})} \geq 0, \tag{15.39}$$

after use is made of the energy balance (15.3) and Gibbs' equation (15.37); the quantity D denotes the positive rate of dissipation function and it is important to note that it is a homogeneous function of degree one in the "fluxes" $\dot{\mathbf{E}}^{(\mathrm{p})}$ and $\dot{\mathbf{T}}^{(\mathrm{p})}$. Similarly, its Legendre transformation D^* defined by

$$D^*(\mathbf{T}, \mathbf{\Phi}^{(\mathrm{p})}) = \mathbf{T} : \dot{\mathbf{E}}^{(\mathrm{p})} - \mathbf{\Phi}^{(\mathrm{p})} : \dot{\mathbf{T}}^{(\mathrm{p})} - D, \tag{15.40}$$

with

$$\mathrm{d}D^* = \dot{\mathbf{E}}^{(\mathrm{p})} : \mathrm{d}T - \dot{\mathbf{T}}^{(\mathrm{p})} : \mathrm{d}\mathbf{\Phi}^{(\mathrm{p})}, \tag{15.41}$$

is homogeneous of degree one in the conjugated variables $\mathbf{T}$ and $\mathbf{\Phi}^{(\mathrm{p})}$, moreover D^* is identically equal to zero in virtue of (15.39). Further information will be drawn from convexity properties as shown in Box 15.1.

Box 15.1 Convex functions and normality conditions Let $D(\dot{\boldsymbol{x}})$ be a positive convex function of the n-dimensional flux $\dot{\boldsymbol{x}}$ and assumed to be homogeneous of degree m: $D(k\dot{\boldsymbol{x}}) = k^m DL(\dot{\boldsymbol{x}})$. In differential form, one has

$$\mathrm{d}D = \frac{\partial D}{\partial \dot{\boldsymbol{x}}} \cdot \mathrm{d}\dot{x} = \mathbf{y} \cdot \mathrm{d}\dot{\boldsymbol{x}}, \tag{15.1.1}$$

with the force (or stress) y defined as

$$\mathbf{y} = \frac{\partial D(\dot{\boldsymbol{x}})}{\partial \dot{\boldsymbol{x}}}, \tag{15.1.2}$$

and, by virtue of Euler's theorem for homogeneous functions,

$$\frac{\partial D}{\partial \dot{\boldsymbol{x}}} \cdot \dot{\boldsymbol{x}} = \boldsymbol{y} \cdot \dot{\boldsymbol{x}} = mD. \tag{15.1.3}$$

In most problems of non-equilibrium thermodynamics, one has $m = 2$. Plasticity constitutes an exception, as the dissipation potential D is homogeneous of degree one and, from (15.1.3), that $\boldsymbol{y}$ is of degree zero in $\dot{\boldsymbol{x}}$ and therefore insensitive to the time-rate at which $\boldsymbol{x}$ evolves. For further purpose, we introduce the Legendre transform $D^*(\boldsymbol{y})$ of $D(\dot{\boldsymbol{x}})$ defined by

$$D^*(\boldsymbol{y}) = \boldsymbol{y} \cdot \dot{\boldsymbol{x}} - D, \tag{15.1.4}$$

from which follows that the dual potential $D^*(\boldsymbol{y})$ is identically equal to zero with

$$\mathrm{d}D^*(\boldsymbol{y}) = \boldsymbol{y} \cdot \mathrm{d}\dot{\boldsymbol{x}} + \dot{\boldsymbol{x}} \cdot \mathrm{d}\boldsymbol{y} - \boldsymbol{y} \cdot \mathrm{d}\dot{\boldsymbol{x}} = \dot{x}\mathrm{d}\boldsymbol{y}, \tag{15.1.5}$$

and

$$\dot{\boldsymbol{x}} = \frac{\partial D^*(\boldsymbol{y})}{\partial \boldsymbol{y}}. \tag{15.1.6}$$

Since our attention is directed to plasticity, we assume that $\mathbf{y}$ is constrained to a closed convex domain $\mathbb{C}$ containing the origin O of $\boldsymbol{y}$-space and bounded by a yield state surface $f(\boldsymbol{y}) = 0$. As far as $\boldsymbol{y}$ is confined inside $\mathbb{C}$, $\dot{\boldsymbol{x}} = 0$ and no dissipation occurs: the deformation is purely elastic, dissipation is observed only when the extremity of $\boldsymbol{y}$ lies on the boundary. Designating by $\boldsymbol{y}^*$ any force inside $\mathbb{C}$, by $y - y^*$ any additional force and by $\dot{\boldsymbol{x}}$ the produced velocity, positiveness of D implies that

$$(\boldsymbol{y} - \boldsymbol{y}^*) \cdot \dot{\boldsymbol{x}} \geq 0. \tag{15.1.7}$$

Inequality (15.1.7) has been interpreted as a principle of maximum dissipation as it asserts that, once the velocity is prescribed, the rate of dissipation of the real force y is never less that the fictitious rate of work of an arbitrary force $\boldsymbol{y}^*$ below or at the yield limit. This criterion was first formulated by von Mises in 1928. In terms of incremental quantities, expression (15.1.7) will take the form proposed by Drucker in 1949,

$$\mathrm{d}\boldsymbol{y} \cdot \mathrm{d}\boldsymbol{x} \geq 0. \tag{15.1.8}$$

Referring to convex analysis (e.g. Germain 1973), this inequality (or (15.1.7)) reflects the normality condition accordingly the velocity $\dot{\boldsymbol{x}}$ lies within the cone generated by the outward normals to the yield surface at the end point of $\boldsymbol{y}$:

$$\dot{\boldsymbol{x}} = \dot{\lambda} \frac{\partial f}{\partial \boldsymbol{y}}, \tag{15.1.9}$$

the upper point in $\dot{\lambda}$ has been introduced for dimensional reason although, paradoxically, there is no time scale corresponding to expression (15.1.9), $\dot{\lambda}$ is a positive scalar with

$$\dot{\lambda} \geq 0 \quad \text{if} \quad f = 0 \quad \text{and} \quad \dot{f} = 0, \tag{15.1.10a}$$

$$\dot{\lambda} = 0 \quad \text{if} \quad f \quad < 0 \quad \text{or} \quad f = 0, \quad \dot{f} < 0, \tag{15.1.10b}$$

the situations $(f = 0, \dot{f} = 0)$, $(f < 0)$ and $(f = 0, \dot{f} < 0)$ describe neutral loading, no plastic flow and unloading respectively.

According to the general considerations of Box 15.1, D^* can be identified with the yield surface $f = 0$ of a closed convex elastic domain $\mathbb{C}$ in the hyperspace of tensors $\mathbf{T}$ and $\mathbf{\Phi}^{(\mathrm{p})}$ with the "fluxes" $\dot{\mathbf{E}}^{(\mathrm{p})}$ and $\dot{\mathbf{T}}^{(\mathrm{p})}$ fulfilling the normality conditions

$$\dot{\mathbf{E}}^{(\mathrm{p})} = \dot{\lambda} \frac{\partial f}{\partial \mathbf{T}}, \qquad \dot{\mathbf{T}}^{(\mathrm{p})} = -\dot{\lambda} \frac{\partial f}{\partial \mathbf{\Phi}^{(\mathrm{p})}}, \tag{15.42}$$

these relations provide the two missing evolution equations of our model, the scalar $\dot{\lambda}$ denotes the so-called plastic multiplier. The first relation (15.42) is well known in the theory of plasticity while the second one is reminiscent of internal variables theories (Maugin 1999).

In whole generality, $\mathbf{\Phi}^{(\mathrm{p})}$ depends on both variables $\mathbf{E}^{(\mathrm{e})}$ and $\mathbf{T}^{(\mathrm{p})}$, however there are many indications that, in plastic flows, the influence of $\mathbf{T}^{(\mathrm{p})}$ is dominant. By analogy with previous developments in fluid mechanics, it is assumed that $\mathbf{\Phi}^{(\mathrm{p})} = \gamma \mathbf{T}^{(\mathrm{p})}$ where γ is a positive constant to guarantee stability of equilibrium. With this particular option, (15.42b) writes as

$$\dot{\mathbf{T}}^{(\mathrm{p})} = -\hat{\lambda} \frac{\partial f}{\partial \mathbf{T}^{(\mathrm{p})}}, \tag{15.43}$$

with $\hat{\lambda} = \dot{\lambda}/\gamma$. Working in the framework of this approximation, the consistency condition (15.1.10) expressing that $f = \dot{f} = 0$ implies that

$$\frac{\partial f}{\partial \mathbf{T}} : \dot{\mathbf{T}} + \frac{\partial f}{\partial \mathbf{T}^{(\mathrm{p})}} : \dot{\mathbf{T}}^{(\mathrm{p})} = 0, \tag{15.44}$$

making use of the normality condition (15.43), one obtains the following expression for $\dot{\lambda}$:

$$\dot{\lambda} = h \frac{\partial f}{\partial \mathbf{T}} : \dot{\mathbf{T}}, \tag{15.45}$$

with the positive scalar coefficient h given by $h = \gamma^{-1}\left[(\partial f/\partial \mathbf{T}^{(\mathrm{p})}) : (\partial f/\partial \mathbf{T}^{(\mathrm{p})})\right]^{-1} \geq 0$. After substitution of (15.45) in (15.42a), one finds back the celebrated normality rule established by Drucker (1949):

$$\dot{\mathbf{E}}^{(\mathrm{p})} = h \frac{\partial f}{\partial \mathbf{T}} \frac{\partial f}{\partial \mathbf{T}} : \dot{\mathbf{T}}. \tag{15.46}$$

Another consequence of the consistency condition written in the form (15.44) is obtained by substituting in it the expressions of $\partial f/\partial \mathbf{T}$ and $\partial f/\partial \mathbf{T}^{(\mathrm{p})}$ drawn respectively from (15.42a) and (15.43), the result is

$$\dot{\mathbf{E}}^{(\mathrm{p})} : \dot{\mathbf{T}} - \gamma \dot{\mathbf{T}}^{(\mathrm{p})} : \dot{\mathbf{T}}^{(\mathrm{p})} = 0. \tag{15.47}$$

In absence of the extra variable $\mathbf{T}^{(\mathrm{p})}$, which means ideal plasticity, we have the strict orthogonality condition

$$\dot{\mathbf{E}}^{(\mathrm{p})} : \dot{\mathbf{T}} = 0. \tag{15.48}$$

In the case that $\mathbf{T}^{(\mathrm{p})}$ is nonzero, we find

$$\dot{\mathbf{E}}^{(\mathrm{p})} : \dot{\mathbf{T}} \geq 0, \tag{15.49}$$

the results (15.48–15.49) are equivalent to Drucker' relation $(\mathbf{T} - \mathbf{T}^{*}) : \dot{\mathbf{E}}^{(\mathrm{p})} \geq 0$ stating that plastic work increment is positive definite.

The description presented in Sects. 15.1–15.15.3 can be viewed as an indirect excursion into the internal structure of the solids and the evolution of the internal structure. Emphasis has been put more on methodology and strategy rather than on practical applications. The principal results which have been obtained can be summarized as follows.

- In thermo-elasticity, there is, as expected, no new information about the elastic behaviour. The original aspect of our study is the occurrence of a new heat transport equation (15.18) of the Cattaneo type.
- In viscoelasticity, we obtain an evolution equation for the anelastic stress tensor, which combined to Hooke's law and Newton's equation of fluid mechanics allows us to recover the classical models of visco-elasticity like these of Maxwell, Voigt, and Jeffreys.

Plasticity is a large and extremely complex subject of which we do not suppose to make justice. Rather, our goal was limited to provide a simple approach based on EIT with the plastic stress tensor elevated to the rank of independent variable.

Contrary to most other applications, plasticity contains no time scale and the corresponding dissipation function is of degree one instead of two. Several features have not been considered, such as thermal effects, the Bauschinger effect, the localized modification of the yield surface due to plastic flow, and rate-dependent plasticity (visco-plasticity). The most important results are embodied in the normality conditions (15.42) and Drucker's results (15.46) and (15.49). As our objective was to present a macroscopic phenomenological description, no effort has been made to connect the macroscopic parameters to specific quantities of the theory of dislocation. Although the connection between microscopic and macroscopic descriptions is of fundamental interest in view of a better comprehension of plasticity (e.g. Kröner 1963; Seeger 1963; Lambermont 1974), we have considered that such a subject is outside the scope of the present book.

15.4 Relation of EIT to Kinetic Polymer Models

It is expected that a kinetic interpretation enlightens and complements a purely continuum approach. A vast amount of work devoted to microscopic descriptions of rheological bodies has been published; valuable results are collected in the classical books by Doi and Edwards (1986) and Bird et al. (1987a,b). It is not our purpose to review the most significant kinetic models but we wish to stress that most of them exhibit a whole relaxation spectrum for the stress tensor. This important property is fairly well described by the beads-springs chain models associated with the names of Rouse (1953) and Zimm (1956). For many years these models have played a key role in the interpretation of rheological phenomena. There have been many extensions of Rouse's and Zimm's works, but although most of these generalisations give a better fitting of the experimental data by introducing more parameters, they do not alter radically the foundations underlying Rouse's and Zimm's approaches. Our purpose here is to show that EIT is capable of coping with the relaxation spectrum of the stress tensor exhibited in the Rouse and Zimm models.

15.4.1 The Rouse and Zimm Models

The current molecular models regard the polymer macromolecules as being formed by assemblies of beads, springs, and rods. In the Rouse model, the molecules are modelled by a chain of N point-mass beads connected by $N - 1$ Hookean springs. The forces acting on each bead can be classified as follows:

a. The hydrodynamic drag force which is the force experienced by the bead as it moves through the polymeric solution. According to Stokes, it is proportional to the difference between the bead velocity and the centre-of-mass velocity of the solution. By hydrodynamic interaction is meant the perturbation of the velocity field of one particular bead by the motion of the other beads. In the Rouse model, in which it is admitted that the motions of the N beads are uncorrelated, this kind of interaction is ignored; it is accounted for in the Zimm model.

b. The Brownian force caused by the thermal fluctuations in the solution.
c. The intramolecular force, which is exerted on one bead through the spring force.
d. The external forces, such as the gravitational or electrical forces.

The Rouse and Zimm models are appropriate for describing dilute polymer solutions and were primarily used in linear viscoelasticity. For simplicity, it is assumed that the total mass density remains constant. It is also supposed that the roles of the solvent and the polymer can be separated. Accordingly, the viscous stress tensor is decomposed into two parts, $\mathbf{T}^v = \mathbf{T}_0 + \mathbf{T}_p$, where subscripts 0 and p denote the contribution of the solvent and the polymer respectively; next, $\mathbf{T}_p$ is decomposed into N normal modes,

$$\mathbf{T}_p = \sum_{\alpha=1}^{N} \mathbf{T}_\alpha, \tag{15.50}$$

and each individual mode α is assumed to satisfy, in the linear regime, a relaxation dynamics of the form

$$\tau_\alpha \frac{\partial \mathbf{T}_\alpha}{\partial t} + \mathbf{T}_\alpha = 2\eta_\alpha \mathbf{V}. \tag{15.51}$$

In the Rouse model, the coefficients τ_α and η_α are given by $\tau_\alpha = \frac{1}{2}\xi / H a_\alpha$ and $\eta_\alpha = n k_\mathrm{B} T \tau_\alpha$; k_B is the Boltzmann constant, T the absolute temperature, n the number of molecules per unit volume, ξ the friction coefficient related to the drag force experienced by the bead, H the Hookean spring constant, and a_α the eigenvalues of the Rouse matrices given by

$$a_\alpha = 4 \sin^2 \left(\frac{\pi \alpha}{2N} \right). \tag{15.52}$$

In Zimm's model, the a_α are replaced by eigenvalues $\overline{a}_\alpha$ of the modified Rouse matrices, which are found in tabular form or given by approximate expressions (Bird et al. 1987).

15.4.2 EIT Description of the Rouse and Zimm Models

The procedure is similar to that developed in Sect. 15.2, but the set of independent variables is now extended in order to include the contributions arising from the N normal modes. In this way, the entropy will depend on $\mathbf{T}_\alpha$ ($\alpha = 0, 1, \ldots, N$) besides the usual variable u (internal energy): $s = s(u, \mathbf{T}_\alpha)$. The temperature is supposed to remain constant as well as the polymer concentration, which therefore has not been introduced into the set of variables. Assuming that the entropy s is analytic in the fluxes, one may write

$$\mathrm{d}s = \frac{1}{T}\mathrm{d}u - \frac{1}{\rho T} \sum_{\alpha=0}^{N} \frac{\tau_\alpha}{2\eta_\alpha} \mathbf{T}_\alpha : \mathrm{d}\mathbf{T}_\alpha \tag{15.53}$$

on condition that we neglect the coupling between the various modes. A more complete treatment in which this coupling is included can be found in Perez-García et al. (1989).

Up to second-order terms in the velocity gradients and pressure tensors, the entropy production can be straightforwardly calculated:

$$T\sigma^s = \sum_{\alpha=0}^{N} \mathbf{T}_\alpha : \left(\mathbf{V} - \frac{\tau_\alpha}{2\eta_\alpha}\frac{\partial \mathbf{T}_\alpha}{\partial t}\right). \tag{15.54}$$

This takes the form of a bilinear relation between fluxes and forces, suggesting the following linear evolution equation:

$$\tau_\alpha \frac{\partial \mathbf{T}_\alpha}{\partial t} + \mathbf{T}_\alpha = 2\eta_\alpha \mathbf{V}, \quad (\alpha = 0, 1, \ldots, N). \tag{15.55}$$

Assuming with Rouse that the solvent is a Newtonian fluid, which means that $\tau_0 \ll \tau_\alpha$, one obtains for the solvent the classical Newton–Stokes equations

$$\mathbf{T}_0 = 2\eta_0 \mathbf{V}, \tag{15.56}$$

while expression (15.55) remains unchanged, provided α runs from 1 to N. Relations (15.55) and (15.56) are identical with the Rouse–Zimm equations, which were derived from kinetic arguments under the condition that the identifications $\tau_\alpha = \frac{1}{2}\xi/Ha_\alpha$ and $\eta_\alpha = nk_\mathrm{B}T\tau_\alpha$ are valid.

15.4.3 *Kinetic Justification of the EIT Results*

Our next objective will be to ground the EIT macroscopic results obtained in this subsection on kinetic foundations. Such as discussion will complement the general results of Chap. 4 on the kinetic theory of ideal monatomic gases. It is shown that the evolution equations and the entropy expression predicted by EIT are confirmed; incidentally, a new insight into the physical meaning of partial stress tensors is gained.

To calculate the polymer contribution to the entropy, one starts from the Boltzmann formula

$$\rho s = -nk_\mathrm{B} \int f \ \ln f \mathrm{d}\Gamma, \tag{15.57}$$

where f is the polymer distribution function and $\mathrm{d}\Gamma$ the volume in the phase space consisting of the positions $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$ and the velocities $\dot{\boldsymbol{r}}_1, \ldots, \dot{\boldsymbol{r}}_N$ of the N beads forming the chain. It is common to take as variables the centre-of-mass coordinate vector $\boldsymbol{r}_c$ and the relative position vectors $\boldsymbol{Q}_1, \ldots, \boldsymbol{Q}_{N-1}$, with $\boldsymbol{Q}_i$ starting from particle i and ending at particle $i+1$. It is also usual to split the distribution function f into two factors, one depending only on the velocities and the other only on the configuration:

$$f = \Xi(\dot{\boldsymbol{r}}_c, \dot{\boldsymbol{Q}}_1, \ldots, \dot{\boldsymbol{Q}}_{N-1})\Psi(\boldsymbol{r}_c, \boldsymbol{Q}_1, \ldots, \boldsymbol{Q}_{N-1}). \tag{15.58}$$

Under the three assumptions that the distribution of polymers in the solution is uniform, the velocity gradient is homogeneous and external forces are position independent, the configuration distribution function Ψ may be expressed as $n\psi(\boldsymbol{Q}_1, \ldots, \boldsymbol{Q}_{N-1})$, with ψ normalized to unity (Bird et al. 1987). Moreover, it is supposed that the velocity-dependent part of the distribution function is given by the Maxwell–Boltzmann local-equilibrium distribution function, from which follows that all the non-equilibrium effects are due to changes in the configurational distribution. This amounts to assuming that the relaxation time of the velocity distribution is much shorter than those associated with the configurational changes.

It is convenient to write the expression (15.57) for the entropy in terms of the equilibrium distribution function f_{eq}:

$$\rho s = -nk_{\mathrm{B}} \int f \ln f_{\mathrm{eq}} \mathrm{d}\Gamma - nk_{\mathrm{B}} \int f \ln(f/f_{\mathrm{eq}}) \mathrm{d}\Gamma. \tag{15.59}$$

The equilibrium distribution function in the canonical ensemble is given by

$$f_{\mathrm{eq}} = [Z\, T, \Omega]^{-1} \exp -E(\Gamma)/k_{\mathrm{B}}T, \tag{15.60}$$

where $E(\Gamma)$ is the energy of the configuration Γ and $Z(T, \Omega)$ the equilibrium partition function with Ω the total volume. Substituting (15.60) into the first term on the right-hand side of (15.59) results in

$$\rho s = \rho u/T + nk_{\mathrm{B}} \ln Z - nk_{\mathrm{B}} \int f \ln(f/f_{\mathrm{eq}}) \mathrm{d}\Gamma. \tag{15.61}$$

In equilibrium, one has

$$\rho s_{\mathrm{eq}}(u_{\mathrm{eq}}) = \rho u_{\mathrm{eq}}/T + nk_{\mathrm{B}} \ln Z, \tag{15.62}$$

whereby (15.61) becomes

$$\rho s - \rho s_{\mathrm{eq}}(u_{\mathrm{eq}}) = \rho(u - u_{\mathrm{eq}})T^{-1} - nk_{\mathrm{B}} \int f \ln(f/f_{\mathrm{eq}}) \mathrm{d}\Gamma. \tag{15.63}$$

It should be noticed that in the kinetic theory of monatomic ideal gases, it is assumed that $u = u_{\mathrm{eq}}$ (see (4.32)) and the first term on the right-hand side of (15.63) is lacking.

Since the non-equilibrium effects arise from changes in the configurational distribution function, the non-equilibrium contribution to s may be written as

$$\rho s - \rho s_{\mathrm{eq}}(u_{\mathrm{eq}}) = \rho T^{-1}(u - u_{\mathrm{eq}}) - nk_{\mathrm{B}} \int \psi \ln(\psi/\psi_{\mathrm{eq}}) \mathrm{d}\boldsymbol{Q}_1 \ldots \mathrm{d}\boldsymbol{Q}_{N-1}. \tag{15.64}$$

Instead of using the relative position vectors $\boldsymbol{Q}_1, \ldots, \boldsymbol{Q}_{N-1}$, we shall introduce the normal coordinates $\boldsymbol{Q'}_1, \ldots, \boldsymbol{Q'}_{N-1}$ of the chain variables. In the Rouse model, the configurational distribution function simply reads (Bird et al. 1987b):

$$\psi(\boldsymbol{Q'}_1, \ldots, \boldsymbol{Q'}_{N-1}, t) = \prod_{j=1}^{N-1} \psi_j(\boldsymbol{Q'}_j, t), \tag{15.65}$$

where ψ_j is the distribution function corresponding to the normal mode j. According to Boltzmann's statistics, ψ_j is given in equilibrium by

$$\psi_{\text{eq}}(\boldsymbol{Q'}_j) = \left(\frac{H}{2\pi k_{\text{B}} T}\right)^{3/2} \exp\left(-\frac{H}{2k_{\text{B}}T}\boldsymbol{Q'}_j \cdot \boldsymbol{Q'}_j\right), \tag{15.66}$$

in which H is an elastic constant characterizing the intramolecular interactions.

The non-equilibrium correction to ψ_j may be derived from its evolution equation. The latter is viewed as a continuity equation in the configuration space, taking into account the various forces acting on the beads. In the absence of external forces, this equation (Bird et al. 1987) is

$$\frac{\partial \psi_j}{\partial t} = -\frac{\partial}{\partial \boldsymbol{Q'}_j} \cdot \left[\nabla \boldsymbol{v} \cdot \boldsymbol{Q'}_j \psi_j - \frac{k_{\text{B}} T a_j}{\xi} \frac{\partial \psi_j}{\partial \boldsymbol{Q'}_j} - \frac{a_j}{\xi} \boldsymbol{F}_j^c \psi_j\right]; \tag{15.67}$$

$\boldsymbol{F}_j^c$ is the Hookean force acting between the beads (in our case $\boldsymbol{F}_j^c = -H\boldsymbol{Q'}_j$), ξ is the friction coefficient describing the hydrodynamic drag force on a bead, and a_j is given by (15.52). Under a given velocity gradient, the steady solution of (15.62) is

$$\psi_j = \psi_{\text{eq}}\left(1 + \frac{\xi}{4a_j k_{\text{B}} T} \text{V} : \boldsymbol{Q'}_j \boldsymbol{Q'}_j\right), \tag{15.68}$$

as it is easily verified. When this result is introduced into (15.64), the entropy for a plane Couette flow with shear rate $\dot{\gamma}$ is

$$\rho s(u, \dot{\gamma}) - \rho s_{\text{eq}}(u_{\text{eq}}) = \frac{1}{2} n k_{\text{B}} \sum_{j=1}^{N-1} (\lambda_j \dot{\gamma})^2, \tag{15.69}$$

where $\lambda_j = (\xi / 2Ha_j)$, which shows explicitly the dependence of s on $\dot{\gamma}$. Expression (15.69) could seem paradoxical in the sense that $s(u, \dot{\gamma})$ is higher in non-equilibrium than in equilibrium. The solution to this apparent paradox is that the internal energy at equilibrium and at a given temperature differs from the internal energy under shear at the same temperature, because under shear the polymer stores an elastic energy as a result of the stretching of the chains. The elastic energy u_{el} is easily evaluated to be

$$\rho u_{\mathrm{el}} = \int \sum_{j=1}^{N-1} \frac{1}{2} H \boldsymbol{Q'}_j \cdot \boldsymbol{Q'}_j \psi\, \boldsymbol{Q'}_1, \ldots, \boldsymbol{Q'}_{N-1}, t \,\mathrm{d}\, \boldsymbol{Q'}_1 \ldots \mathrm{d}\boldsymbol{Q'}_{N-1}. \tag{15.70}$$

By taking (15.65) and (15.68) into account, one finds that

$$\rho(u - u_{\mathrm{eq}}) = nk_{\mathrm{B}}T \sum_{j=1}^{N-1} (\lambda_j \dot{\gamma})^2. \tag{15.71}$$

Combining (15.69) and (15.71) results in

$$\rho s(u, \dot{\gamma}) - \rho s_{\mathrm{eq}}(u_{\mathrm{eq}}) = \frac{\rho}{T}(u - u_{\mathrm{eq}}) - \frac{1}{2} nk_{\mathrm{B}} \sum_{j=1}^{N-1} (\lambda_j \dot{\gamma})^2, \tag{15.72}$$

or, what is the same,

$$\rho s(u, \dot{\gamma}) - \rho s_{\mathrm{eq}}(u_{\mathrm{eq}}) = \rho s_{\mathrm{eq}}(u) - \frac{1}{2} nk_{\mathrm{B}} \sum_{j=1}^{N-1} (\lambda_j \dot{\gamma})^2, \tag{15.73}$$

after use of the expansion

$$s_{\mathrm{eq}}(u) - s_{\mathrm{eq}}(u_{\mathrm{eq}}) = \left(\frac{\partial s}{\partial u}\right)_{\mathrm{eq}} (u - u_{\mathrm{eq}}) + \mathcal{O}(2). \tag{15.74}$$

According to the macroscopic theory (see (15.53)), the contribution of the fluxes to the entropy is

$$\rho s(u, \dot{\gamma}) = s_{\mathrm{eq}}(u) - \frac{1}{4} \sum_{j=1}^{N} \frac{\tau_j}{\rho \eta_j T} \mathbf{T}^v_j : \mathbf{T}^v_j. \tag{15.75}$$

To check whether the microscopic expression (15.73) is compatible with the macroscopic result (15.75) predicted by EIT, a microscopic evaluation of the relaxation times and the viscosities is needed. To proceed in the simplest way, we recall two equivalent expressions of the polymeric contribution to the viscous stress tensor, namely the Kramers and Giesekus tensors. The former reads (Bird et al. 1987b)

$$\mathbf{T}^v = nH \sum_{j=1}^{N-1} \left\langle \mathbf{Q}'_j \mathbf{Q}'_j \right\rangle - (N-1) nk_{\mathrm{B}} T \mathrm{U}, \tag{15.76}$$

with . . . standing for an average over the configuration space, i.e.

$$\left\langle \boldsymbol{Q'}_j \boldsymbol{Q'}_j \right\rangle = \int \psi(\boldsymbol{Q'}_1, \ldots, \boldsymbol{Q'}_{N-1}, t) \boldsymbol{Q'}_j \boldsymbol{Q'}_j \mathrm{d}\boldsymbol{Q'}_1 \ldots \mathrm{d}\boldsymbol{Q'}_{N-1}. \tag{15.77}$$

Expression (15.76) exhibits the microscopic meaning of the splitting of $\mathbf{T}^v$ as a sum of several terms: each of them is related to the contribution of one normal mode. To the $N-1$ modes appearing in (15.76) should be added the contribution of the motion of the centre of mass. The sum over the modes should therefore really extend to N instead of $N-1$.

We now turn to the Giesekus expression for $\mathbf{T}^v$ (Bird et al. 1987a):

$$\mathbf{T}^v = -\frac{1}{2}n\xi \sum_{j=1}^{N-1} \frac{1}{a_j} D^{\uparrow} \langle \boldsymbol{Q}'_j \boldsymbol{Q}'_j \rangle, \tag{15.78}$$

whith $D^{\uparrow}$ denoting the contravariant convected time derivative. After applying $D^{\uparrow}$ to (15.76) and using definition (15.78), one obtains

$$\mathbf{T}^v + \lambda_j D^{\uparrow}\mathbf{T}^v = 2nk_{\mathrm{B}}T\lambda_j \mathbf{V}, \tag{15.79}$$

where the relation $D^{\uparrow}\mathbf{U} = -2\mathbf{V}$ has been taken into account. Comparison of (15.79) with (15.55) allows us to identify the relaxation time and the viscosity related to each partial viscous pressure tensor as $\tau_j = \lambda_j$, $\eta_j = nk_{\mathrm{B}}T\lambda_j$. With these identifications in mind and in the particular case of a plane Couette flow for which $\mathbf{T}^v_j : \mathbf{T}^v_j = 2\eta_j^2\dot{\gamma}^2$, it is seen that the microscopic (15.73) and macroscopic (15.75) expressions are identical.

Whereas in the Rouse model the hydrodynamic interactions are neglected, in the Zimm model they are introduced in an average form. But this changes only the values of the eigenvalues a_j, in such a way that the basic formalism remains the same, and the agreement with extended irreversible thermodynamics is still achieved (Camacho and Jou 1990).

15.5 Non-Newtonian Fluids

Because of technical progresses in plastic polymers, polymer solutions, and pharmaceutical industry, non-Newtonians fluids have been the subject of intense interest. After general considerations, we will propose an EIT modelling and compare with experimental data. For simplicity, only incompressible materials without bulk effects are considered.

15.5.1 General Considerations

We examine the response of a rheological fluid under a simple shearing flow between two parallel horizontal planes separated by a distance h. If one of the planes, for instance the upper one, is moved in the x direction with a constant velocity v_0, the velocity field of the fluid is $v_x = \dot{\gamma}y$, $v_y = v_z = 0$, $\dot{\gamma} = v_0/h$, with

y in the direction normal to the planes, z the neutral direction, and $\dot{\gamma}$ the constant shear rate.

For a Newtonian incompressible fluid, the components of the stress tensor are given by $T_{xz} = T_{yz} = 0$, $T_{xx} = T_{yy} = T_{zz} = -p$, and $T_{xy} = \eta\dot{\gamma}$. Defining the first normal stress N_1 and the second normal stress N_2 as $N_1 = P_{yy} - P_{xx}$, $N_2 = T_{zz} - T_{yy}$, one sees straightforwardly that for a Newtonian fluid both N_1 and N_2 are zero. The linear constitutive relation $T_{xy} = \eta_0\dot{\gamma}$ together with a constant viscosity η_0 and the absence of normal stresses are the main properties of a Newtonian fluid. In contrast, non-Newtonian fluids are characterized by a shear-rate-dependent viscosity and non-vanishing normal stresses. It is common to introduce the 'apparent' viscosity μ and the first and second normal stress coefficients Ψ_1 and Ψ_2 by

$$T_{xy} = \mu(\dot{\gamma})\dot{\gamma} \quad (\mu > 0), \tag{15.80a}$$

$$N_1 = -\Psi_1(\dot{\gamma})\dot{\gamma}^2 \quad (\Psi_1 > 0), \tag{15.80b}$$

$$N_2 = -\Psi_2(\dot{\gamma})\dot{\gamma}^2 \quad (\Psi_2 < 0), \tag{15.80c}$$

where μ, Ψ_1, and Ψ_2 are generally referred to as the viscometric functions. Experimental data indicate that Ψ_1 is positive and Ψ_2 negative. While the dependence of μ with respect to $\dot{\gamma}$ gives rise to velocity profiles totally unusual in Newtonian flows, the normal stress coefficients are responsible for the well-known Weissenberg rod-climbing effect (Lodge 1964; Astarita and Marucci 1974). Non-zero values of Ψ_2 have been detected for several substances but usually Ψ_2 remains very small; $\Psi_2 = 0$ is known as Weissenberg's hypothesis.

A widely used model for the apparent viscosity μ is the Ostwald power law

$$\mu = m\dot{\gamma}^{n-1}, \tag{15.81}$$

where m and n are parameters characteristic of a given fluid allowed to depend on the temperature. However, the power law (15.81) is not realistic because it gives $\mu = \infty$ for $\dot{\gamma} = 0$ when $n < 1$, which is the most usual situation. To circumvent this difficulty, Carreau (1972) has proposed the following viscosity equation:

$$\frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty} = \left[1 + (\tau\dot{\gamma})^2\right]^{\frac{n+1}{2}}, \tag{15.82}$$

involving four parameters: a zero-shear-rate viscosity μ_0 an infinite shear-rate viscosity μ_∞, a time constant τ, and a supplementary constant n. This formula describes fairly well most engineering experiments.

The main problem in non-Newtonian fluid mechanics is that of formulating a constitutive equation for $\mathbf{T}$ containing the smallest number of parameters and applicable to the widest range of fluid responses.

The simplest generalisation of Newton's law is the Reiner–Rivlin non-linear fluid model,

$$\mathbf{T} = -p\mathbf{U} + 2\eta\mathbf{V} + 4\alpha_1\left[\mathbf{V}\cdot\mathbf{V} - \frac{1}{3}(\mathbf{V}:\mathbf{V})\mathbf{U}\right], \tag{15.83}$$

with $p = -\frac{1}{3}\mathrm{Tr}\,\mathbf{T}$. Expression (15.83) contains two material functions η and α_1 that depend on the second and third principal invariants of $\mathbf{V}$: $\mathrm{II}_v = \mathbf{V} : \mathbf{V}$, $\mathrm{III}_v = \det \mathbf{V}$. The quantities η and α_1 do not depend on the first invariant $\mathrm{I}_v = \nabla \cdot \boldsymbol{v}$, since it vanishes for an incompressible fluid. On continuum mechanics grounds, it has been shown by Astarita and Marucci (1974) that η and α_1 cannot be simultaneously taken constant, unless $\alpha_1 = 0$, in which case Newton's law is recovered.

Going back to the Reiner–Rivlin model, it is directly shown that for a steady shear flow, the viscometric functions are related to the material coefficients η and α_1 by $\mu = \eta$, $\Psi_1 = 0$, and $\Psi_2 = \alpha_1$. The result $\Psi_1 = 0$ is at variance with experimental observations and this means that the Reiner–Rivlin model does not provide a realistic description of non-Newtonian fluids.

To correct for these undesirable features, one can use the more sophisticated model of Rivlin–Ericksen (1985). To meet the principle of frame indifference, Rivlin and Ericksen introduced the following tensors, which reflect the above requirement:

$$\mathrm{A}^{(0)} = \mathbf{U}, \tag{15.84a}$$

$$\mathrm{A}^{(1)} = 2\mathbf{V}, \tag{15.84b}$$

$$\mathrm{A}^{(n)} = \frac{\mathrm{d}\mathrm{A}^{(n-1)}}{\mathrm{d}t} + (\nabla\boldsymbol{v}) \cdot \mathrm{A}^{(n-1)} + \mathrm{A}^{(n-1)} \cdot (\nabla\boldsymbol{v})^T \quad (n = 2, 3, \ldots). \tag{15.84c}$$

The tensors $\mathrm{A}^{(n)}$ are the Rivlin–Ericksen tensors. The simplest Rivlin–Ericksen fluid is the second-order fluid

$$\mathbf{T} = -p\mathbf{U} + \eta\mathrm{A}^{(1)} + \alpha_2\mathrm{A}^{(2)} + \alpha_1\left[\mathrm{A}^{(1)} \cdot \mathrm{A}^{(1)} - \frac{1}{3}(\mathrm{A}^{(1)} : \mathrm{A}^{(1)})\mathbf{U}\right], \tag{15.85}$$

that depends on three material coefficients, η, α_1, and α_2, which may be functions of the temperature but not of the velocity gradient. It is found experimentally that this assumption is not very satisfactory. By setting α_2 equal to zero in (15.85), one obtains again the Reiner–Rivlin model. It is instructive to consider what predictions follow from (15.85) under a steady shearing flow. The material constants η, α_1, and α_2 are related to the usual viscometric functions by $\eta = \mu$, $\alpha_1 = \Psi_1 + \Psi_2$, and η, α_1, and $\alpha_2 = -\frac{1}{2}\Psi_1$. Working within the framework of rational thermodynamics, Dunn and Fosdick (1974) have shown that the second principle of thermodynamics and stability of equilibrium require that

$$\alpha_2 > 0 \quad (\text{or } \Psi_1 < 0), \qquad \alpha_1 + \alpha_2 = 0 \quad \left(\text{or } \Psi_2 = -\frac{1}{2}\Psi_1 < 0\right). \tag{15.86}$$

However, both from experimental data and theoretical considerations it can be concluded that Ψ_1 should be positive and that Ψ_2 is usually not equal to $-\frac{1}{2}\Psi_1$. In the face of these contradictory results, we are confronted with two alternatives. Either the Rivlin–Ericksen model is at variance with thermodynamics and cannot pretend to model real fluids for which $\Psi_1 > 0$, or rational thermodynamics contains some deficiencies that rule out a realistic physical model. We shall come back to this problem at the end of Sect. 15.5.2.

The Rivlin–Ericksen second-order fluid has been extended in several ways. A natural generalisation is that of Criminale et al. (1957) who used equation (15.85), but with shear-rate dependent and are not very useful in practical problems.

An alternative approach consists in expressing the viscous stress tensor by means of an integral dependence of the whole strain history,

$$\mathbf{T}^{v} = \int_{-\infty}^{t} K(t-t')\mathbf{V}(t')\mathrm{d}t', \tag{15.87}$$

where $K(t-t')$ is the memory kernel. A typical history dependence is provided by Green–Rivlin (1954) equation

$$\begin{aligned}\mathbf{T}^{v} = &\int_{-\infty}^{t} K_1(t-t')\mathbf{V}(t')\mathrm{d}t' \\ &\times \int_{-\infty}^{t}\mathrm{d}t''\int_{-\infty}^{t} K_2(t-t',t-t'')\,\mathbf{V}(t')\cdot\mathbf{V}(t'')+\mathbf{V}(t'')\cdot\mathbf{V}(t')\,\mathrm{d}t',\end{aligned} \tag{15.88}$$

All the aforementioned models are explicit in the pressure tensor, meaning that $\mathbf{T}^{v}$ can be substituted in the momentum equation to give a flow problem for the velocity.

Another possibility, still mentioned earlier, is to describe the behaviour of fluids exhibiting elastic effects by means of rate equations. Examples of rate-equation models are provided by the generalised Maxwell equation

$$\tau\mathrm{D}\mathbf{T}^{v} + \mathbf{T}^{v} = 2\eta\mathbf{V}, \tag{15.89}$$

where D is an objective time derivative (examples of which are given by expressions (1.90)–(1.92)); the substitution of D for $\partial/\partial t$ is dictated by the frame-indifference criterion of viscometric coefficients. Higher-order expansions in terms of the Rivlin–Ericksen tensors $\mathbf{A}^{(n)}$ $(n>2)$ have also been proposed but they lead to a proliferation of parameters

Oldroyd (1958) suggested an extension of (15.89) by including all possible non-linear terms involving the products of stress tensors and velocity gradients as well as products of velocity gradients with each other. This yields the well established 8-constant Oldroyd model:

$$\begin{aligned}&\mathbf{T}^{v} + \lambda_1\mathrm{D}\mathbf{T}^{v} + \lambda_2(\mathrm{Tr}\,\mathbf{T}^{v})\mathbf{V} + \lambda_0(\mathbf{T}^{v}\cdot\mathbf{V} + \mathbf{T}^{v}\cdot\mathbf{V}) + \lambda_4(\mathbf{T}^{v}:\mathbf{V})\mathbf{U} \\ &+\lambda_5\mathbf{V} + \lambda_6\mathrm{D}\mathbf{V} + \lambda_7(\mathbf{V}\cdot\mathbf{V}) + \lambda_8(\mathbf{V}:\mathbf{V})\mathbf{U} = 0.\end{aligned} \tag{15.90}$$

Flow problems involving non-Newtonian fluids demand in general lengthy numerical solutions: these methods are the object of several papers and books (e.g. Crochet et al. 1984) and will not be reviewed here. We shall no longer discuss the properties of the several rheological models found in the literature. We wish only to stress that none of these models is applicable to the study of all the motion states of a given particular non-Newtonian fluid. Several constitutive equations may be needed to describe the behaviour of one single fluid, depending on the particular circumstances under which the motion takes place. For instance, blood is rather well represented by Newton's law in large capillaries, while in narrow capillaries its flow properties require a non-Newtonian description.

15.5.2 EIT Description of Second-Order Non-Newtonian Fluids

As repeatedly mentioned, EIT is by no means restricted to linear evolution equations. Our aim in this sub-section is to show that a description of second-order non-Newtonian fluids stems naturally from EIT. Two particular models are derived: a three-parameter model and Giesekus four-parameter model. In particular, the simple three-parameter description is seen to yield the correct signs of the material coefficients of the Rivlin–Ericksen model, in agreement with observations. We also examine to what extent the three-parameter model is able to cope with experimental dependence of the material functions on shear rate in steady shearing flows.

Heat effects are again assumed to be negligible, and only isotropic and incompressible fluids are considered. For incompressible fluids, bulk viscous effects are negligible in the linear theory, but they must be taken into account when non-linear contributions (of the order of $\dot{\gamma}^2$) are included.

15.5.2.1 A Three-Parameter Model

The basic variables are selected to be the same as for an ordinary Newtonian fluid, namely u and $\mathbf{T}^v$, and the corresponding Gibbs equation is

$$T_0 \mathrm{d}s = \mathrm{d}u - \frac{1}{\rho_0} A \mathbf{T}^v : \mathrm{d}\mathbf{T}^v, \tag{15.91}$$

where A is a scalar coefficient which may depend on u and the invariants of $\mathbf{T}^v$. The convexity of s implies that $\partial^2 s/(\partial \mathbf{T}^v : \partial \mathbf{T}^v) < 0$, from which it follows that $A > 0$. Combining Gibbs' equation with the balance law of energy yields the following expression of the entropy production:

$$T_0 \sigma^s = \mathbf{T}^v : (\mathbf{V} - A\dot{\mathbf{T}}^v). \tag{15.92}$$

We identify the generalised thermodynamic force X as the quantity between the brackets:

$$\mathrm{X} = \mathbf{V} - A\dot{\mathbf{T}}^v. \tag{15.93}$$

It is noted that $T_0\sigma^s$ takes the form of a bilinear expression in the flux $\mathbf{T}^v$ and the force X. On the other hand, we can formulate another expression for X if it is imposed that X must be constructed as the most general second-order traceless tensor depending on $\mathbf{T}^v$ accordingly, we are allowed to write $\mathbf{X}$ as

$$\mathbf{X} = a_1\mathbf{T}^v - a_2(\mathbf{T}^v \cdot \mathbf{T}^v - \pi^v\mathbf{U}), \tag{15.94}$$

where $\pi^v = \frac{1}{3}(\mathbf{T}^v : \mathbf{T}^v)$, a_1 and a_2 are functions of u and the invariants of $\mathbf{T}^{\tilde{v}}$ The positiveness of $T\sigma^s$ requires that $a_1 > 0$. Equating the right-hand sides of (15.88) and (15.89), one obtains the evolution equation for the viscous stress tensor

$$\frac{A}{a_1}\dot{\mathbf{T}}^v = \frac{1}{a_1}\mathbf{V} - \mathbf{T}^v + \frac{a_2}{a_1}(\mathbf{T}^v \cdot \mathbf{T}^v - \pi^v\mathbf{U}). \tag{15.95}$$

For latter purpose, we set $A/a_1 = \tau$, $1/a_1 = 2\eta$, and $a_2/a_1 = a$, where τ and η have the dimensions of time and viscosity respectively and a is a coefficient that takes account of the non-linear correction to Newton's law. To satisfy the criterion of frame indifference, the time derivative in (15.90) must be replaced by an objective time derivative. Since a macroscopic theory cannot discriminate amongst the several objective time derivatives, we choose the Jaumann's derivative D_J, which guarantees the form invariance of the entropy production. It follows that the final expression for the evolution equation reads

$$\tau\mathrm{D}_J\mathbf{T}^v = 2\eta\mathbf{V} - \mathbf{T}^v + a(\mathbf{T}^v \cdot \mathbf{T}^v - \pi^v\mathbf{U}). \tag{15.96}$$

This relation is the cornerstone of the model and a similar result was obtained by Müller and Wilmanski (1986). For negligible values of τ (in ordinary fluids, τ is of the order of the collision time, i.e. 10^{-12} s) and $a = 0$, one recovers Newton's law.

Combining the constraints $A > 0$ and $a_1 > 0$, one obtains, in virtue of the above definitions of τ and η, that $\tau > 0$, $\eta > 0$. This result indicates that the evolution equation (15.96) is characterized by a positive viscosity and a positive relaxation time. No information about the sign of a is available. The positiveness of τ and η together with (15.96) provide the essential features of the model. The latter involves three parameters: η, τ., and a, to be determined from experimental observations or microscopic theories.

It is interesting to investigate the transition from the rate-type equation (15.96) to constitutive equations like those of Rivlin–Ericksen and Reiner–Rivlin. To this end, let us rewrite (15.96) in terms of the Rivlin–Ericksen time derivative $\mathbf{P}^{(2)}$ defined by (15.84): it is found that

$$\mathbf{T}^v = 2\eta\mathbf{V} - \tau\mathbf{T}^{(2)} + a(\mathbf{T}^v \cdot \mathbf{T}^v - \pi^v\mathbf{U}) + \tau(\mathbf{T}^v \cdot \mathbf{V} + \mathbf{V} \cdot \mathrm{T}^v), \tag{15.97}$$

where use has been made of the result

$$\mathrm{D}_J\mathbf{T}^v = \mathbf{T}^{(2)} - (\mathbf{T}^v \cdot \mathbf{V} + \mathbf{V} \cdot \mathbf{T}^v). \tag{15.98}$$

In the first-order approximation and in the limit $\tau = 0$, (15.97) reduces to

$$_{(1)}\mathbf{T}^{v} = 2\eta\mathbf{V}, \tag{15.99}$$

which is the Navier–Stokes relation; subscript $_{(1)}$ refers to the first-order approximation. For a non-vanishing relaxation time, still in the first-order approximation, expression (15.97) becomes

$$_{(1)}\mathbf{T}^{v} = 2\eta\mathbf{V} - \tau\frac{\partial_{(1)}\mathbf{T}^{v}}{\partial t}, \tag{15.100}$$

which is the basic equation of Maxwell's model.

The second-order approximation with $\tau = 0$ is obtained by substituting $\mathbf{T}^{v}$ by its value (15.99) into the right-hand side of (15.97). This operation leads to the Reiner–Rivlin equation,

$$_{(2)}\mathbf{T}^{v} = 2\eta\mathbf{V} + 4\eta^{2}a\left[\mathbf{V}\cdot\mathbf{V} - \tfrac{1}{3}\mathbf{V}:\mathbf{V}\mathbf{U}\right]. \tag{15.101}$$

If the relaxation time does not vanish, one obtains from (15.97)

$$(2)\mathbf{T}^{v} = 2\eta\mathbf{V} - 2\tau\eta\mathbf{V}^{(2)} + 4\eta\,(\eta a + \tau)\left[\mathbf{V}\cdot\mathbf{V} - \tfrac{1}{3}\,(\mathbf{V}:\mathbf{V})\,\mathbf{U}\right]. \tag{15.102}$$

Comparison between (15.102) and the Rivlin–Ericksen equation (15.85) allows one to express the coefficients Ψ_1 and Ψ_2 (see (15.80) in terms of the parameters η, τ and a:

$$\Psi_1 + \Psi_2 = \eta\tau + \eta^{2}a, \tag{15.103a}$$

$$\Psi_1 = 2\eta\tau. \tag{15.103b}$$

Recalling that τ and η are positive, it is clear from equation (15.103b) that Ψ_1 is a positive quantity, in accordance with experiments. Moreover, combining the two equations in (15.103) leads to $\Psi_2 = -\frac{1}{2}\Psi_1 + \eta^{2}a$, which shows that Ψ_2 is generally different from $-\frac{1}{2}\Psi_1$. As experiments suggest that $-\Psi_2/\,\Psi_1$ takes values between 0.1 and 0.4, it is expected that the coefficient a is positive.

By working in the framework of rational thermodynamics, Dunn and Fosdick (1974) have found that $\Psi_1 < 0$ and $\Psi_2 = -\frac{1}{2}\Psi_1$, in contradiction with experiments. Therefore, it can be concluded that by considering Rivlin–Ericksen's equation to be an approximation of the more general rate-type model (15.97), one avoids the problems raised by Dunn and Fosdick's work. The essential conclusions are that $\Psi_1 > 0$ is not in contradiction with the second law of thermodynamics and that EIT is a good candidate for describing second-order non-Newtonian fluids.

A further check of the quality of the model can be obtained by calculating the viscometric functions μ, Ψ_1 and Ψ_2 and by comparing them with experimental results. This is done in Box 15.2, where steady shearing flows of polymer solutions are studied.

Box 15.2 Steady shearing flows Let us determine the dependence of the viscometric functions μ, Ψ_1 and Ψ_2 with respect to the shear rate for a steady shearing flow in the x direction. Inserting the velocity field $v_x = \dot{\gamma} y$ into the evolution equation (15.96), and making use of the definitions (15.80) of the viscometric functions, one obtains the following set of non-linear algebraic equations:

$$4\tau\mu^2 - \Psi_1(2\eta - \tau\Psi_1\dot{\gamma}^2) = 0, \tag{15.2.1a}$$

$$\tau\mu\,(\Psi_1 + 2\Psi_2) + a\Psi_1\Psi_2\,(\Psi_1 + \Psi_2)\,\dot{\gamma}^2 - a\mu^2\Psi_1 = 0, \tag{15.2.1b}$$

$$3\Psi_1 - 6\mu\tau - a\Psi_1\,(\Psi_1 + 2\Psi_2)\,\dot{\gamma}^2 = 0. \tag{15.2.1c}$$

The unknowns in (15.2.1) are μ, Ψ_1 and Ψ_2, while $\dot{\gamma}$ is the independent variable. To calculate μ, Ψ_1 and Ψ_2 it is necessary to know the behaviour of η, τ, and a. Preliminary information is obtained by assuming that τ and η are constant and that a is negligibly small. In view of (15.2.1) it follows that

$$\mu = \frac{\eta}{1 + \tau^2\dot{\gamma}^2}, \quad \Psi_1 = \frac{2\tau\eta}{1 + \tau^2\dot{\gamma}^2}, \quad \Psi_2 = -\frac{1}{2}\Psi_1. \tag{15.2.2}$$

These results indicate that the three viscometric functions are even functions of $\dot{\gamma}$, and that Ψ_1 is positive and Ψ_2 is negative: although these conclusions are corroborated experimentally, the model is too crude. At high shear rates, it is found that η behaves like $\dot{\gamma}^{-2}$, which is not very realistic. On the other hand the asymptotic behaviour of Ψ_1 is proportional to $\dot{\gamma}^{-2}$, which is closer to experimental observations. It is also seen that the ratio $-\Psi_2/\Psi_1$ is equal to 0.5, higher than the experimental values, which lie between 0.1 and 0.4.

A more realistic description is obtained by supposing that the material coefficients η, τ, and a are allowed to depend on the invariants of T^v. Moreover, we do not alter the generality by considering that η, τ and a are functions of $\dot{\gamma}$ rather than of $\mathbf{T}^v$, because in steady motions both quantities are related by (15.80a).

The problem is of course to find the most adequate dependence of the parameters with respect to $\dot{\gamma}$. To achieve this task, we rely on the fact that, for steady shearing, it is generally accepted that the apparent viscosity μ and the first normal stress coefficient Ψ_1 are well accounted for by Ostwald's power laws (15.81) (Tanner 1985). It is also widely admitted that Ψ_2 is proportional to Ψ_1 and can therefore be described by a power law as well. We are thus allowed to write

$$\mu = \mu_0\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^{n_\mu}, \quad \Psi_1 = \Psi_0^1\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^{n_1}, \quad \Psi_2 = \Psi_0^2\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^{n_2}; \tag{15.2.3}$$

$\dot{\gamma}_0$ represents a reference value for $\dot{\gamma}$ and is introduced for dimensional reasons; μ_0, n_μ, Ψ_0^1, n_1 Ψ_0^2, and n_2 are undetermined constants.

Substitution of (15.2.3) into (15.2.1) shows that the parameters η, τ, and a have also to satisfy the following Ostwald power laws:

$$\eta = \eta_0 \left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^{n_\eta}, \quad \tau = \tau_0 \left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^{n_\tau}, \quad a = a_0 \left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^{n_a}. \qquad (15.2.4)$$

The assumption that τ is shear dependent is a direct consequence of the present formalism but is also confirmed by other rheological models, such as the White–Metzner model (Bird et al. 1987a).

Table 15.1 Some values of adjustable constants in (15.2.3) for viscometric coefficients

Solution	μ_0	Ψ_0^1	Ψ_0^2	n_μ
PAA	6.10×10^1	4.12×10^2	-2.41×10^1	-0.774
Oppanol B200	1.71×10^{-1}	5.53×10^{-2}	-8.02×10^{-4}	-0.302
Oppanol B50	1.41×10^{-1}	2.66×10^{-5}	2.66×10^{-6}	-0.323

After introducing (15.2.3) and (15.2.4) into (15.2.1), we observe that the 12 unknown constant parameters appearing in (15.2.3) and (15.2.4) are not independent but are related by $n_1 = n_2 = n_\mu - 1$, $n_a = -1 - n_\eta$, $n_\tau = -1$, $n_\mu = n_\eta$, plus three relations identical to (15.2.1), with every quantity affected by a subscript 0. Finally, bearing all these results in mind, we are left with four independent adjustable constants that can be selected as μ_0, Ψ_0^1, Ψ_0^2, and n_η. This choice is dictated by the fact that these quantities are easily obtained from experimental measurements.

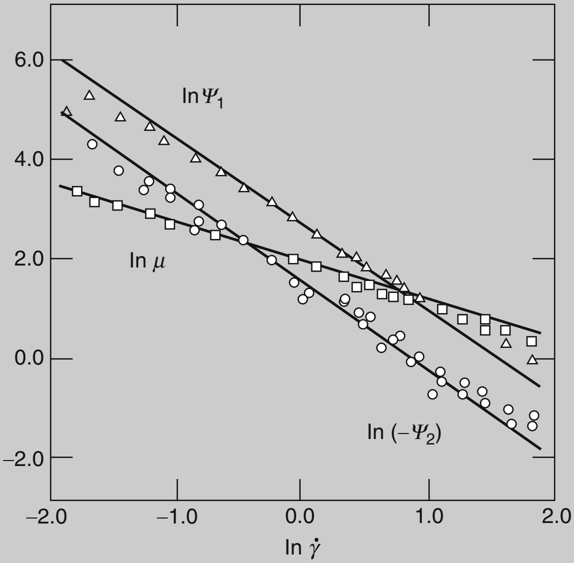


Fig. 15.2.1 Dependence of the viscometric functions on the shear rate for PAA: comparison between theoretical and experimental results. Squares, triangles, and open circles represent, respec-

tively, experimental data for the viscosity, and the first and second normal stress coefficients. The solid lines are the theoretical results (Reprinted from Lebon G et al. (1990) Rheol Acta 29:127)

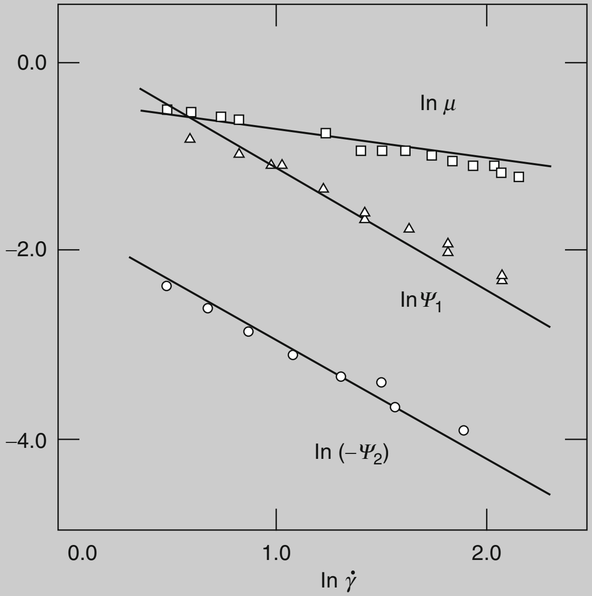


Fig. 15.2.2 Dependence of the viscometric functions on the shear rate for Oppanol B200: comparison between theoretical and experimental results. Squares, triangles, and circles represent experimental data for μ, Ψ_1, and Ψ_2, respectively; the solid lines are the theoretical results (Reprinted from Lebon G et al. (1990) Rheol Acta 29:127)

Comparison with experimental data is performed with three polymeric solutions: a 2.5% solution of polyacrylamide in a 50% water and 50% glycerine solution (PAA), a 1.1% polyisobutylen solution in decahydronaphtalene (Oppanol B200), and an 8.7% polyisobutylen-decalin solution ‘D2b’ (Oppanol B50). The reason for choosing the PAA and Oppanol B200 solutions is that in these cases all three viscometric functions η, Ψ_0^1, Ψ_0^2 have been determined experimentally (Christiansen and Leppard 1974). We have also checked our model on Oppanol B50 because it is, to our knowledge, the only polymeric solution for which η and Ψ_0^1 have been measured at very large values of $\dot{\gamma}$ up to $10^6\,\mathrm{s}^{-1}$ (Lodge 1989); for this particular solution we have imposed $\Psi_2/\Psi_1 = -0.1$ because no experimental data are available for the viscometric function Ψ_2. The values of the adjustable constants are reported in Table 15.1 and given in SI units (Lebon et al. 1990)

Comparison between experimental and theoretical results is shown in Figs. 15.2.1–3. A very satisfactory agreement is achieved in all the cases: it is worth noticing that even at very high values of the shear rate, as in Oppanol B50 (Fig. 15.2.3), the model accounts for the experimental data to a very high degree of accuracy.

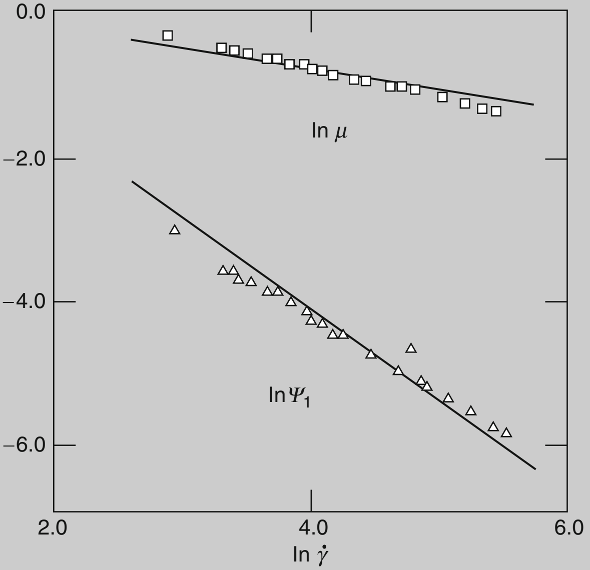


Fig. 15.2.3 The viscosity and the first normal stress coefficient as a function of the shear rate for Oppanol B50: comparison between theoretical and experimental results. Squares and triangles correspond, respectively, to experimental data for the viscosity and the first normal stress. Solid lines are the theoretical results (Reprinted from Lebon G et al.(1990) Rheol Acta 29:127)

15.5.2.2 Giesekus Four-Parameter Model

In the previous subsection, we discussed a non-Newtonian model characterized by the three parameters η, τ, and α. We show here that more complicated descriptions, such as the Giesekus four-parameter model, can easily be generated if it is admitted that the total viscous stress tensor $\mathbf{T}^v$ is the sum of a contribution $\mathbf{T}_0$ from the solvent and a contribution $\mathbf{T}_p$ from the polymer chains: $\mathbf{T}^v = \mathbf{T}_0 + \mathbf{T}_p$. As in the Rouse–Zimm model, it is supposed that the solvent is an incompressible Newtonian fluid, so that $\mathbf{T}_0$ is related to $\mathbf{V}$ by Newton's law, $\mathbf{T}_0 = 2\eta_0\mathbf{V}$, and η_0 is the shear viscosity of the solvent. As a consequence, $\mathbf{T}_0$ will not be considered as independent variable and the Gibbs equation will take the same form as (15.91), with $\mathbf{T}^v$ replaced by $\mathbf{T}_p$:

$$T\mathrm{d}s = \mathrm{d}u - \frac{1}{\rho}A_p\mathbf{T}_p : \mathrm{d}\mathbf{T}_p. \tag{15.104}$$

From the concavity property of entropy, it is inferred that $A_p > 0$. The corresponding entropy production is given by

$$T\sigma^s = \mathbf{T}_0 : \mathbf{V} + \mathbf{T}_p : \mathbf{X}, \tag{15.105}$$

where $\mathbf{X}$ is given by (15.93), with $\mathbf{T}^v$ replaced by $\mathbf{T}_p$. Repeating the procedure followed in the preceding subsection, it is found that $\mathbf{T}_p$ satisfies the evolution equation

$$\tau_p \mathrm{D}_J \mathbf{T}_p = 2\eta_p \mathbf{V} - \mathbf{T}_p + a_p \left(\mathbf{T}_p \cdot \mathbf{T}_p - \pi_p \mathbf{U}\right), \tag{15.106}$$

which contains the three parameters τ_p, η_p, and a_p, and the quantity π_p given by $\pi_p = \frac{1}{3}\left(\mathbf{T}_p : \mathbf{T}_p\right)$. Eliminating $\mathbf{T}_p$ in terms of $\mathbf{T}^v$ and $\mathbf{T}_0$ and using $\mathbf{T}_0 = 2\eta_0 \mathbf{V}$, one obtains the following evolution equation for the total stress tensor:

$$\tau_p \mathrm{D}_J \mathbf{T}^v + \mathbf{T}^v + \frac{a\tau_p}{\eta}(\mathbf{T}^v \cdot \mathbf{T}^v - \pi^v U) - 2a\lambda_G(\mathbf{V} \cdot \mathbf{T}^v + \mathbf{T}^v \cdot \mathbf{V} - \overline{\pi}\mathbf{U})$$
$$L = 2\eta\left[\mathbf{V} + \lambda_G \mathrm{D}_J \mathbf{V} - 2a\frac{\lambda_G^2}{\tau_p}(\mathbf{V} \cdot \mathbf{V} - \overline{\overline{\pi}}\mathbf{U})\right], \tag{15.107}$$

where the unidentified coefficients η, a, λ_G, $\overline{\pi}$, and $\overline{\overline{\pi}}$ stand respectively for $\eta = \eta_0 + \eta_p$, $a = -(\eta a_p/\tau_p)$, $\lambda_G = -(\eta_0 \tau_p/\eta)$, $\overline{\pi} = \frac{2}{3}(\mathbf{T}^v : \mathbf{V})$, and $\overline{\overline{\pi}} = \frac{1}{3}(\mathbf{V} : \mathbf{V})$.

Expression (15.107) is the same as the Giesekus (1982) constitutive equation except for the terms in π^v, $\overline{\pi}$, and $\overline{\overline{\pi}}$, which appear here as a consequence of the hypothesis of the absence of bulk effects. The adjustable parameters in Giesekus' model are η_0, a_p, η_p, and τ_p, or equivalently η, a, λ_G, and τ_p. The result (15.107) is particularly promising, since it allows one to derive the Giesekus equations from very simple macroscopic considerations.

It is interesting to note that by setting into (15.107) the coefficient $a = 0$ one recovers Jeffreys' model

$$\tau_p \mathrm{D}_J \mathbf{T}^v + \mathbf{T}^v = 2\eta\ (\mathbf{V} + \lambda_G \mathrm{D}_J \mathbf{V}). \tag{15.108}$$

It is worth stressing that the above results were obtained by simply requiring that the stress tensor is selected as an independent variable and that it obeys a non-linear evolution equation of the relaxation type. It is possible to complicate the model by assuming that a non-Newtonian solvent or by introducing viscous bulk effects. This would result in more realistic descriptions and generate other rheological models, such as the Oldroyd's 8-constant model (Dauby and Lebon 1990). This is a further step in the formulation of the theory but it does not raise any fundamental difficulty. Indeed, the thermodynamical formalism presented here exhibits such a flexibility and power of generalisation that it can successfully deal with more sophisticated systems.

15.6 Problems

15.1. Consider a dilute polymeric solution modelled by rigid dumbbells, each of them characterized by a director vector $\boldsymbol{u}$. The orientational equilibrium distribution function is the isotropic distribution $\psi_{\mathrm{eq}} = \frac{1}{4}\pi$. In a plane Couette flow with shear rate $\dot{\gamma} = (\partial v_x / \partial y)$, the steady state distribution function is, up to the first order in $\dot{\gamma}$,

$$\psi(\boldsymbol{u}) = \psi_{\mathrm{eq}}(1 + 3u_x u_y \tau \dot{\gamma}),$$

with the relaxation time τ given by $\tau = \zeta L^2 (12 K_{\mathrm{B}} T)^{-1}$, L being the length of the dumbbell and ζ. the friction coefficient between the beads of the dumbbell and the solvent. If the entropy of the dumbbells is given by

$$s = -k_{\mathrm{B}} \int \psi \ln \psi \mathrm{d}\boldsymbol{u},$$

show that the non-equilibrium entropy at steady shear flow is

$$s(u, \dot{\gamma}) = s_{\mathrm{eq}}(u) - \tfrac{3}{10} n k_{\mathrm{B}} (\tau \dot{\gamma})^2.$$

(Camacho J, Jou D (1990) J Chem Phys 92:1339)

15.2. The steady-state viscosity of a dilute solution of rigid dumbbells is $\eta = n k_{\mathrm{B}} T \tau$, with n the number of dumbbells per unit volume and τ the relaxation time as given in Problem 15.1. (a) Compare the expression for the non-equilibrium entropy obtained in the above problem with the following expression

$$s = s_{\mathrm{eq}} - \frac{\tau}{2T} (\eta \dot{\gamma})^2.$$

Is this result satisfactory? (b) The viscous stress tensor for a rigid dumbbell solution has the form

$$\mathbf{T}^v = 2\eta_s \mathbf{V} + \mathbf{T}_1^v + \mathbf{T}_2^v,$$

with

$$\mathbf{T}_1^v = 3 n k_{\mathrm{B}} T \left(\langle \boldsymbol{uu} \rangle - \frac{1}{3} \mathbf{U} \right)$$

and

$$\mathbf{T}_2^v = 6 n k_{\mathrm{B}} T \tau \, \langle \boldsymbol{uuuu} \rangle : \mathbf{V}.$$

The quantity η_s is the viscosity of the pure solvent, $\mathbf{V}$ the symmetric part of the velocity gradient, and $\boldsymbol{u}$ the director vector of the rigid dumbbells. It may be shown that the part $\mathbf{T}_1^v$ has a relaxation time $\tau_1 = \tau$ and that the corresponding shear viscosity is $\eta_1 = \frac{3}{5} n k_{\mathrm{B}} T \tau$, while the part $\mathbf{T}_2^v$ has a relaxation time $\tau_2 = 0$ and a viscosity $\eta_2 = \frac{2}{5} n k_{\mathrm{B}} T \tau$ (Bird RB et al. 1977b). Show that the above decomposition of the viscous stress tensor is consistent with the following expression for the entropy:

$$s = s_{\mathrm{eq}} - \frac{1}{2T} (\tau_1 \eta_1 + \tau_2 \eta_2) \dot{\gamma}^2$$

15.3. In ideal gases and in polymeric solutions described by rigid dumbbells, a shear flow does not change the internal energy of the system at a given temperature T. However, for elastic dumbbells, the shear flow produces a stretching of the dumbbells and consequently induces a change of the internal energy at constant T. The elastic potential energy of the dumbbells may be obtained from

$$u_d = \int \tfrac{1}{2} H \boldsymbol{Q}^2 \psi(\boldsymbol{Q}) \mathrm{d}\boldsymbol{Q},$$

where H is the elastic constant of the dumbbells, $\boldsymbol{Q}$ the bead-to-bead vector, and $\psi(\boldsymbol{Q})$ the distribution function of the dumbbells. Up to the first order in the shear rate $\dot{\gamma}$, the distribution function is

$$\psi(\boldsymbol{Q}, \dot{\gamma}) = \psi_{\mathrm{eq}}(\boldsymbol{Q}) \left(1 + \frac{\zeta}{4k_{\mathrm{B}}T} \mathbf{V} : \boldsymbol{Q}\boldsymbol{Q} \right),$$

where $\psi_{\mathrm{eq}}(\boldsymbol{Q})$ is the equilibrium distribution function (15.66), V the traceless symmetric part of the velocity gradient, and ζ the friction coefficient between the beads and the solvent. Assuming constant n (number of dumbbells per unit volume) and T (temperature), show that the difference in internal energy per unit volume between a steady state and an equilibrium state is

$$u(n, T, \dot{\gamma}) - u_{\mathrm{eq}}(n, T) = n k_{\mathrm{B}} T (\tau \dot{\gamma})^2,$$

with the relaxation time τ given by $\tau = \zeta / 4H$.

15.4. The entropy of a dilute solution of Hookean dumbbells under shear $\dot{\gamma}$ is

$$s(u, \dot{\gamma}) = s_{\mathrm{eq}}(u_{\mathrm{eq}}) + n k_{\mathrm{B}} \ln \sqrt{1 + (\tau \dot{\gamma})^2}.$$

(a) Find the expression of $s(u, \dot{\gamma}) - s_{\mathrm{eq}}(u_{\mathrm{eq}})$ at low $\tau \dot{\gamma}$. Should it be surprising that the non-equilibrium entropy $s(u, \dot{\gamma})$ is higher than the equilibrium entropy $s_{\mathrm{eq}}(u_{\mathrm{eq}})$? (b) Taking into account the expression for $u - u_{\mathrm{eq}}$ found in Problem 15.3, calculate the difference $s(u, \dot{\gamma}) - s_{\mathrm{eq}}(u)$. (c) Compare the expressions for $s(u, \dot{\gamma})$, $s_{\mathrm{eq}}(u)$ and $s_{\mathrm{eq}}(u_{\mathrm{eq}})$.

15.5. The evolution equation for $\mathbf{T}^v$ in the upper convected Maxwell model is

$$\dot{\mathbf{T}}^v - (\nabla \boldsymbol{v})^{\mathbf{T}} \cdot \mathbf{T}^v - \mathbf{T}^v \cdot (\nabla \boldsymbol{v}) = -\frac{1}{\tau} \mathbf{T}^v + \frac{2\eta}{\tau} \mathbf{V}$$

with $\mathbf{V}$ being the symmetric part of the velocity gradient. (a) Show that, in a steady pure shear flow, $\mathbf{T}^v$ is given by

$$\mathbf{T}^v = \begin{pmatrix} 2\tau\eta\dot{\gamma}^2 & \eta\dot{\gamma} & 0 \\ \eta\dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

(b) Show that the normal stress coefficients are $\Psi_1(\dot{\gamma}) = 2\tau\eta$ and $\Psi_2(\dot{\gamma}) = \tilde{0}$

15.6. Determine the expression for $\mathbf{T}^v$ in a steady shear flow if the lower-convected derivative (1.91) or the Jaumann derivative (1.90) are used in Problem 15.5 instead of the upper-convected derivative.

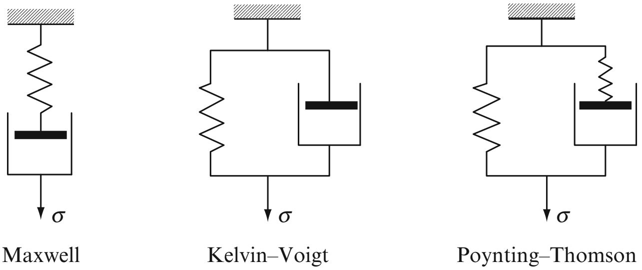
15.7. A planar extensional flow is defined by a velocity gradient of the form

$$\nabla v = \begin{pmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

with $\dot{\varepsilon}$ being the extensional rate. Show that for the upper convected Maxwell model in the steady state the viscous stress tensor reads

$$\mathbf{T}^v = \begin{pmatrix} 2\eta\dot{\varepsilon}(1-2\tau\dot{\varepsilon})^{-1} & 0 & 0 \\ 0 & -2\eta\dot{\varepsilon}(1+2\tau\dot{\varepsilon})^{-1} & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

15.8. Show that the constitutive equations of the Maxwell, Kelvin–Voigt, and Poynting–Thomson bodies are easily interpretable in terms of the following mechanical models involving coupling of springs and dashpots.



15.9. Repeat the demonstration leading to (15.102) when, in the evolution equation (15.96) for $\mathbf{T}^v$, the Jaumann derivative is replaced by the lower-convected and the upper-convected time derivatives, respectively.

15.10. Determine the dependence of the viscometric functions μ, Ψ_1 and Ψ_2 in terms of the supposed constant parameters η, τ, and a for a material described by an evolution equation of the form (15.96) for: (a) a steady shearing flow $v_x = \dot{\gamma}y$;(b) a time-dependent shear flow $v_x = \dot{\gamma}(t)y$; (c) a small amplitude oscillatory shearing flow.

15.11. Show that the Gibbs equations for a Kelvin–Voigt and a Poynting–Thomson material at uniform temperature are respectively given by

$$T\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\mathrm{d}u}{\mathrm{d}t} + \frac{1}{\rho}\mathbf{T}^{(e)} : \frac{\mathrm{d}\mathbf{E}}{\mathrm{d}t} \text{ (Kelvin–Voigt)},$$

$$T\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\mathrm{d}u}{\mathrm{d}t} + \frac{1}{\rho}\mathbf{T}^{(e)} : \frac{\mathrm{d}\mathbf{E}}{\mathrm{d}t} - \frac{1}{\rho}\mathbf{T}^{(i)} : \frac{\mathrm{d}\mathbf{E}^{(i)}}{\mathrm{d}t} \text{ (Poynting–Thomson)},$$

wherein the inelastic strain $\mathbf{E}^{(i)}$ is defined through

$$\frac{\mathrm{d}\mathbf{E}^{(i)}}{\mathrm{d}t} = \frac{1}{2\eta}\mathbf{T}^{(i)}.$$

15.12. Consider a viscoelastic material subject to external sinusoidal oscillations. Assuming one-dimensional deformations with strain and stress of the form

$$\varepsilon = \hat{\varepsilon}\exp(\mathrm{i}\omega t), \; T = \hat{T}\exp(\mathrm{i}\omega t).$$

Defining the complex modulus $G^* = G' + iG''$ by $\hat{T} = 2G^*\hat{\varepsilon}$, show that

$$G^*(\omega) = \frac{1 + \mathrm{i}\omega\tau_\sigma}{1 + \mathrm{i}\omega\tau_\varepsilon}G,$$

and that the phase shift δ defined by $\tan\delta = G''/G'$ is given by

$$\tan\delta = \frac{\omega}{(\boldsymbol{G}/\eta + \omega^2\tau_\varepsilon\,[1 + \boldsymbol{G}\tau_\varepsilon/\eta]}.$$

For an elastic body, one has $\tau_\varepsilon = \eta = 0$ so that $\delta = 0$; for a viscous fluid, $\tau_\varepsilon = G = 0$ and $\delta = \pi/2$.

15.13. *Plane harmonic waves*: Study wave propagation in a Poynting–Thomson body described by expression (15.29), temperature is uniform. In the one-dimensional case, the propagation of waves is governed by the momentum equation

$$\rho\frac{\partial^2 u_x}{\partial t^2} = \frac{\partial}{\partial x}T_{xx},$$

where u is the displacement vector in the x direction and

$$T_{xx} = 2G\overset{0}{\varepsilon}_{xx} + T_{xx}^{(i)}.$$

Select a reference state $u_x = \text{const}$, $T_{xx}^{(i)} = 0$ and superpose upon this basic solution a plane harmonic wave $\exp[\mathrm{i}(\omega t - kx)]$ where ω is the (real) frequency and $k = k' + k''$ the complex wave number. Show the dispersion relation between ω and k is given by

$$\rho\omega^2 = \frac{4}{3}\frac{G(1+\mathrm{i}\omega\tau_\varepsilon)}{1+\mathrm{i}\omega\tau}k^2.$$

Determine the corresponding phase velocity $v_{\mathrm{ph}} = \omega/k'$ and the attenuation factor $\Gamma = k''/k'$. In particular, derive their expressions in the limiting cases of low ($\omega\tau \ll 1$) and high frequencies ($\omega\tau \gg 1$).

Chapter 16

Thermodynamics of Polymer Solutions Under Shear Flow

In Chaps. 3 and 9 we studied effects of a heat flux on the thermodynamics of non-equilibrium steady states. Here, we deal with another interesting situation that of polymer solutions under shear flow. The presence of a shear results not only in drastic changes in the phase diagram of the solution but is also able to modify the kinetics of chemical reactions taking place within it (Jou et al. 2001). Various thermodynamic approaches have been concerned with the study of the interaction between the flow and the thermodynamic properties of a fluid with internal structure; some of them are based on internal variables (Maugin and Muschik 1994) and others on Hamiltonian formalisms (Öttinger 2005). The difference between extended irreversible thermodynamics (EIT) and other theories is that the former uses as variables the shear viscous pressure or the shear rate, whereas the latter prefer variables related with the internal structure of the fluid, as for instance, the configuration tensor. The relation between the two classes of variables has already been discussed in Sect. 15.3. The EIT variables are especially useful in macroscopic analyses while the internal variables are more suitable for a microscopic understanding. Let us also mention that EIT predicts modifications of the thermodynamic equations of state not only for fluids with internal structure but also for ideal monatomic gases or for liquids of spherical particles. These systems have been the subject of many computer simulations, some of which have been discussed in Sect. 9.5, and of several kinds of microscopic analyses, ranging from the kinetic theory of gases to renormalization group techniques (Onuki and Kawasaki 1979; Loose and Hess 1989).

The study of polymer solutions under shear is particularly interesting because the effects of shear are more perceptible than in ordinary liquids or gases. Besides its theoretical interest, this study is also important in engineering, since most of polymer processings take place under motion. The phase diagrams established for equilibrium situations cannot be trusted in the presence of flows since the latter may enhance or reduce the solubility of the polymer and the conditions under which the phase separation occurs.

Many works in laboratories and in industry have been devoted to flow-induced changes in phase diagrams of polymer solutions (Rangel-Nafaile et al. 1984). It is obvious that the classical local-equilibrium thermodynamics must be modified in such a way that the equations of state incorporate explicitly the influence of the flow. Moreover, the equilibrium thermodynamic stability conditions cannot be

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_16, © Springer Science+Business Media LLC 2010

blindly extrapolated to non-equilibrium steady states, but a justification based on dynamic arguments is needed and shall be found in Sect. 16.4. Another problem is the effect of a shear on chemical equilibrium, which is treated in Sect. 16.2, and applied to thermodynamically-induced polymer degradation under flow. Polymer degradation under elongational flow has been extensively studied from kinetic arguments (Nguyen and Kausch 1992).

Several authors bypass thermodynamics and analyse phase separation or phase homogenisation under shear by writing directly the relevant dynamical equations and investigating afterwards the stability of their solutions (Onuki 1989, 1990). At first sight, it may be thought that such a procedure has a wider range of potentialities than a pure thermodynamic analysis, as the latter cannot provide details about the process of segregation of the different phases or the changes in viscosity observed during such a process. However, it is our opinion that the coexistence of both approaches should be fostered because the dynamical method is helpful to specify the range of validity of thermodynamics and, reciprocally, the dynamical analysis asks for equations of state which are supplied by thermodynamics.

As the chemical potential plays a prominent role in all these problems, we examine in Sect. 16.1 the effects of a shear on the expression of this potential and the consequences on phase diagrams of polymeric solutions.

16.1 The Chemical Potential Under Shear: Flow-Induced Changes in the Phase Diagram of Solutions

A basic quantity in multicomponent mixtures is the chemical potential. Recall that in Chap. 3 thermal and caloric equations of state for a fluid in non-equilibrium were proposed. In this section, we shall determine the expressions of the Gibbs function and the chemical potential of a fluid under shear. Assume that temperature and pressure remain constant and that heat flux, diffusion flux and bulk viscous pressure are negligible. Define the Gibbs function g per unit mass as

$$g = u - \theta s + \pi \mathrm{v}. \tag{16.1}$$

The corresponding Gibbs equation at constant temperature and pressure reads as

$$\mathrm{d}g = \sum_k \mu_k \mathrm{d}c_k + \frac{\tau \mathrm{v}}{2\eta} \mathbf{P}^v : \mathrm{d}\mathbf{P}^v \tag{16.2}$$

and, after integration,

$$g(c_i, \mathbf{P}^v) = g_{\mathrm{eq}}(c_i) + \tau \mathrm{v}/(4\eta) \mathbf{P}^v : \mathbf{P}^v, \tag{16.3}$$

where τ designates the relaxation time of the viscous pressure tensor. Note that for the sake of commodity, the constant pressure and temperature have not been written explicitly.

In a steady shear, the components of the viscous pressure tensor for the Maxwell upper-convected model (see Problem 15.5) are

$$\mathbf{P}^v = \begin{pmatrix} -2\tau\eta\dot{\gamma} & -\eta\dot{\gamma} & 0 \\ -\eta\dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{16.4}$$

from which it follows that (16.3) takes the form

$$g(c_i,\dot{\gamma}) = g_{\text{eq}}(c_i) + \tfrac{1}{2}\tau\eta \text{v}\dot{\gamma}^2 + \mathcal{O}(\dot{\gamma}^4), \tag{16.5a}$$

or equivalently

$$g(c_i, P_{12}^v) = g_{\text{eq}}(c_i) + \tfrac{1}{2}J\text{v}(P_{12}^v)^2 + \mathcal{O}(P_{12}^v)^4, \tag{16.5b}$$

where the quantity $J = \tau/\eta$ is the so-called steady-state compliance.

More information about the non-equilibrium free energy can be obtained from microscopic considerations: the Rouse–Zimm model predicts that, for arbitrary laminar motions, the flow contribution to the Helmholtz free energy f is (Bird et al. 1987)

$$\Delta f = -\tfrac{1}{2}nk_{\text{B}}T\left\{\text{Tr}(\mathbf{P}^v)' + \ln|\det[(U - (\mathbf{P}^v)']|\right\}, \tag{16.6}$$

where Δf stands for $\Delta f = f(T, \text{v}, c, (\mathbf{P}^v)') - f(T, \text{v}, c, 0), n$ is the number of macro-molecules per unit volume and $(\mathbf{P}^v)' = (nk_{\text{B}}T)^{-1}\mathbf{P}^v$. Note that $\Delta g = \Delta f + p\Delta\text{v}$ at constant pressure, with, according to (16.3),

$$\Delta\text{v} = \frac{\partial}{\partial p}\left(\frac{1}{4}J\text{v}\right)\mathbf{P}^v : \mathbf{P}^v. \tag{16.7}$$

For an incompressible fluid $\partial\text{v}/\partial p = 0$, J does not depend on pressure, and therefore $\Delta\text{v} = 0$, and $\Delta g = \Delta f$.

In a Maxwell model, the viscosity η and the relaxation time τ are related by $\eta = nk_{\text{B}}T\tau$. Substitution of (16.4) into (16.6) gives

$$\Delta g = \frac{1}{2}\left[2\tau\eta\dot{\gamma}^2 - nk_{\text{B}}T\ln\left|1 + \frac{2\tau\eta}{nk_{\text{B}}T}\dot{\gamma}^2 - \frac{\eta^2}{(nk_{\text{B}}T)^2}\dot{\gamma}^2\right|\right]. \tag{16.8}$$

For small values of $\dot{\gamma}$ one has, up to the second order in $\dot{\gamma}$, $\Delta g = \frac{1}{2}\tau\eta\dot{\gamma}^2 = \frac{1}{2}J(P_{12}^v)^2$ which is equivalent to (16.5). At high values of the shear rate, the first term in (16.8) is dominant and therefore $\Delta g = \tau\eta\dot{\gamma}^2 = J(P_{12}^v)^2$.

The presence of non-equilibrium contributions may drastically change the phase diagram and the value of the critical point of polymer solutions. At equilibrium, the Gibbs free energy of mixing is given by the well-known Flory–Huggins formula (Jou et al. 2001; Rangel-Nafaile et al. 1984),

$$(RT)^{-1}(\Delta G)_{\mathrm{FH}} = n_1 \ln(1-\phi) + n_2 \ln\phi + \chi N\phi(1-\phi), \tag{16.9}$$

where G is the free energy per unit volume, ϕ the volume fraction of the polymer, and n_1 and n_2 the number of moles per unit volume of the polymer and the solvent, respectively; N is given by $N = n_1 + mn_2$, with m the ratio of the molar volume of the polymer and the molar volume of the solvent, so that $\phi = n_2 m(n_1 + mn_2)^{-1}$. The interaction parameter χ in (16.9) is assumed to depend on the temperature according to

$$\chi = \frac{1}{2} + \psi\left(\frac{\Theta}{T} - 1\right), \tag{16.10}$$

with ψ being a constant and Θ the so-called theta temperature of the quiescent solution.

In non-equilibrium situations, expression (16.5b) suggests to add to (16.9)a corrective term of the form

$$\Delta G_f = \mathrm{v}_1 NJ(P^v_{12})^2, \tag{16.11}$$

with v_1 the molar volume of the solvent. Note that, in general, J may depend on ϕ and it will be determined from experiments.

The chemical potential of the ith component is defined as usually by

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,Z} = \left(\frac{\partial G}{\partial \phi}\right)\left(\frac{\partial \phi}{\partial n_i}\right)_{T,p,Z}, \tag{16.12}$$

with Z a non-equilibrium parameter, either the shear rate or the viscous pressure, depending on the external constraints acting on the system. Note that different choices of Z lead to different expressions for the chemical potential, so that the selection of Z is important in formulating a coherent theory (see Problem 16.2).

From (16.9) and (16.11) it is inferred that the changes in the chemical potentials of the polymer and the solvent due to mixing are

$$\frac{\Delta\mu_1}{RT} = \ln(1-\phi) + \left(1 + \frac{1}{m}\right)\phi + \chi\phi^2 + \frac{\mu_{1f}}{RT}, \tag{16.13a}$$

$$\frac{\Delta\mu_2}{RT} = \ln\phi + (1-m)(1-\phi) + \chi m(1-\phi)^2 + \frac{\mu_{2f}}{RT}. \tag{16.13b}$$

In (16.13) the subscripts 1 and 2 refer as above to the polymer and the solvent, respectively, and use was made of $\partial\phi/\partial n_1 = -(\phi/N)$ and $\partial\phi/\partial n_2 = -(m/N)(1-\phi)$, with μ_{1f} and μ_{2f} the non-equilibrium contributions to the change of the chemical potential due to mixing, i.e. $\mu_{if} = (\partial\Delta G_f/\partial n_i)_{T,p,Z}$.

The spinodal line in the (T,ϕ)-plane is given by the relation

$$\left(\frac{\partial\Delta\mu_1}{\partial\phi}\right)_{T,p,Z} = 0, \tag{16.14}$$

and the critical point, corresponding to the maximum of the spinodal line, is specified by the supplementary relation

$$\left(\frac{\partial^2 \Delta\mu_1}{\partial\phi^2}\right)_{T,p,Z} = 0. \tag{16.15}$$

Since these expressions are directly borrowed from equilibrium thermodynamics, their applicability to non-equilibrium situations must be conforted by dynamical arguments. We leave such discussion to Sect. 16.4.

From (16.13) one obtains for the spinodal line and the critical point

$$\frac{1}{RT}\left(\frac{\partial \Delta\mu_1}{\partial\phi}\right) = -\frac{1}{1-\phi} + \left(1 - \frac{1}{m}\right) + 2\chi\phi + \frac{1}{RT}\left(\frac{\partial \mu_{1f}}{\partial\phi}\right) = 0, \tag{16.16a}$$

$$\frac{1}{RT}\left(\frac{\partial^2 \Delta\mu_1}{\partial\phi^2}\right) = -\frac{1}{(1-\phi)^2} + 2\chi + \frac{1}{RT}\left(\frac{\partial^2 \mu_{1f}}{\partial\phi^2}\right) = 0. \tag{16.16b}$$

The coordinates of the critical point of the quiescent solution are obtained from (16.15) by setting $\mu_{1f} = 0$; this leads to

$$\phi_c = \left(1 + m^{1/2}\right)^{-1}, \quad \chi_c = \tfrac{1}{2}\left(1 + m^{-1/2}\right)^2. \tag{16.17}$$

When m is very high (high molecular mass), ϕ_c tends to zero and χ_c to $\frac{1}{2}$, i.e. the critical temperature T_c tends to the theta temperature Θ. The parameters Θ and ψ in the original Flory–Huggins model for a solution of PS in TD are $\psi = 0.50$ and $\Theta = 294.4\,\mathrm{K}$ (Criado-Sancho et al. 1995). In addition, starting from the values for the molar volumes given by $V_1 = 1.586 \times 10^3\,\mathrm{m^3\,mol^{-1}}$ and $V_2 = 0.486\,\mathrm{m^3\,mol^{-1}}$ when the PS mass is $520\,\mathrm{kg\,mol^{-1}}$, one finds $m = 3\,064$. With these values of ψ, Θ, and m, one obtains from the Flory–Huggins theory, $T_c = 284.1\,\mathrm{K}$ for the equilibrium critical temperature.

The shear contribution μ_{1f} modifies not only the positions of the critical point, but also the spinodal and the coexistence lines (Fig. 16.1). To obtain them, explicit expressions for J as a function of ϕ are needed; these have been established by Rangel-Nafaile et al. (1984) for polystyrene in dioctylphtalate and by Wolf (1984) for polystyrene in transdecalin on experimental bases. For polystyrene in dioctylphtalate, the experimental shifts of the critical temperature with respect to the quiescent solution are 4 K at $P_{12}^v = 100\,\mathrm{N\,m^{-2}}$, 14 K at $P_{12}^v = 200\,\mathrm{N\,m^{-2}}$, and 24 K at $P_{12}^v = 400\,\mathrm{N\,m^{-2}}$. In the aforementioned examples, the critical temperature is enhanced by the shear flow, but this is not a general rule. As shown in the next section and confirmed by Wolf observations, for low-molecular-weight polymers there is a decrease in the critical temperature, whereas for high molecular weights there is an increase.

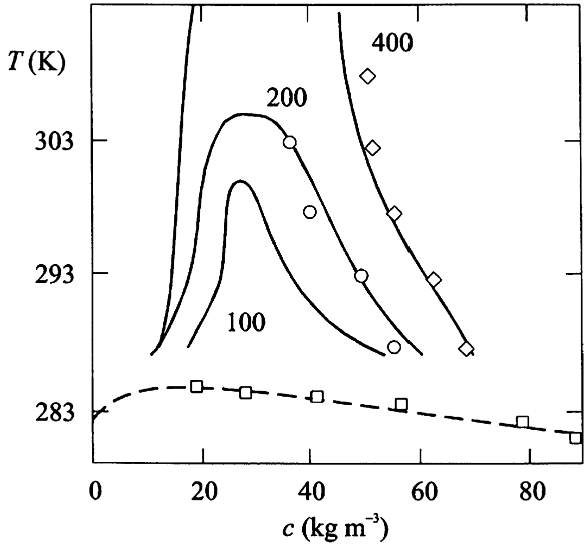


Fig. 16.1 Phase diagram of a binary solution of polystyrene in dioctylphtalate for several values of P_{12}^{v} (expressed in N m^{-2}). The dashed curve is the equilibrium spinodal line ($P_{12}^{v} = 0$) (reprinted from Rangel-Nafaile et al. (1984) Macromolecules 17:1187)

16.2 Explicit Solution for the Rouse–Zimm Model

It is well known that the equations of state for real polymer solutions are obtained experimentally; however, in some occasions the experimental data are scarce and, frequently, their analytical fit is not an easy task. For these reasons, we shall illustrate the general considerations of Sect. 16.1 by appealing to the well-known Rouse–Zimm microscopic model which was already introduced in Sect. 15.4. We also analyse the influence of the nature of hydrodynamic interactions on the shift of the critical point, and compare the phase diagram at constant shear viscous pressure and at constant shear rate to emphasize the role of different constraints (Criado-Sancho et al. 1995). The price to be paid for making use of this simple model is a restriction to relatively low values of the shear rate.

Our purpose is to modify the Flory–Huggins equilibrium model (16.9) taking into account the non-equilibrium correction. To do that, it is necessary to know how the steady-state compliance J depends on the composition of the mixture. This dependence is easily obtained by assuming that the polymer behaves as a linear generalised Maxwell model (see Sect. 15.1), for which

$$J = \frac{CM_1}{cRT}\left(1 - \frac{\eta_s}{\eta}\right)^2, \tag{16.18}$$

where c is the polymer concentration expressed in terms of mass per unit volume, η the viscosity of the solution, η_s the solvent viscosity, M_1 the polymer molar mass and C a parameter whose value shall be discussed below.

It is important to have in mind that η depends on the concentration. The latter dependence is crucial in the analysis of the shift of the critical point: predictions based on the hypothesis that $J \sim c^{-1}$ yield unsatisfactory results (see Problem 16.4). It is usually assumed that $\eta(c)$ takes the form (Rangel-Nafaile et al. 1984)

$$\frac{\eta}{\eta_s} = 1 + [\eta]c + k[\eta]^2c^2, \tag{16.19}$$

where k is the so-called Huggins constant and $[\eta]$ stands for the intrinsic viscosity, defined, as usually, by

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_s}{\eta_s}. \tag{16.20}$$

For the system TD/PS with a polymer molecular mass of 520 kg mol^{-1}, $k = 1.40$ (Wolf 1984), $[\eta] = 0.043\,\mathrm{m^3\,kg^{-1}}$, and the solvent viscosity $\eta_s = 0.0023$ Pa s. With these values, (16.19) describes fairly well the viscosity in a concentration range for which the product $c[\eta]$ is less than 1. Since the critical density of the system is found in this range, this limitation is not too restrictive.

When hydrodynamic interactions are ignored, as in the Rouse model, the parameter C in (16.18) takes the value 0.4, whereas accounting for hydrodynamic interactions, as in the Zimm model, the value of C is 0.206. A comparison with experimental data shows that Zimm's theory is useful at low concentrations, whereas at high concentrations, the behaviour of the system is well described by the Rouse model. There is thus a shift from the Zimm to Rouse model with increasing polymer concentration, which may be described, by assuming that C is a function of the composition, via a reduced concentration $\tilde{c}$ defined by $\tilde{c} = [\eta]c$. Since the functional dependence $C = C(\tilde{c})$ is unknown we propose to describe the gradual transition from the Zimm to the Rouse behaviour by means of

$$C(\tilde{c}) = 0.206 + \frac{0.194\alpha\tilde{c}\,^{,}}{1 + \alpha\tilde{c}} \tag{16.21}$$

where α is a parameter which measures how steep is the transition.

We may summarize our hypotheses by the following expression for (16.11)

$$\frac{(\Delta G)_f}{RT} = BC(\tilde{c})\frac{(P_{12}^v)^2}{T^2}NF(\tilde{c}), \tag{16.22}$$

where B is a constant given by $B = V_1M_1[\eta]/R^2$ and $F(\tilde{c})$ a function of the reduced concentration defined as

$$F(\tilde{c}) = \tilde{c}\left(\frac{1 + k\tilde{c}}{1 + \tilde{c} + k\tilde{c}^2}\right)^2. \tag{16.23}$$

The results for the shift in the spinodal line are given in Box 16.1.

Box 16.1 Shear-induced shift of spinodal curve It is interesting to discuss the consequences of keeping constant either the shear rate $\dot{\gamma}$ or the shear viscous pressure P_{12}^{v}. These different constraints will lead to different non-equilibrium phase diagrams. Let $(\mu_1)_{P_{12}^{v}}$ be the chemical potential at constant shear viscous pressure and $(\mu_1)_{\dot{\gamma}}$ the chemical potential at constant shear rate, defined respectively as

$$(\mu_1)_{P_{12}^{v}} = \left(\frac{\partial \Delta G^{(s)}}{\partial n_1}\right)_{P_{12}^{v}}, \quad (\mu_1)_{\dot{\gamma}} = \left(\frac{\partial \Delta G^{(s)}}{\partial n_1}\right)_{\dot{\gamma}}. \tag{16.1.1}$$

At constant P_{12}^{v} the explicit expression for the chemical potential is

$$\frac{1}{RT}(\mu_1)_{P_{12}^{v}} = -\frac{2B(P_{12}^{v})^2}{T^2} C \frac{P_5(\tilde{c})}{P_6(\tilde{c})} - \frac{B(P_{12}^{v})^2}{T^2} C' \tilde{c} F(\tilde{c}), \tag{16.1.2}$$

where C' stands for the derivative of $C(\tilde{c})$ with respect to $\tilde{c}$, with the auxiliary functions $P_5(\tilde{c})$ and $P_6(\tilde{c})$ given by

$$P_5(\tilde{c}) = (k-1)\tilde{c}^2 + (k^2-3k)\tilde{c}^3 - 3k^2\tilde{c}^4 - k^3\tilde{c}^5, \quad P_6(\tilde{c}) = (1+\tilde{c}+k\tilde{c}^2)^3. \tag{16.1.3}$$

At constant shear rate $\dot{\gamma}$, the explicit expression for the chemical potential is

$$\frac{(\mu_1)_{\dot{\gamma}}}{RT} = \frac{(\mu_1)_{P_{12}^{v}}}{RT} - \frac{2B\eta_s^2\dot{\gamma}^2}{T^2} C\Omega(\tilde{c}), \tag{16.1.4}$$

where Ω is defined as $\Omega(\tilde{c}) = \tilde{c}(1+\tilde{c}+k\tilde{c}^2)(1+2k\tilde{c}^2)F(\tilde{c})$. It is easy to show that the expression for the chemical potential at constant $\dot{\gamma}$ is smaller than the chemical potential at constant P_{12}^{v}, because the corrective term in (16.1.4) is positive.

We are now in position to examine the consequences issued from the thermodynamic criterion for the limit of stability. From $(\partial\mu/\partial\tilde{c}) = 0$, we obtain the following expression for the spinodal line

$$\frac{\partial}{\partial\tilde{c}}\left(\frac{\mu_1}{RT}\right) = \frac{\partial}{\partial\tilde{c}}\left(\frac{\mu_1^{(0)}}{RT}\right) + \frac{\partial}{\partial\tilde{c}}\left(\frac{(\mu_1)_s}{RT}\right) = 0 \qquad (s = P_{12}^{v}, \dot{\gamma}), \tag{16.1.5}$$

where the first derivative on the right-hand side is given by

$$\frac{\partial}{\partial\tilde{c}}\left(\frac{\mu_1^{(0)}}{RT}\right) = -\frac{\nu}{1-\nu\tilde{c}} + \left(1-\frac{1}{m}\right)\nu + 2\chi\nu^2\tilde{c}, \tag{16.1.6}$$

with ν a constant defined as $\nu = V_1/M_1[\eta]$. For $(\mu_1)_{P_{12}^{v}}$ and $(\mu_1)_{\dot{\gamma}}$ the corrective terms in (16.1.1) are respectively

$$\frac{\partial}{\partial \tilde{c}}\left(\frac{1}{RT}(\mu_1)_{P_{12}^v}\right) = -\frac{2B(P_{12}^v)^2}{T^2}\left[C\frac{P_6P_5' - P_5P_6'}{(P_6)^2} + C'\left(\frac{P_5}{P_6} + F\right) + C''\tilde{c}F\right],$$

$$\frac{\partial}{\partial \tilde{c}}\left(\frac{1}{RT}(\mu_1)_{\dot{\gamma}}\right) = \frac{\partial}{\partial \tilde{c}}\left(\frac{1}{RT}(\mu_1)_{P_{12}^v}\right) \tag{16.1.7}$$

$$-\frac{2B\eta_s^2\dot{\gamma}^2}{T^2}\left[C\frac{\Omega_2(1+\tilde{c}+k\tilde{c}^2) - \Omega_1(1+2k\tilde{c})}{(1+\tilde{c}+k\tilde{c}^2)^2} + C'\Omega\right]. \tag{16.1.8}$$

In the latter expressions, P_n' stands for the derivative of P_n with respect to $\tilde{c}$, and C' and C'' are the two first derivatives of (16.21) with respect to $\tilde{c}$. Furthermore, we have introduced the auxiliary functions

$$\Omega_1(\tilde{c}) = \tilde{c}^2 + 4k\tilde{c}^3 + 5k^2\tilde{c}^4 + 2k^3\tilde{c}^5, \tag{16.1.9a}$$

$$\Omega_2(\tilde{c}) = 2\tilde{c} + 12k\tilde{c}^2 + 20k^2\tilde{c}^3 + 10k^3\tilde{c}^4. \tag{16.1.9b}$$

To obtain numerical values, consider a solution of polystyrene of molecular mass 520 kg mol^{-1} in transdecalin. The corresponding equilibrium and non-equilibrium spinodal lines are shown in Fig. 16.2, where it is seen that at constant $\dot{\gamma}$ the presence of a shear rate lowers the critical temperature, in agreement with experiments (Rangel-Nafaile et al. 1984).

When the same system is submitted to a constant P_{12}^v, the conclusion drawn from (16.1.7–16.1.8) is that the critical temperature is increased, as seen in Fig. 16.3 for different values of the shear viscous pressure. Since the temperature shifts are important, it is clear that equilibrium thermodynamics is inadequate for describing

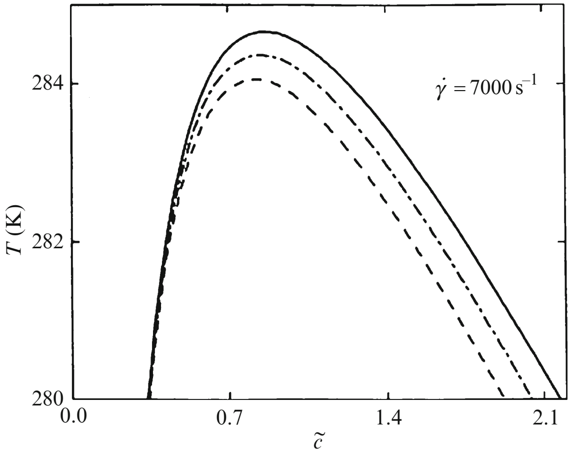


Fig. 16.2 Spinodal curve of a solution of polystyrene in transdecalin at equilibrium (*dashed line*) and in a non-equilibrium steady state at constant shear rate $\dot{\gamma} = 1500\,\mathrm{s}^{-1}$ (*continuous line*) (reprinted from Criado-Sancho M et al. (2002) Physica A 309:1)

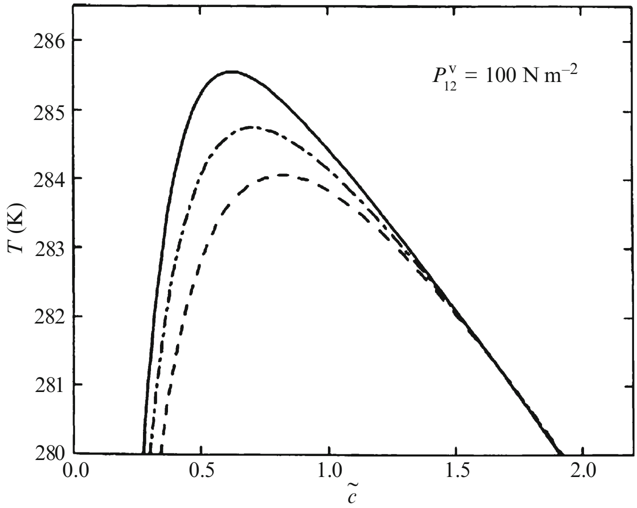


Fig. 16.3 Spinodal curve of a Rouse–Zimm binary solution at equilibrium (Flory–Huggins) and in a non-equilibrium steady state at constant shear viscous pressure $P^{v}_{12} = 100\,\mathrm{N\,m^{-2}}$. The figure collects the results corresponding to the Rouse (no hydrodynamic interactions), the Zimm (hydrodynamic interactions) and two intermediate models corresponding to the values $\alpha = 0.5$ and $\alpha = 1.5$ of the parameter α describing the transition from the Rouse model to the Zimm model for increasing values of the concentration according to Eq. (16.21). The higher the hydrodynamic interactions, the lower the shift of the critical temperature (reprinted from Criado-Sancho M et al. (2002) Physica A 309:1)

polymer solutions in the presence of a shear pressure. However, the above theoretical predictions about the temperature shifts are still lower than the actual values; the agreement is nevertheless improved when the effects of shear-enhanced concentration fluctuations are taken into account in a dynamical approach (Sancho et al. 1994, 1997).

Another interesting result derived from Fig. 16.3 is the effect of hydrodynamic interactions on the shift of the critical point: when they are neglected, as in the Rouse model, the shift is maximum, while it is minimum in the Zimm model, where they are relevant. Our model shows that hydrodynamic interactions are more important in the shift (increase) of the critical temperature T_c than in the shift (decrease) of the critical concentration.

These phenomena have practical applications in macromolecular separation, as the non-equilibrium effective diffusion coefficient strongly depends on the macromolecular mass in a more sensitive way than the equilibrium diffusion coefficient. As a consequence, in the steady state, the radial distribution of macromolecules depends acutely on the mass: those with higher molecular mass will tend to accumulate near the axis of symmetry.

An analogous situation is found for solutions flowing along a cylindrical duct. A consequence of the dependence of the chemical potential on the shear rate has a strong influence on polymer extraction from a porous matrix; this effect makes the extraction process less effective when the shear rate in the extracting duct is high, because of a reduction in the number of microstates accessible to a macromolecule.

16.2 Chemical Reactions Under Flow

It is expected that the application of a shear pressure will modify the properties of a chemical reaction taking place in the system, and in particular the chemical equilibrium constant. After general considerations, we shall examine as an illustration the interesting problem of the thermodynamic degradation of polymers under flow.

16.2.1 Shear-Induced Effect on the Affinity

The change of chemical potential due to the presence of a shear pressure will be reflected in the expression of the affinity, and consequently in that of chemical equilibrium constant. To see that, consider a chemical reaction in a system submitted to a steady shear flow; the generalised Gibbs equation will take the form

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \sum_k \mu_k \mathrm{d}N_k + V\tau/(2\eta)\mathbf{P}^v : \mathrm{d}\mathbf{P}^v, \tag{16.24}$$

where G is the global Gibbs function. By equating the cross derivatives

$$\left(\frac{\partial \mu_k}{\partial \mathbf{P}^v}\right)_{T,p,N_j} = \frac{\partial}{\partial N_k}\left(\frac{V\tau}{2\eta}\right)_{T,p,N_j} \mathbf{P}^v, \tag{16.25}$$

and after integration, one obtains for the generalised chemical potential

$$\mu_k(T, p, N_j, \mathbf{P}^v) = \mu_{k,\mathrm{eq}}(T, p, N_j) + \frac{1}{4}\frac{\partial(V\tau/\eta)}{\partial N_k}\mathbf{P}^v : \mathbf{P}^v, \tag{16.26}$$

where $\mu_{k,\mathrm{eq}}$ is the local-equilibrium chemical potential, independent of $\mathbf{P}^v$; it is usual to write $\mu_{k,\mathrm{eq}}$ as

$$\mu_{k,\mathrm{eq}}(T, p, N_j) = \mu^0_{k,\mathrm{eq}}(T, p) + RT \ln a_k, \tag{16.27}$$

with a_k being the activity of component k. If we use $\mathrm{d}N_k = \nu_k \mathrm{d}\xi$, where ν_k is the stoichiometric coefficient of component k and ξ the rate of advancement of the reaction, (16.24) reads as

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p - \mathcal{A}\mathrm{d}\xi + V\tau/(2\eta)\mathbf{P}^v : \mathrm{d}\mathbf{P}^v, \tag{16.28}$$

where

$$\mathcal{A} = -(\partial G/\partial \xi)_{T,p,\mathbf{P}^v} = -\sum_k \nu_k \mu_k \tag{16.29}$$

denotes the affinity of the reaction. At chemical equilibrium in the absence of a shear pressure, it is well known that G is minimum from which it follows that $\mathcal{A} = 0$, at constant T and p. According to expression (16.28), the same properties hold in the presence of a shear pressure but now the minimum of G corresponds to fixed values of T, p and $\mathbf{P}^v$, and is generally shifted compared with the classical case where $\mathbf{P}^v = 0$. As a consequence, we are still allowed to put $\mathcal{A} = 0$, so that

$$\sum_k \nu_k \mu_k = 0. \tag{16.30}$$

Substituting in this relation the expression for the chemical potential given by (16.26) and taking (16.27) into account, one obtains

$$\sum_k \nu_k \left[\frac{\mu^0_{k,\text{eq}}}{RT} + \ln a_k + \frac{1}{4RT}\frac{\partial}{\partial N_k}\left(\frac{V\tau}{\eta}\right)\mathbf{P}^v : \mathbf{P}^v \right] = 0. \tag{16.31}$$

Defining the equilibrium constant K by

$$\ln K(T,p) = -\frac{1}{RT}\sum_k \nu_k \mu^0_{k,\text{eq}} \tag{16.32}$$

and a function λ describing the effects of the viscous shear by

$$\ln \lambda = -\frac{1}{4RT}\sum_k \nu_k \frac{\partial}{\partial N_k}\left(\frac{V\tau}{\eta}\right)\mathbf{P}^v : \mathbf{P}, \tag{16.33}$$

it is found that at chemical equilibrium under a shear flow

$$K(T,p) = \frac{1}{\lambda}\prod_k a_k^{\nu_k}. \tag{16.34}$$

Note that when $\mathbf{P}^v = 0$, $\lambda = 1$ and one recovers the classical expression relating the values of the activities a_k in chemical equilibrium to the equilibrium constant. The above result is important, as it shows that even chemical equilibrium may be influenced by non-equilibrium constraints.

16.2.2 Illustration: Polymer Degradation Under Flow

As an illustration of the above general considerations, we shall examine the problem of polymer degradation. The latter is usually solved by chemical kinetics (Nguyen and Kausch 1992). The first hypothesis underlying any kinetic mechanism for polymer degradation is to assume that each chain is broken only at one point (i.e. only two fragments are produced per each broken macromolecule). The second hypothesis states that each elementary reaction

$$\mathrm{P}_j \to \mathrm{P}_i + \mathrm{P}_{j-i} \tag{16.35}$$

follows a first-order kinetics, i.e.

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = k_{ij} n_j, \tag{16.36}$$

where n_i and n_j stand for the number of macromolecules with i and j degrees of polymerization, respectively, and k_{ij} is the kinetic constant describing the breaking of a macromolecule with i monomers into a macromolecule with j monomers and another with $i - j$ monomers.

Besides numerical difficulties, the only (and non trivial) problem is to know the values of the kinetic constants k_{ij}. Three situations are often analysed (Basedow et al. 1978): (1) the simplest one is to assume that all bonds have the same breaking probability, so that the value of k_{ij} is independent of i and j and the macromolecular fragmentation is a random process; (2) a slightly more complicated situation occurs when the kinetic constant depends on the length of the chain which is broken, but not on the length of the ensuing fragments, i.e. the value of k_{ij} depends on i but not on j; (3) the most complicated case arises when k_{ij} depends on the position of the breaking point: this situation is usually dealt with by assuming that the value of the kinetic constant for the breaking of any chain is given by a Gaussian function whose parameters are obtained by fitting experimental data.

The kinetic mechanism proposed in (16.35) is not the most general, and it may be considered as a particular case of a degradation-combination scheme of the form

$$\mathrm{P}_j \rightleftarrows \mathrm{P}_i + \mathrm{P}_{j-i} \tag{16.37}$$

In this event, the mass action law (16.36) will contain a new kinetic constant κ_{ij} which corresponds to the recombination of the chains P_i and P_{j-i} and which is related to the chemical equilibrium constant K_{ij} by $K_{ij} = k_{ij}/\kappa_{ij}$.

In the present approach, the system is viewed as a multicomponent mixture, constituted by the solvent (component 1) and a set of polymeric species P_i (with i the degree of polymerization), whose chemical potentials for macromolecules with different lengths will be written as

$$\mu_j = \mu_{j,\mathrm{eq}} + RT \left(\frac{\partial \Delta G_s}{\partial n_j} \right)_{n_k, \dot{\gamma}}, \tag{16.38}$$

where ΔG_s is the non-equilibrium contribution to the Gibbs function and j refers to the number of monomeric units in the chain.

Furthermore, the average character of the polymeric molecular mass in the solution amounts to admit that M_1 appearing in (16.18) is a function of n_i. It is also assumed that in equilibrium the n_i are distributed according to some well-known equilibrium distribution functions of the number of particles, as for instance the so-called most probable distribution (Criado-Sancho et al. 1995; Basedow et al. 1978).

Applying the result (16.26) to reaction (16.35) and considering for simplicity an ideal mixture, one may write

$$\frac{N_j}{N_i N_{j-1}} = \frac{N_j^{(0)}}{N_i^{(0)} N_{j-1}^{(0)}} \lambda(i, j)^{-1}, \tag{16.39}$$

where N_k is the number of chains with k units while the superscript (0) refers to values with $\dot{\gamma} = 0$. The function λ that takes into account the non-equilibrium effects is obtained from (16.33) and it is given explicitly in (Sancho et al. 1994, 1997) for a solution of polystyrene in transdecalin.

The results are summarized in Fig. 16.4, where the differential mass fraction $W(i)$ (the polymeric mass with a degree of polymerization between i and $i + \mathrm{d}i$, considering i as a continuous variable) is plotted as a function of i for a solution of polystyrene of mean molecular mass 1170 kg mol^{-1} in transdecalin. To describe the

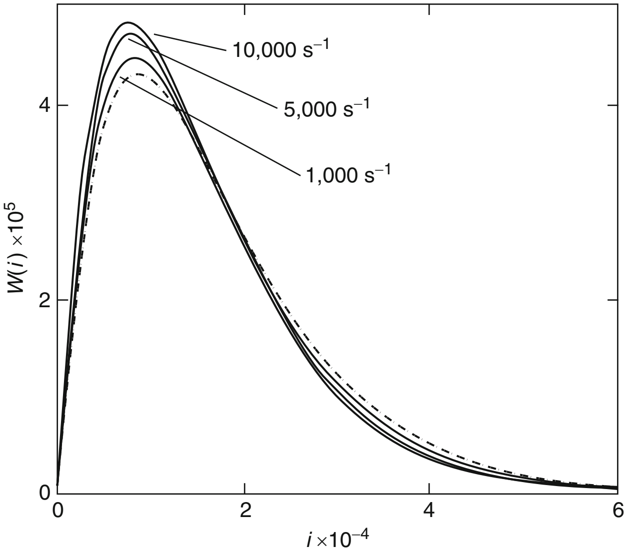


Fig. 16.4 Differential mass fraction of polystyrene in a polystyrene–transdecalin solution for an equilibrium mean molecular weight of 1, 170 Kg mol^{-1} under several shear rates. The dashed line corresponds to a quiescent situation. It has been assumed that the form of the curve is given by the so-called most-probable distribution (reprinted from Sancho et al. M et al. (1994) J Non Equilib Thermodyn 19:1)

form of $W(i)$ at equilibrium we have used the so-called most-probable distribution $W(i) = \alpha^2 i(1-\alpha)^{i-1}$, where α is a parameter describing the width of the distribution. The parameters of the equilibrium distributions without shear rate and with shear rate are related by the expression $\alpha(1-\alpha)^{-1} = \alpha^{(0)}[1-\alpha^{(0)}]^{-1}\lambda$. Figure 16.4 exhibits a tendency towards an enhancement of the number of smaller particles, in such a way that the mean molecular mass diminishes by 5% for a shear rate $\dot{\gamma} = 10^4\,\mathrm{s}^{-1}$ A detailed analysis shows a slight dependence of the results with the form used to describe the distribution function and with the ratio between the weight average and the number average (Basedow et al. 1978).

16.4 Dynamical Approach

Our purpose in this section is to justify from dynamical bases the use of the thermodynamic stability criterion (16.14) in non-equilibrium situations (Casas-Vazquez et al. 1993). Let us start from the general results of Sect. 13.4 about the coupling between viscous pressure and diffusion. According to (13.35–13.37), the diffusion flux and the viscous pressure in a steady state are related by

$$\boldsymbol{J}_1 = -D'\nabla\tilde{\mu} + D'T\nabla\cdot(\beta\mathbf{P}^v), \tag{16.40}$$

$$\mathbf{P}^v = -2\eta(\nabla\boldsymbol{v})^s + 2\eta T\beta(\nabla\boldsymbol{J}_1)^s, \tag{16.41}$$

with $\tilde{\mu} = \mu_1 - \mu_2$ being the difference between the specific chemical potentials of the solute and the solvent. The coefficient D' is related to the diffusivity D through $D = D'(\partial\tilde{\mu}_{\mathrm{eq}}/\partial n_1)_{T,p}$, where n_1 is the concentration of the solute.

When diffusion effects are negligible compared with those of $\mathbf{P}^v$ (for instance, when the system is subjected to a relatively high shear pressure and the diffusion flux is very weak), one has (see (16.26))

$$\tilde{\mu}(n_1, P^v) = \tilde{\mu}_{\mathrm{eq}}(n_1) + \frac{1}{4}\left[\frac{\partial}{\partial n_1}\left(\frac{\tau v}{\eta}\right)\right]_{T,p} \mathbf{P}^v : \mathbf{P}^v. \tag{16.42}$$

Our purpose is to determine under which conditions the classical thermodynamic stability criterion $(\partial\tilde{\mu}/\partial n_1) \geq 0$ used in (16.14) to obtain the spinodal curve in the presence of a shear, is supported by a dynamical theory.

First of all, in the absence of coupling effects, i.e. when $\beta = 0$, (16.40) reduces to

$$\boldsymbol{J}_1 = -D'(n_1, \dot{\gamma})\nabla\tilde{\mu}(n_1, \dot{\gamma}). \tag{16.43}$$

Note that both $\tilde{\mu}$ and D' may depend not only on n_1 but also on $\dot{\gamma}$. For a homogeneous shear rate, i.e. an uniform value of $\dot{\gamma}$, (16.43) can be written as

$$\boldsymbol{J}_1 = -D'(n_1, \dot{\gamma})(\partial\tilde{\mu}/\partial n_1)_{T,\dot{\gamma}}\nabla n_1. \tag{16.44}$$

Expression (16.53) allows one to identify an effective diffusion coefficient D_{eff} by

$$D_{\text{eff}} = D'(n_1, \dot{\gamma})(\partial\tilde{\mu}/\partial n_1)_{T,\dot{\gamma}}. \tag{16.45}$$

According to the positiveness of entropy production, $D'(n_1, \dot{\gamma})$ is always positive. When D_{eff} becomes negative the inhomogeneities are amplified so that the homogeneous state becomes unstable. Thus, for $(\partial\tilde{\mu}/\partial n_1)_{T,\dot{\gamma}} > 0$, one has $D_{\text{eff}} > 0$, and the states are stable whereas when $(\partial\tilde{\mu}/\partial n_1)_{T,\dot{\gamma}}$ is negative, D_{eff} is also negative and the homogeneous states are unstable. As a consequence, it can be said that the criterion $(\partial\tilde{\mu}/\partial n_1)_{T,\dot{\gamma}} = 0$ yields the border between stable and unstable states, both from the thermodynamical and the dynamical points of view. Of course, the dynamical approach may predict the details of phase separation (droplets, percolating structures, etc.) and the rate of separation, in contrast with the purely thermodynamic analysis. An illustration of the above considerations for a sheared suspension flow was treated by Nozieres and Quemada (1986).

When the coefficient β is different from zero, the diffusion flux is coupled with the viscous pressure tensor. Take a steady state and a plane shear flow with velocity distribution of the form $v_x(y)$; then (16.40) for the component J_y of the diffusion flux normal to the velocity, which is responsible for the appearance of inhomogeneities in the fluid, can be written as

$$J_y = -D'(n_1, \dot{\gamma})\frac{\partial}{\partial y}\left[\tilde{\mu}(n_1, \dot{\gamma}) - T\beta P^v_{yy}\right], \tag{16.46}$$

provided that the quantities appearing in (16.40) do not change along the direction of the flow.

As in (13.45), one may identify a generalised chemical potential $\tilde{\mu}''$ as

$$\tilde{\mu}''(n_1, \gamma) = \tilde{\mu}(n_1, \gamma) - T\beta P^v_{yy} = \tilde{\mu}(n_1, \gamma) + \bar{\mathrm{v}} P^v_{yy}. \tag{16.47}$$

Then, (16.46) can simply be expressed as

$$J_y = -D'(n_1, \dot{\gamma})\frac{\partial}{\partial y}\mu''(n_1, \dot{\gamma}). \tag{16.48}$$

In this case, the dynamical stability condition of a positive effective diffusion coefficient is

$$\frac{\partial\tilde{\mu}''}{\partial n_1} > 0, \tag{16.49}$$

instead of $(\partial\tilde{\mu}/\partial n_1)_{T,\dot{\gamma}} > 0$. Condition (16.49) is equivalent to that obtained by Onuki (1989, 1990) from a full hydrodynamic analysis. This means that when the normal viscous pressure P^v_{yy} is zero (as, for instance, in Maxwell upper-convected models, where the normal pressure along the x direction is different from zero but the normal pressure along the y and z directions are zero), the chemical potential $\tilde{\mu}''(n_1, \dot{\gamma})$ coincides with $\tilde{\mu}(n_1, \dot{\gamma})$. Since this condition is satisfied in the analysis presented in Sect. 16.2, the results presented there are valid.

In general terms, it is clear that more experimental and theoretical work is needed. The spinodal curves should be examined for a larger variety of flows and materials. The composition of the individual phases should also be measured carefully. Spectrographic techniques rather than simple visual observation of the turbidity should be used in order to improve the accurateness of the data. An open problem is to formulate some general criteria to predict, for a particular material, whether shear-induced solubility or shear-induced phase separation will occur.

16.5 Shear-Induced Migration of Polymers

The coupling between shear effects and diffusion is nowadays one of the most active topics in rheology. In particular, shear-induced migration of polymers deserves a great attention, both for its practical aspects (chromatography, separation techniques, flow through porous media) and its theoretical implications in non-equilibrium thermodynamics and transport theory (Larson 1992; Prakash and Mashelkar 1991, 1992). The subject is especially attractive, as it concerns the coupling of vectorial fluxes and tensorial forces, which lies outside the range of applicability of classical irreversible thermodynamics, and because it puts forward a testing ground for non-equilibrium equations of state. The basic frame of this section is provided by Eqs. (16.40–16.41).

Recently, MacDonald and Muller (1996), to whom we refer for a wide bibliography on this topic, have studied the evolution of the concentration profile of a polymer under the effect of a shear pressure in a cone-and-plate configuration. Their conclusions are extremely challenging, as they observe a discrepancy of two to three orders of magnitude between theoretical predictions and experimental observations.

The constitutive equation for the diffusion flux $\boldsymbol{J}$ proposed by MacDonald and Muller is

$$\boldsymbol{J} = -D\nabla n - \frac{D}{RT}\nabla \cdot \mathbf{P}^v, \tag{16.50}$$

where n is the polymer concentration (in moles per unit volume), D the diffusion coefficient and R the ideal gas constant. This constitutive equation has been examined from different macroscopic and microscopic points of view (Mavrantzas 1992; Beris 1994; Ottinger 1992, 2005).

MacDonald and Muller have applied Eq. (16.50) in the particular case of a cone-and-plate configuration, where the only non-zero components of the viscous pressure tensor are given by

$$P^v_{\phi\phi} = -2RTn(\tau\dot{\gamma})^2, \qquad P^v_{\phi\theta} = -RTn(\tau\dot{\gamma}), \tag{16.51}$$

where we have considered that $\eta = nRT\tau$, and the subscripts ϕ and θ refer to the axial and azymuthal directions respectively, and τ is the polymer relaxation time.

By combining (16.50) and (16.59) with the mass balance equation

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{\partial n}{\partial t} + \boldsymbol{v} \cdot \nabla n = -\nabla \cdot \boldsymbol{J}, \tag{16.52}$$

and since the convection term vanishes identically in this geometry, one has

$$\frac{\partial n}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial n}{\partial r} + \beta_{\mathrm{MM}} r n \right), \tag{16.53}$$

with the parameter $\beta_{\mathrm{MM}} = 2(\tau\dot{\gamma})^2$. To obtain (16.51) it has been assumed that the steady viscometric flow has only one non-zero component of the velocity (the ϕ component) which depends on the r and θ coordinates, that the shear-induced flux in the θ direction is negligible when the angle between the cone and the plate is small (as occurred in the experiments), and that the contribution of convection of molecules by migration to the viscous pressure is negligible. The term in β_{MM}, arising from the second term in the right-hand side of (16.53), induces a flux of solute towards the apex of the cone (designated by arrows 1 in Fig. 16.5) and it is usually believed to be responsible for induced migration.

But, according to MacDonald and Muller, this contribution cannot explain by itself the actual rate of migration. Indeed, they have calculated a short-time solution of (16.62) for $n(r,t)$ and have compared it with their experimental results for polystyrene macromolecules of different molecular weights 2×10^3 and $4 \times 10^3\,\mathrm{kg\,mol^{-1}}$ (denoted by 2M and 4M respectively) in a solvent of oligomeric polystyrene molecules of $0.5\,\mathrm{kg\,mol^{-1}}$, in a cone-and-plate configuration sheared

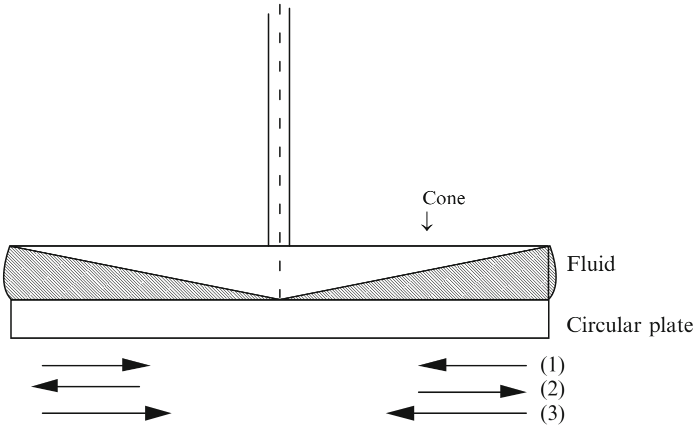


Fig. 16.5 The flows of matter are indicated in the cone-and-plate configuration. *Arrows* (1) shows the shear-induced flow described by the second term in the right-hand side of Eqs. (16.50) and (16.54); *arrows* (2) and (3) indicate the diffusion flux corresponding to the first term in the right-hand side of Eq. (16.54). When the effective diffusion coefficient (16.58) is positive, the diffusion flux (2) is opposite to the shear-induced flow (1), whereas when it is negative, the diffusion flux (3) enhances the shear-induced effects

at $\dot{\gamma} = 2\,\mathrm{s}^{-1}$. The initial homogeneous concentration of the molecules of each solution was 0.20% and 0.12% in weight for the 2M and 4M solutions, respectively. Taking an average value of τ obtained from steady-state data for the shear viscosity, they found for the 2M and 4M solutions the theoretical values $\beta_{2\mathrm{MM}} = 240$ and $\beta_{4\mathrm{MM}} = 1{,}500$ respectively.

However, when MacDonald and Müller compare the result obtained from (16.53) with the experimental concentration profiles, they notice a dramatic difference with a migration motion much faster than that predicted by Eq. (16.53). They tried to fit the data by allowing either β_{MM} or D to be adjustable parameters: to comply with the data it is necessary to take $\beta_{2\mathrm{MM}} = 200{,}000$ and $\beta_{4\mathrm{MM}} = 1{,}100{,}000$ instead of the values mentioned previously.

It is interesting to stress that (16.40), instead, alleviates this severe discrepancy. We write it as

$$\boldsymbol{J} = -D'\nabla\mu - \frac{D}{RT}\nabla\cdot\mathbf{P}^v, \tag{16.54}$$

where $D' = (\partial\mu_{\mathrm{eq}}/\partial n)D$. The essential point is that in the presence of a non-vanishing $\mathbf{P}^v$, μ is not only a function of n but may contain contributions of $\mathbf{P}^v$. This gives rise to a new coupling neglected up to now, between viscous effects and diffusion, besides the term in $\nabla\cdot\mathbf{P}^v$.

To be explicit, μ may be expressed as

$$\mu = \mu_{\mathrm{eq}} + \frac{1}{V}(1 - V'n)\left(\frac{\partial G}{\partial n}\right)_{T,p,\mathbf{P}^v}, \tag{16.55}$$

where $V' = \partial V/\partial N$ is the partial molar volume of the solute and $N = nV$. The terms within parentheses in (16.55) take into account that a variation of N at constant p produces a change in the total volume V.

According to (16.11) and (16.55), the chemical potential of the solute is

$$\mu = \mu_{\mathrm{eq}} + \frac{1}{4V}(1 - V'n)\frac{\partial}{\partial n}(JV)\mathbf{P}^v : \mathbf{P}^v. \tag{16.56}$$

The use of the generalised chemical potential suggests to introduce an effective diffusion coefficient as $D_{\mathrm{eff}} = D'(\partial\mu/\partial n)$ or, by writing D' in terms of the classical diffusion coefficient D,

$$D_{\mathrm{eff}} = \frac{D}{(\partial\mu_{\mathrm{eq}}/\partial n)}\left(\frac{\partial\mu}{\partial n}\right). \tag{16.57}$$

Introduction of (16.56) into (16.57), leads to

$$D_{\mathrm{eff}} = D\left\{1 + \frac{1}{(\partial\mu_{\mathrm{eq}}/\partial n)}\frac{\partial}{\partial n}\left[\frac{(1 - V'n)}{4V}\frac{\partial}{\partial n}(JV)\mathbf{P}^v : \mathbf{P}^v\right]\right\}. \tag{16.58}$$

If the contribution of the term in $\mathbf{P}^v : \mathbf{P}^v$ is negative and in absolute value larger than one, so that $D_{\text{eff}} < 0$, it induces a flow of solute towards higher solute concentrations, i.e. in opposite direction of the usual Fickian diffusion. Such an effect coupled to the contribution of the term containing $\nabla \cdot \mathbf{P}^v$ in (16.54) will drastically fasten the migration process of the solute towards the center, as shown in Fig. 16.5.

To see whether the non-equilibrium contribution to D_{eff} is negative requires a detailed knowledge of μ_{eq}, V' and J with respect to the concentration. We consider polystyrene in transdecalin, whose non-equilibrium chemical potential under flow has been studied in detail (Jou et al. 2001; Criado-Sancho et al. 1991, 1993, 1995; Lebon et al. 1993). In Fig. 16.6 is represented $(\partial\mu/\partial n)$ as a function of n for a given $\mathbf{P}^v$. To obtain this figure we have used for the equilibrium chemical potential the Flory–Huggins model and to evaluate the non-equilibrium contribution we have taken for J the formula (16.18). The explicit expression for the non-equilibrium contribution to the chemical potential of the solute is given by (16.25).

It is seen in Fig. 16.6 that for sufficiently low values of the concentration, $(\partial\mu/\partial\tilde{c})$, and therefore D_{eff}, is positive, whereas for higher concentrations $(\partial\mu/\partial\tilde{c})$ and consequently D_{eff} is negative; this transition is observed for $\tilde{c} \approx 0.5\,\tilde{c}$. This value corresponds to a mass percentage of 1.3%.

An estimation of the order of magnitude of $D_{\text{eff}}/D = (\partial\mu/\partial n)/(\partial\mu_{\text{eq}}/\partial n)$ for the situations described in Fig. 16.6, i.e. for $\tau\dot{\gamma} \approx 12$ and $\tau\dot{\gamma} \approx 25$ (corresponding to the experiments by MacDonald and Muller), yields values of order 10^3 and 10^4

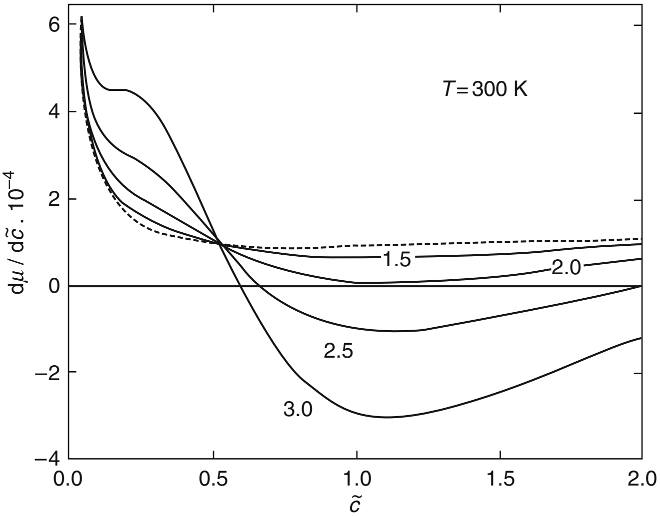


Fig. 16.6 The variation of $(\partial\mu/\partial\tilde{c})$ – which is proportional to the polymer effective diffusivity – in terms of the reduced concentration $\tilde{c}$ is presented for different values of $\tau\dot{\gamma}$, for polystyrene in transdecalin solution. The dashed line corresponds to the equilibrium Flory–Huggins contribution. For $\tilde{c}$ higher than a critical value approximately equal to 0.5, and for high values of $\tau\dot{\gamma}$ the effective diffusivity becomes negative (reprinted from del Castillo LF et al. (2000) Polymer 41:2633)

respectively, which are consistent with the experimental observations (Del Castillo et al. 2000). These results confirm that the corrections introduced in our analysis are all but negligible.

These phenomena have practical applications in macromolecular separation, as the non-equilibrium effective diffusion coefficient strongly depends on the macromolecular mass, in a more sensitive way than equilibrium diffusion coefficient. As a consequence, in the steady state, the radial distribution of macromolecules depends acutely on the mass: those with higher molecular mass will tend to accumulate near the axis of symmetry. An analogous situation is found for solutions flowing along a cylindrical duct. The dependence of the chemical potential on the shear rate has a strong influence on polymer extraction from a porous matrix; this effect makes the extraction process less effective when the shear rate in the extracting duct is high, because of a reduction in the number of microstates accessible to a macromolecule.

To conclude, let us emphasize that for a given concentration (higher than a critical value), the effective diffusion coefficient is reduced when the shear viscous pressure increases, and may become negative. In this regime, the non-equilibrium contribution to the chemical potential considerably enhances the polymer migration, and makes it much faster. In contrast, at low shear rates, the only thermodynamic force leading to migration is the second term on the right-hand side of (16.63), and migration is very slow. While many authors generalise the transport equations far from equilibrium, most of them do not modify the equations of state. The example in this section is highly representative of the shortcomings of this procedure, as it indicates clearly and explicitly that including the fluxes in the equations of state is not merely an academic exercise for systems out of equilibrium, but their contribution may be decisive to account for the experimental observations.

16.6 Problems

16.1.(a) Show that, according to Problem 15.5, one may write

$$\mathrm{Tr}\,\mathbf{P}^v = -2J(P_{12}^v)^2,$$

with $J = \tau/\eta$ the steady-state shear compliance. (b) Starting from the microscopic expression for the non-equilibrium contribution to the Gibbs free energy

$$\Delta G = -\tfrac{1}{2}Nk_\mathrm{B}T\left[\mathrm{Tr}\,(\mathbf{P}^v)' + \ln|\det(\mathbf{U} - (\mathbf{P}^v)')|\right],$$

where N is the total number of macromolecules in the volume V and the $(\mathbf{P}^v)'$ given by $(\mathbf{P}_i^v)' = (nk_\mathrm{B}T)^{-1}\mathbf{P}_i^v$ show that for high values of the shear rate, when the second term may be neglected in this expression for ΔG, one has $G = G_\mathrm{eq} + \frac{1}{2}V\,\mathrm{Tr}\,\mathbf{P}^v$.

16.2. Starting from the definition of chemical potential,

$$\mu_i = \left(\frac{\partial g}{\partial n_i} \right)_{T,p,n_j},$$

with n_i the number of moles of the species i and the non-equilibrium Gibbs free energy derived in (16.5b)

$$g(T,p,c_i,P_{12}^v) = g_{\text{eq}}(T,p,c_i) + \tfrac{1}{2} J v (P_{12}^v)^2$$

show that the expressions for the chemical potentials at constant viscous pressure $\mathbf{P}^v$ and at constant shear rate $\dot{\gamma}$ for a polymeric solution satisfying the Zimm scaling relations $\tau \propto M^{3/2}$, $\eta \propto cM^{1/2}$, and $J \propto c^{-1}M$ are $\mu_{\mathbf{P}^v} = \mu_{\text{eq}} - \frac{1}{2}(J/c)(P_{12}^v)^2$ and $\mu_{\dot{\gamma}} = \mu_{\text{eq}} + \frac{1}{2}(\tau\eta/c)\dot{\gamma}^2 = \mu_{\text{eq}} + \frac{1}{2}(J/c)(P_{12}^v)^2$ respectively.

16.3. A polymer solution has an equilibrium critical temperature of $T_c = 285\,\text{K}$. Under a shear pressure P_{xy}^v, the critical temperature is shifted according to the law $T_c = 5 \times 10^{-2} (\text{K}\,\text{m}^2\,\text{N}^{-1})(P_{xy}^v)^2$, while the critical composition remains practically unchanged. A solution of critical composition is kept at 300 K and has a viscosity of $10^2\,\text{N}\,\text{s}\,\text{m}^{-2}$. What is the maximum rate flow of the solution through a cylindrical tube of radius 10^{-2} m without splitting into two phases of different composition?

16.4. Show that if instead of the expression (16.18) for the steady-state compliance J one uses the simple scaling-law relation $J = CM_1/(cRT)$, Eqs. (16.14–16.5) yield a negative value for the shear-induced shift of the critical temperature. Thus, it is seen how the detailed form of the equation of state for J is important in the predictions of shear-induced thermodynamic effects.

16.5. A chemical reaction $A + B \rightleftarrows C$ takes place in a viscous solvent subjected to a shear flow, at constant shear rate $\dot{\gamma}$. Evaluate the influence of the shear rate on the equilibrium constant. (*Hint*: Express the influence of the shear flow on the chemical potential of each species from the result

$$G(T,p,n_i,\dot{\gamma}) = G_{\text{eq}}(T,p,n_i) + \sum_i V \tau_i \eta_i \dot{\gamma}^2.$$

Take $\eta_i = \eta \left[1 + \frac{5}{2} \left(\frac{4}{3} \pi r_i^3 n_i \right) \right]$ and $\tau_i = m_i (6\pi\eta r)^{-1}$, where η is the viscosity of the pure solvent and r_i the radius of molecules of species i, and n_i the number of molecules per unit volume. Make numerical estimations for globular macromolecules A, B, and C with a radius of the order of 10^{-6} m in water at $\dot{\gamma} = 10\,\text{s}^{-1}$.

16.6. A dynamical interpretation of the effects of a shear flow on the equilibrium chemical composition in ideal gases may be obtained from the kinetic theory. Assume a reaction $A + A \to B + C$ for a dilute gas. The rate of the chemical reaction may be expressed in microscopic terms as

$$J = -\iiint f(\boldsymbol{r},\boldsymbol{c},t) f(\boldsymbol{r},\tilde{\boldsymbol{c}},t)|\boldsymbol{c}-\tilde{\boldsymbol{c}}|\sigma_r(\boldsymbol{c}-\tilde{\boldsymbol{c}})\mathrm{d}\boldsymbol{c}\mathrm{d}\tilde{\boldsymbol{c}}\mathrm{d}\Omega,$$

where all the symbols have the same meaning as in Sect. 5.1, and where $\sigma_r(\boldsymbol{c}-\tilde{\boldsymbol{c}})$ is the cross section for reactive collisions. Assume that $\sigma_r(\boldsymbol{c}-\tilde{\boldsymbol{c}}) = 0$ for $\varepsilon < \varepsilon^*$ and $\sigma_r(\boldsymbol{c}-\tilde{\boldsymbol{c}}) = \sigma[1-(\varepsilon/\varepsilon^*)]$ for $\varepsilon > \varepsilon^*$, where $\varepsilon = \frac{1}{4}m(\boldsymbol{c}-\tilde{\boldsymbol{c}})^2$ is the kinetic energy of the collision in the centre of mass reference frame and ε^* is an activation energy. Show that in the presence of a viscous pressure $\mathbf{P}^v$, and if one uses expression (5.36) (with $\boldsymbol{q} = 0$) for the distribution function f, then the reaction rate is given by

$$J = -4n^2\sigma^2\sqrt{\frac{\pi k_\mathrm{B}T}{m}}\exp\left[-\frac{\varepsilon^*}{k_\mathrm{B}T}\right]$$
$$\left\{1-\frac{2}{15(k_\mathrm{B}Tn)^2}\left[\left(\frac{\varepsilon^*}{k_\mathrm{B}T}\right)^2-\frac{\varepsilon^*}{k_\mathrm{B}T}-\frac{1}{4}\right]\mathbf{P}^v:\mathbf{P}^v\right\}.$$

This shows how $\mathbf{P}^v$ changes the reaction rate. If the change on the rate of the direct and the inverse reactions is different, the equilibrium constant of the reaction will be also changed (see Cukrowski AS, Popielawski J (1986) Chem Phys 109:215 and Eu BC, Li KW (1977) Physica 88A:135).

16.7. By using an approach analogous to that followed in (5.84–5.86), show that in a plane Couette flow with vanishing heat flux and $P_{12}^v = -\eta\dot{\gamma}$, the second moments of the fluctuations of the viscous pressure tensor and the correlation of the energy fluctuations with the fluctuations of the viscous pressure are given by

$$\langle\delta P_{12}^v\delta P_{12}^v\rangle = \frac{k_\mathrm{B}\eta T}{\tau_2 V}\left(1+\frac{20}{3}\tau^2\dot{\gamma}^2\right),$$
$$\langle\delta u\delta P_{12}^v\rangle = -2\frac{k_\mathrm{B}T}{M}\left(1+\frac{20}{3}\tau\dot{\gamma}\right).$$

For a more general analysis of non-equilibrium fluctuations of the shear stress in viscoelastic liquids see Dyre JC (1993) Phys Rev E 48:400; and for a molecular dynamics analysis of the effects of a shear flow on fluctuations see Baranyiai, Cummings (1995).

16.8. *Shear-induced chromatography*: A practical application of shear-induced diffusion is shear-induced chromatography. i.e. the separation of macromolecules of different molecular mass under the action of a flow on a polymer solution. Taking into account the explicit dependence of J on the molecular mass M given in (16.18), discuss which macromolecules will exhibit a higher accumulation near the apex of the cone in the cone-and-plate experiment discussed in Sect. 16.5. (For a more detailed analysis including the dependence of the viscosity on the macromolecular mass, see Jou, Criado-Sancho, del Castillo, Casas-Vazquez (2001)).

16. 9. In the entangled regime, the steady-state compliance of a polymer solution is given by

$$J = \frac{2M_e}{ck_{\mathrm{B}}T}\left(1 - \frac{\eta_s}{\eta}\right)^2 .$$

The main differences with the dilute regime discussed in (16.18) are the following ones: M_e is the mass of the average length of polymer between successive entanglements and, consequently, it decreases when the concentration increases, as $M_e \cong c^{-2}$; the viscosity η_s of the solute is negligible as compared to the total viscosity η of the solution, in such a way that the parenthesis may be equated to 1. (a) Estimate the form of the non-equilibrium chemical potential. (b) Show that a shear flow under a constant pressure increases the stability of the solution, in contrast with the behaviour observed in the dilute regime.

Chapter 17
Relativistic Formulation

The standard first-order relativistic thermodynamic theories developed by Eckart (1940) and Landau and Lifshitz (1985) suffer from two main drawbacks: firstly, they predict an infinite speed for the propagation of thermal and viscous signals. This fact may be uncomfortable in classical thermodynamics, because of its inconsistency with the principle of causality and some experimental data, but it is certainly intolerable in any relativistic theory. Secondly, the transport equations of the first-order theory lead to some undesirable generic instabilities: as a matter of fact, small-amplitude disturbances from equilibrium diverge exponentially with time on very short time scales (Hiscock and Lindblom 1985).

These shortcomings are avoided when use is made of the relativistic version of extended irreversible thermodynamics (EIT). It can be shown that within a given range of values of the parameters, the equilibrium is stable and the characteristic speeds are lower than the speed of light in vacuo. This has prompted an intensive activity on relativistic EIT (e.g. Israel 1976; Pavón et al. 1982; Liu et al. 1986). In Chap. 2 we recalled that the finite value of propagation of thermal and viscous signals was one of the first motivations for EIT. In fact, the present chapter deals with a basic general aspect of the theory, and could have been included in the introductory chapters. However, we have deferred the relativistic presentation to the last chapters for pedagogical purposes and in order to provide a joint exposition of macroscopic aspects and kinetic foundations.

The motivations for a relativistic formulation are not purely conceptual: applications are found in several outstanding fields as nuclear physics, astrophysics and cosmology. In Chap. 18 we pay a special attention to viscous cosmological models, where bulk viscosity provides a source of dissipation which may have relevant effects on the dynamics of the Universe. In Sect. 17.4 we briefly comment some aspects of the extended Gibbs relation for nuclear matter and of the relaxational transport equations, which may be of interest in the hydrodynamic analysis of high-energy collisions of atomic nuclei to explore the formation of quark-gluon plasmas. In astrophysics, the role of thermal conductivity and viscosity of a gas of neutrinos is essential in phenomena like stellar collapse.

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_17,

17.1 The Macroscopic Theory

In this section, we briefly summarize the main characteristics of the relativistic formulation of EIT. In contrast with classical relativistic irreversible thermodynamics (Eckart 1940; Landau and Lifshitz 1985), one assumes that the dissipative fluxes are independent variables. The general formulation parallels that of the classical non-relativistic theory. In the theory of relativity, the basic variables are the four-current vector J^{μ} and the second-order symmetric energy–momentum tensor $T^{\mu\nu}$. For a local observer at rest with respect to the average motion of the particles, J^{μ} and $T^{\mu\nu}$ are related to the four-velocity vector u^{μ}, the heat flux vector q^{μ}, the specific internal energy ε, and the pressure tensor $P^{\mu\nu}$ by

$$J^{\mu} = \rho u^{\mu}, \tag{17.1a}$$

$$T^{\mu\nu} = \rho\varepsilon u^{\mu}u^{\nu} + 2c^{-1}q^{(\mu}u^{\nu)} + P^{\mu\nu}. \tag{17.1b}$$

Greek superscripts or subscripts run from 1 to 4, c is the velocity of light in vacuo, ρ the mass density, and u^{μ} a dimensionless hydrodynamic velocity satisfying $u^{\mu}u_{\mu} = -1$; in the reference frame attached to a comoving observer, u^{μ} reduces to the usual velocity. Parentheses around a set of indices denote symmetrization. Both q^{μ} and $P^{\mu\nu}$ are of spatial type,

$$q^{\mu} = \Delta^{\mu}_{\nu} q^{\nu} \text{ and } P^{\mu\nu} = \Delta^{\mu}_{\rho}\Delta^{\nu}_{\sigma}P^{\rho\sigma},$$

i.e. they obey $q^{\mu}u_{\mu} = u_{\mu}P^{\mu\nu} = P^{\mu\nu}u_{\nu} = 0$, where $\Delta^{\mu\nu}$ is the symmetric spatial projector $\Delta^{\mu\nu} = g^{\mu\nu} + u^{\mu}u^{\nu}$, and $g^{\mu\nu}$ the metric tensor of the space-time. The pressure tensor splits into

$$P^{\mu\nu} = p\Delta^{\mu\nu} + \Pi\Delta^{\mu\nu} + \Pi^{\mu\nu},$$

with p and Π being the equilibrium pressure and the bulk viscous pressure respectively, and $\Pi^{\mu\nu}$ the traceless viscous pressure tensor. We prefer this notation, instead of p^{v} and $\overset{0}{\mathbf{P}}{}^{v}$ used throughout the book, because it is much more usual in the relativistic literature; therefore, the researchers interested by these chapters will feel more at ease with this notation without being a difficulty for the reader who has read the previous chapters.

The decomposition (17.1b) is not unique. A different splitting can be devised by an observer drifting slowly in the direction of the heat flux, with velocity adjusted in such a way that the mass–energy counterflow of particles relative to his frame cancels exactly the heat flux (Israel 1976, 1981). It turns out that in the frame attached to such an observer, the heat flux vanishes (see Landau and Lifshitz 1985). Here, we choose to follow the scheme consistent with (17.1), first proposed by Eckart. The two descriptions are nearly equivalent, although their decomposition of the invariant fields J^{μ} and $T^{\mu\nu}$ is different.

The conservation equations read

$$J^{\mu}_{;\nu} = 0 \tag{17.2}$$

(or equivalently $\rho\dot{\mathrm{v}} = u^{\mu}_{;\mu}$) and

$$T^{\mu\nu}_{;\nu} = 0, \tag{17.3}$$

where the semicolon stands for the covariant derivative. The temporal and the spatial parts of (17.3) correspond to the energy and the momentum conservation laws respectively. They can be explicitly written as

$$\rho(\dot{\varepsilon} + p\dot{v}) = -\frac{1}{c}\left(q^{\mu}_{;\mu} + q^{\mu}\dot{u}_{\mu}\right) - \left(\Pi\Delta^{\mu\nu} + \Pi^{\mu\nu}\right)u_{(\mu;\nu)} \tag{17.4}$$

and

$$\rho\varepsilon\dot{u}^{\lambda} + \frac{1}{c}\left(\dot{q}^{\lambda} - u^{\lambda}q_{\mu}\dot{u}^{\mu} + q^{\lambda}u^{\nu}_{;\nu} + u^{\lambda}_{;\nu}q^{\nu}\right) + \Delta^{\lambda}_{\mu}P^{\mu\nu}{}_{;\nu} = 0, \tag{17.5}$$

where the upper dot denotes differentiation along the four-velocity, i.e. $\dot{A}^{\nu} = u^{\mu}A^{\nu}{}_{;\mu}$.

To determine the evolution equations of the fluxes, we postulate, in the spirit of EIT, the existence of a non-equilibrium entropy flux vector S^{μ} depending on the whole set of variables. Up to the second order in the fluxes, one has

$$\begin{aligned} S^{\mu} = &\left(s_{\mathrm{eq}} - v\alpha_1 T^{-1}q^{\nu}q_{\nu} - v\alpha_0 T^{-1}\Pi^2 - v\alpha_2 T^{-1}\Pi^{\lambda\nu}\Pi_{\lambda\nu}\right)u^{\mu} \\ &+ \frac{1}{cT}q^{\mu} + \beta_0\Pi q^{\mu} + \beta_2\Pi^{\lambda\mu}q_{\lambda}, \end{aligned} \tag{17.6}$$

The standard form of the entropy balance equation reads

$$S^{\mu}_{;\mu} = \sigma^{s} \geq 0. \tag{17.7}$$

The four-divergence of S^{μ} may be calculated from (17.6) by taking into account that

$$\dot{s}_{\mathrm{eq}} = T^{-1}\dot{\varepsilon} + T^{-1}p\dot{v} \tag{17.8}$$

and by making use of (17.4). Then, by neglecting second-order contributions to the equations of state, one can write the entropy production in the bilinear form

$$\sigma^{s} = T^{-1}\left(q^{\mu}X^{1}_{\mu} + \Pi X^{0} + \Pi^{\mu\nu}X^{2}_{\mu\nu}\right), \tag{17.9}$$

with

$$X^1_\mu = \Delta^\nu_\mu \left[-(cT)^{-1}(T_{,\nu} + T\dot{u}_{,\nu}) - 2\alpha_1 \dot{q}_\nu + T\beta_0 \Pi_{;\nu} + T\beta_2 \Pi^\lambda{}_{\nu;\lambda} \right],$$
$$X^0 = -u^\mu{}_{;\mu} - 2\alpha_0 \dot{\Pi} + T\beta_0 q^\mu{}_{;\mu},$$

and

$$X^2_{\mu\nu} = \Delta^\lambda_{(\mu\Delta^\rho_\nu)} \left[u_{(\lambda;\rho)} - 2\alpha_2 \dot{\Pi}_{\lambda\rho} + T\beta_2 q_{(\lambda;\rho)} \right].$$

Here, the semicolon means partial derivative, and the quantities β_0 and β_2 are assumed to be constant; this is consistent with the approximation of neglecting non-linear terms, made in the non-relativistic description.

In analogy with the treatment of Chap. 2, we may take X^1_μ, X^0, and $X^2_{\mu\nu}$ proportional to q_μ, Π, and $\Pi_{\mu\nu}$, respectively, with positive proportionality coefficients to ensure the positive semi-definite character of the entropy production. As a consequence, the evolution equations of the fluxes read

$$\tau_1 \dot{q}_\mu = -q_\mu - \lambda T \Delta^\nu_\mu \left[(cT)^{-1} T_{,\nu} + T\dot{u}_\nu + T\beta_0 \Pi_{,\nu} + T\beta_2 \Pi^\lambda{}_{\nu;\lambda} \right], \tag{17.10}$$
$$\tau_0 \dot{\Pi} = -\Pi - \zeta u^\mu{}_{;\mu} - T\beta_0 \zeta q^\mu{}_{;\mu}, \tag{17.11}$$
$$\tau_2 \dot{\Pi}_{\mu\nu} = \langle -\Pi_{\mu\nu} - 2\eta(u_{\lambda;\rho} + T\beta_2 q_{\lambda;\rho}) \rangle, \tag{17.12}$$

where the angular brackets $\langle \cdots \rangle$ mean the symmetric, trace-free spatial part of the corresponding tensor. Also the left-hand side of (17.10) and (17.12) have to be understood as the projected part of the corresponding quantities. These equations generalise the non-relativistic ones (2.70–2.72). Note that in the classical limit the relativistic equation for the heat flux does not reduce exactly to the classical Fourier law, but contains a supplementary term which depends on the acceleration $\dot{u}^\mu$, as first noted by Eckart (1940). Its physical meaning is connected with the inertia of heat; effectively, a heat flux will set in through accelerated matter even in the absence of temperature gradients (Pavón et al. 1980).

In Table 17.1 are reported the values of the coefficients appearing in (17.10–17.12) as a function of the relaxation times τ_1, τ_0, and τ_2. Two systems are considered: an ideal monatomic gas in the ultrarelativistic limit ($\beta = mc^2/(k_B T) \ll 1$) and a radiative fluid consisting of a mixture of photons and electrons, the above results are drawn from the kinetic theory. The quantities Ω and Ω_m are given by

Table 17.1 Coefficients of (17.10–17.12) for an ultrarelativistic ideal gas and for a mixture of photons and electrons (β stands for $mc^2/(k_B T)$ and a is the radiation constant)

Fluid	λ	ζ	η	β_0	β_2
Relativistic ideal gas	$\frac{8}{5}\frac{p}{\rho T}\tau_1$	$\frac{1}{108}\frac{p\beta^4}{\rho}\tau_0$	$\frac{4}{3}\frac{p}{\rho}\tau_2$	$\frac{6}{pT\beta^2}$	$-\frac{1}{4pT}$
Photons and electrons	$\frac{4}{3}aT^3c^2\tau_1$	$4aT^4\Omega^2\tau_0$	$\frac{4}{15}aT^4\tau_2$	$4aT^5\left(\frac{\Omega}{\Omega_m}\right)^2$	$-\frac{3}{4aT^5}$

$\Omega = \frac{1}{3} - (\partial p/\partial T)_n(\partial \rho/\partial T)_n^{-1}$ and $\Omega_m = \frac{1}{3} - (\partial p_m/\partial T)_n(\partial \rho_m/\partial T)_n^{-1}$, where p and ρ are the pressure and density of the total fluid and p_m and ρ_m the pressure and density of the matter. The values of the relaxation times depend of the kind of theory used to describe the interaction between matter and radiation. For pure Thomson scattering (i.e. scattering of electromagnetic radiation by free charged particles in the classical non-relativistic theory), the values of the relaxation times are $\tau_1 = \frac{9}{10}\tau_2$ and $\tau_0 = \infty$.

17.2 Characteristic Speeds

A relevant calculation is that of the characteristic speeds associated with (17.10–17.12), to ascertain whether their values remain finite (Hiscock and Lindblom 1983). To this end, we use the linear equations (17.10–17.12). These nine equations, together with the 5 conservation laws (17.2–17.3), provide a set of 14 equations for the 14 unknowns $\rho,\ \varepsilon,\ u_\mu,\ \Pi,\ q_\mu$, and $\Pi_{\mu\nu}$.

The complete set of first-order and quasi-linear equations can be expressed in the simplified form

$$a^{AB\mu}(\alpha,\beta,u_\nu)\partial_\mu y_B = D^A(y), \quad (A, B = 1,\dots,14). \tag{17.13}$$

The right-hand side contains all the collision terms, and the coefficients $a^{AB\mu}$ are purely thermodynamical functions. The wavefront speeds are determined by the condition

$$\det\left[a^{AB\mu}(\partial_\mu\phi)\right] = 0, \tag{17.14}$$

where $\phi(x_\mu) =$ constant is a characteristic surface of (17.13), that is, a 3-dimensional space across which the variables y_A are continuous but their first derivatives are allowed to exhibit discontinuities $[\partial_\mu y_A]$ normal to the surface, i.e. $[\partial_\mu y_A] = Y_A(\partial_\mu\phi)$. The characteristic velocities are independent of the details of the collisions.

To solve the characteristic equation (17.14) consider a coordinate system (x^1, x^2, x^3, x^4) chosen in such a way that at any point in the fluid the system of reference is orthogonal and comoving, with the property

$$g^{\mu\nu}\partial_\mu\partial_\nu = -(\partial_1)^2 + (\partial_2)^2 + (\partial_3)^2 + (\partial_4)^2, \quad u^\mu\partial_\mu = \partial_1, \tag{17.15}$$

and assume that ϕ is a function of only (x^1, x^2). In this coordinate system, the characteristic equation simplifies to

$$\det\left[v' a^{AB1} - a^{AB2}\right] = 0, \tag{17.16}$$

where v' is the characteristic velocity defined by $v' = -(\partial_1\phi)/(\partial_2\phi)$. The form of the characteristic matrix simplifies further if use is made of the following set of 14 perturbation variables: $y_B = (T\delta\theta, T^{-1}\delta T, \delta\Pi, \delta u^2, \delta q^2, \delta\Pi^{22}, \delta u^3, \delta q^3, \delta\Pi^{32}$, δu^4, $\delta q^4, \delta\Pi^{33}$, $-\delta\Pi^{44}, \delta\Pi^{42}, \delta\Pi^{34})$, where $\theta = (\rho T^{-1})(\varepsilon + p) - s$. With this choice of variables, and after some lengthy calculations, the characteristic matrix may be written as (Hiscock and Lindblom 1983)

$$v'\boldsymbol{a}^1 - \boldsymbol{a}^2 = \begin{pmatrix} \mathbf{Q} & 0 & 0 & 0 \\ 0 & \mathbf{R} & 0 & 0 \\ 0 & 0 & \mathbf{R} & 0 \\ 0 & 0 & 0 & \mathbf{S} \end{pmatrix}. \tag{17.17}$$

The blocks **Q**, **R** and **S** are respectively given by

$$\mathbf{Q} = \begin{pmatrix} \frac{v'}{T}\left(\frac{\partial\rho}{\partial\theta}\right)_T & \frac{v'}{T}\left(\frac{\partial\rho}{\partial T}\right)_\theta & 0 & -\rho & 0 & 0 \\ \frac{v'}{T}\left(\frac{\partial\varepsilon}{\partial\theta}\right)_T & \frac{v'}{T}\left(\frac{\partial\varepsilon}{\partial T}\right)_\theta & 0 & -(\varepsilon + p) & -1 & 0 \\ 0 & 0 & -\alpha_0 v' & -1 & -\beta_0 & 0 \\ -\rho & -(\varepsilon + p) & -1 & -(\varepsilon + p)v' & -v' & -1 \\ 0 & -1 & -\beta_0 & -v' & -\alpha_0 v' & -\beta_2 \\ 0 & 0 & 0 & -1 & -\beta_2 & \frac{3}{2}\alpha_2 v' \end{pmatrix}, \tag{17.18a}$$

$$\mathbf{R} = \begin{pmatrix} v'(\varepsilon + p) & v' & -1 \\ v' & \alpha_1 v' & \beta_2 \\ -1 & \beta_2 & 2\alpha_2 v' \end{pmatrix}, \tag{17.18b}$$

$$\mathbf{S} = \begin{pmatrix} 2\alpha_2 v' & 0 \\ 0 & \alpha_2 v' \end{pmatrix}. \tag{17.18c}$$

The total determinant now reduces to

$$\det\left[v'\boldsymbol{a}^1 - \boldsymbol{a}^2\right] = (\det\mathbf{Q})(\det\mathbf{R})^2(\det\mathbf{S}). \tag{17.19}$$

The roots of the characteristic equation (17.14) are the ensemble of roots obtained after setting to zero the determinant of each of the matrix blocks. The main results may be summarized as follows.

1. The determinant of **R** is given by

$$\det\mathbf{R} = v'\left\{2\alpha_2\left[(\varepsilon + p)\alpha_1 - 1\right]v'^2 - \left[(\varepsilon + p)\beta_2^2 + 2\beta_2 + \alpha_1\right]\right\}. \tag{17.20}$$

This yields a vanishing and two non-vanishing characteristic velocities

$$(v'_t)^2 = \frac{(\varepsilon + p)\beta_2^2 + 2\beta_2 + \alpha_1}{2\alpha_2\left[\alpha_1(\varepsilon + p) - 1\right]}. \tag{17.21}$$

These are transverse velocities because they refer to (δq^3, $\delta\Pi^{32}$, δu^3) and (δq^4, $\delta\Pi^{42}$, δu^4), the components of the perturbation variables which are tangent to the characteristic surface, and therefore transverse to the direction of propagation.

2. The determinant of matrix **Q**, related to the variables ($T\delta\theta$, $T^{-1}\delta T$, $\delta\Pi$, δu^2, δq^2, $\delta\Pi^{22}$), is

$$\det Q = \frac{3}{2}v'^2\left(Av'^4 + Bv'^2 + C\right)\left[\left(\frac{\partial\rho}{\partial\theta}\right)_T\left(\frac{\partial\varepsilon}{\partial T}\right)_\theta - \left(\frac{\partial\rho}{\partial T}\right)_\theta\left(\frac{\partial\varepsilon}{\partial\theta}\right)_T\right], \tag{17.22}$$

with

$$\begin{aligned} A &= \alpha_0\alpha_2\left[\alpha_1(\varepsilon+p)-1\right], B = -(\varepsilon+p)D - \alpha_1 E - 2F,\\ C &= (DE - F^2)(\alpha_0\alpha_2)^{-1},\\ D &= \alpha_0\alpha_2\left[\frac{\beta_0^2}{\alpha_0} + \frac{2\beta_2^2}{3\alpha_2} + \frac{1}{\rho T^2}\left(\frac{\partial T}{\partial s}\right)_n\right],\\ E &= \alpha_0\alpha_2\left[\frac{1}{\alpha_0} + \frac{2}{3\alpha_2} + (\varepsilon+p)\left(\frac{\partial p}{\partial\varepsilon}\right)_s\right],\\ F &= \alpha_0\alpha_2\left[\frac{\beta_0}{\alpha_0} + \frac{2\beta_2}{3\alpha_2} - \frac{\rho}{T}\left(\frac{\partial T}{\partial\rho}\right)_s\right]. \end{aligned}$$

It is checked that **Q** has two vanishing and four non-vanishing characteristic velocities. The latter are the roots of

$$Av_l'^4 + Bv_l'^2 + C = 0, \tag{17.23}$$

and correspond to longitudinal velocities, the first pair to sound propagation and the second pair to temperature waves or second sound.

3. The determinant of the matrix **S** corresponding to the variables ($\delta\Pi^{33}$, $-\delta\Pi^{44}$, $\delta\Pi^{34}$) is simply

$$\det \mathbf{S} = 2(\alpha_2 v')^2, \tag{17.24}$$

and the two associated characteristic velocities vanish.

We are thus able to express the characteristic velocities in terms of thermodynamic parameters. Hiscock and Lindblom (1983) have shown that when thermodynamic stability conditions are satisfied, the characteristic speeds are lower than the speed of light. Explicit values for the velocities may be obtained by using the equations of state derived from kinetic theory. Stewart (1977) has found that for a Boltzmann gas in the ultrarelativistic limit, the velocities of the transverse modes increase monotonically between $\frac{7}{5}k_B T/m \le v_l^2 \le \frac{1}{5}c^2$, whereas the two longitudinal speeds satisfy $1.35\,(k_B T/m) \le v_{l1}^2 \le \frac{1}{3}c^2$ and $5.18(k_B T/m) \le v_{l2}^2 \le \frac{3}{5}c^2$. Other analyses of the properties of waves in relativistic hyperbolic heat-conducting and viscous fluids can be found in Bressan ((1978) and van Weert (1982).

17.3 Relativistic Kinetic Theory

Supplementary information about the coefficients appearing in the entropy and the entropy flux can be drawn from a kinetic approach. Here we follow the work of Israel and Stewart (1979); other significant references on the connection between relativistic kinetic theory and EIT may be found in (Kranys 1967, 1972; Schweizer 1985; Liu et al. 1986; Dreyer and Weiss 1986; Boillat and Ruggeri 1996; Struchtrup 1998; Banach 2000). We study here the general case of quantum relativistic gases, following the main lines of Grad's classical analysis, and for the sake of simplicity, we will skip all the details of calculations which are rather cumbersome.

The microscopic expression for the four-dimensional current vector J^{μ}, the energy–momentum tensor $T^{\mu\nu}$, and the entropy four-vector S^{μ} are

$$J^{\mu} = c\int \mathrm{d}P p^{\mu} f(x^{\nu}, p^{\lambda}), \tag{17.25a}$$

$$T^{\mu\nu} = c\int \mathrm{d}P p^{\mu} p^{\nu} f(x^{\rho}, p^{\lambda}), \tag{17.25b}$$

$$S^{\mu} = -k_{\mathrm{B}} c\int \mathrm{d}P p^{\mu}\left[f \ln\frac{f}{y} \mp \left(1 \pm \frac{f}{y}\right)\ln\left(1 \pm \frac{f}{y}\right)\right], \tag{17.25c}$$

where p^{μ} is the four-momentum of a particle, with $p^{\mu}p_{\mu} = m^2c^2$, $\mathrm{d}P = (-g)^{1/2}\mathrm{d}p/p_0$, the invariant volume element (g is the determinant of $g_{\mu\nu}$), and $y = (2s+1)/h^3$, with s being the spin of the particle. In (17.25c) upper sign refers to bosons and lower sign to fermions. Remember that $T^{\mu\nu}$ may be decomposed in terms of the heat flux q^{μ}, viscous pressure Π and viscous pressure tensor $\Pi^{\mu\nu}$:

$$T^{\mu\nu} = \varepsilon u^{\mu}u^{\nu} + (p+\Pi)\Delta^{\mu\nu} + 2c^{-1}q^{(\mu}u^{\nu)} + \Pi^{\mu\nu}. \tag{17.26}$$

The distribution function $f(x^{\mu}, p^{\nu})$ gives the number density of particles in the element $\mathrm{d}x\mathrm{d}p$ at (x^{μ}, p^{ν}). In equilibrium, $f(x^{\mu}, p^{\nu})$ is given by the Jüttner expression

$$f_{\mathrm{eq}} = \left[\exp\left(\frac{\alpha}{k_{\mathrm{B}}} + \frac{u_{\mu}p^{\mu}}{k_{\mathrm{B}}T}\right) \mp 1\right]^{-1}. \tag{17.27}$$

Introduction of (17.27) into (17.25c) leads to the equilibrium entropy expression

$$S^{\mu}_{\mathrm{eq}} = p(\alpha,\beta)\beta^{\mu} - \alpha J^{\mu} - \beta_{\lambda}T^{\lambda\mu}, \tag{17.28}$$

with $\beta^{\mu} = 1/(k_{\mathrm{B}}T)u^{\mu}$, $\beta = mc^2(k_{\mathrm{B}}T)^{-1}u^{\mu}$ and $\alpha = -\mu/T$. Out of equilibrium, f obeys the relativistic Boltzmann equation

$$p^{\mu}\frac{\partial f}{\partial x^{\mu}} - \Gamma^{\mu}_{\nu\lambda}p^{\nu}p^{\lambda}\frac{\partial f}{\partial p^{\mu}} = \mathcal{J}(f), \tag{17.29}$$

with $\Gamma^{\mu}_{\nu\lambda}$ being the Christoffel symbols and $\mathcal{J}(f)$ the collision operator. It is not necessary to solve (17.29) to obtain an expression for the stationary distribution function. Rather, we shall follow an approach similar to the non-relativistic Grad formalism. To this end we set

$$\ln\left[\frac{f}{y}\left(1 \pm \frac{f}{y}\right)^{-1}\right] = \Delta \tag{17.30}$$

and expand Δ in its first moments with respect to p^{μ}:

$$\Delta = \Delta_{\mathrm{eq}} + \varepsilon(x) + m^{-1}\varepsilon_{\lambda}(x)p^{\lambda} + m^{-2}\varepsilon_{\lambda\mu}(x)p^{\lambda}p^{\mu}_{.} \tag{17.31}$$

The 14 parameters $\varepsilon(x)$, $\varepsilon_{\lambda}(x)$ and $\varepsilon_{\lambda\mu}(x)$ will be related to the dissipative fluxes. Note that the non-equilibrium distribution function may be written in terms of Δ as

$$f - f_{\mathrm{eq}} = \left[f_{\mathrm{eq}}\left(1 \pm \frac{f_{\mathrm{eq}}}{y}\right)\right]^{-1}\delta\Delta, \tag{17.32}$$

with $\delta\Delta = \Delta - \Delta_{\mathrm{eq}}$ given by (17.31). Accordingly,

$$f - f_{\mathrm{eq}} = \frac{\varepsilon(x) + m^{-1}\varepsilon_{\lambda}(x)p^{\lambda} + m^{-2}\varepsilon_{\lambda\mu}(x)p^{\lambda}p^{\mu}}{f_{\mathrm{eq}}\left[1 \pm (f_{\mathrm{eq}}/y)\right]}. \tag{17.33}$$

We assume that the tensor $\varepsilon_{\lambda\mu}$ is trace-free, i.e. $\varepsilon_{\lambda\lambda} = 0$. The actual non-equilibrium distribution function is thus specified by (17.33). Introduction of (17.33) into (17.29) leads to the evolution equations for ε, ε_{λ} and $\varepsilon_{\lambda\mu}$.

We now calculate the change of J^{μ}, $T^{\mu\nu}$, and S^{μ} with respect to their equilibrium values in terms of $f - f_{\mathrm{eq}}$. First of all, we define $\phi(f)$ as

$$\phi(f) = \frac{f}{y}\ln\frac{f}{y} \mp \left(1 \pm \frac{f}{y}\right)\ln\left(1 \pm \frac{f}{y}\right), \tag{17.34}$$

and expand it around $\phi(f_{\mathrm{eq}})$ up to the second order, it is found that

$$\phi(f) = \phi(f_{\mathrm{eq}}) + \phi'(f_{\mathrm{eq}})(f - f_{\mathrm{eq}}) + \tfrac{1}{2}\phi''(f_{\mathrm{eq}})(f - f_{\mathrm{eq}})^2, \tag{17.35}$$

where

$$\phi'(f) = \ln\frac{f/y}{1 \pm (f/y)} \tag{17.36a}$$

and

$$\phi''(f) = \frac{1}{[1 \pm (f/y)]\,(f/y)} \tag{17.36b}$$

are the first and second functional derivatives of ϕ with respect to f. Introducing (17.35) into expression (17.25c) for the entropy yields

$$S^\mu = -k_\mathrm{B}c\int \mathrm{d}P\phi(f)p^\mu = S^\mu_\mathrm{eq} - T^{-1}q^\mu - \tfrac{1}{2}k_\mathrm{B}c\int \mathrm{d}P\phi''(f_\mathrm{eq})(f-f_\mathrm{eq})^2 p^\mu. \tag{17.37}$$

Taking into account (17.33), one finds for the non-equilibrium expressions of J^μ and $T^{\mu\nu}$

$$\begin{aligned} J^\mu &= \varepsilon c\int \mathrm{d}P\phi''(f_\mathrm{eq})p^\mu + \varepsilon_\lambda(c/m)\int \mathrm{d}P\phi''(f_\mathrm{eq})p^\lambda p^\mu \\ &\quad + \varepsilon_{\lambda\nu}(c/m^2)\int \mathrm{d}P\,\phi''(f_\mathrm{eq})p^\lambda p^\nu p^\mu \qquad (17.38) \\ T^{\mu\nu} &= \varepsilon c\int \mathrm{d}P\phi''(f_\mathrm{eq})p^\mu p^\nu + \varepsilon_\lambda(c/m)\int \mathrm{d}P\phi''(f_\mathrm{eq})p^\mu p^\lambda p^\nu \\ &\quad + \varepsilon_{\lambda\rho}(c/m^2)\int \mathrm{d}P\phi''(f_\mathrm{eq})p^\mu p^\nu p^\lambda p^\rho \qquad (17.39) \end{aligned}$$

respectively. We require that the local-equilibrium particle and energy densities $\rho(\alpha,\beta)$ and $\varepsilon(\alpha,\beta)$ equal their actual densities, given by $u_\mu J^\mu$ and $u_\mu u_\nu T^{\mu\nu}$ respectively (this is equivalent to the requirements (4.31) in classical kinetic theory) and we fix the nine remaining variables in terms of q^μ, Π, and $\Pi^{\mu\nu}$. From (17.38) and (17.39) it follows that (Israel and Stewart 1979; Udey and Israel 1982)

$$\varepsilon_{\lambda\mu} = B_0(\Delta_{\lambda\mu} + 3u_\lambda u_\mu)\Pi + \tfrac{1}{2}B_1(u_\lambda q_\mu + q_\lambda u_\mu) + B_2\Pi_{\lambda\mu}, \tag{17.40a}$$

$$\varepsilon_\mu = D_0 u_\mu \Pi + D_1 q_\mu,\ \varepsilon = E_0\Pi. \tag{17.40b}$$

The coefficients in (17.40a and b) are given by

$$\begin{aligned} &B_0 = -\frac{m}{4k_\mathrm{B}T\zeta'\Omega},\ B_1 = -\frac{1}{k_\mathrm{B}T\Lambda n},\ B_2 = -\frac{m}{2k_\mathrm{B}T\zeta'},\ D_0 = -3B_0C_2, \\ &D_1 = B_1\frac{J_{41}}{J_{31}},\ E_0 = 3B_0C_1,\ \zeta' = (\varepsilon+p)\frac{k_\mathrm{B}T}{m},\ \Omega = 3\left(\frac{\partial\ln\zeta'}{\partial\ln\rho}\right)_{\zeta/\rho} - 5 \\ &\Lambda = \frac{D_{31}}{J_{21}^2},\ C_1 = -1 - \frac{4J_{31}J_{30} - J_{41}J_{20}}{D_{20}},\ C_2 = \frac{J_{31}J_{20} - J_{41}J_{10}}{D_{20}},' \end{aligned}$$

with

$$J_{nq} = \frac{4\pi y m^2}{(2q+1)!!}\int_0^\infty \mathrm{d}\chi\left(\frac{f_\mathrm{eq}}{y}\right)\left(1+\frac{f_\mathrm{eq}}{y}\right)\sinh^{2(q+1)}\chi\cosh^{n-2q}\chi, \tag{17.41}$$

where χ is obtained from $m\cosh\chi = -p_\mu u^\mu$. In terms of (17.27), f_eq/y takes the simple form

$$\frac{f_\mathrm{eq}}{y} = \frac{1}{\exp(\beta\cosh\chi - \alpha) \pm 1}, \tag{17.42}$$

with α and β as defined in (17.28). This is a usual variable transform in relativistic kinetic theory, in terms of which $\mathrm{d}P = 4\pi m^2\sinh^2\chi\mathrm{d}\chi$. Though the procedure is simple from a conceptual point of view, to obtain the above coefficients is very intricate. The interested reader is advised to go to the work of Israel and Stewart (1979).

Once ε, ε_μ, and $\varepsilon_{\lambda\mu}$ have been expressed in terms of the fluxes, one may substitute (17.33) in (17.37) to obtain the non-equilibrium entropy

$$\begin{aligned} S^\mu = {} & S^\mu_{\text{eq}} + T^{-1}q^\mu - u^\mu vT^{-1}\left(\alpha_0\Pi^2 + \alpha_1 q^\lambda q_\lambda + \alpha_2 \Pi^{\rho\lambda}\Pi_{\lambda\rho}\right) \\ & +\beta_0\Pi q^\mu + \beta_2\Pi^{\mu\nu}q_\nu, \end{aligned} \tag{17.43}$$

where the coefficients α_i, β_i stand for

$$\alpha_1 = \frac{1}{2vT}D_{41}nm\Lambda^2 J_{21}J_{31},\ \alpha_2 = \frac{1}{4vT}\beta\zeta'^2 J_{52}, \tag{17.44a}$$

$$\begin{aligned} \alpha_0 = {} & \frac{3}{2vT\Omega^2}\beta\zeta' \\ & \left[5J_{52} - 3\frac{J_{31}(J_{30}J_{31} - J_{41}J_{20}) + J_{41}(J_{41}J_{10} - J_{31}J_{20})}{D_{20}}\right], \end{aligned} \tag{17.44b}$$

$$\begin{aligned} \beta_0 &= (D_{41}D_{20} - D_{31}D_{30})T\Lambda\zeta' J_{21}J_{31}, \\ \beta_2 &= -(J_{41}J_{42} - J_{31}J_{52})T\Lambda\zeta' J_{21}J_{31}, \end{aligned} \tag{17.44c}$$

with D_{qn} defined by $D_{qn} = J_{q+1,n}J_{q-1,n} - J^2_{qn}$. In the limit of non-degenerate gases, i.e. $\alpha \gg 1$ in (17.42), the asymptotic expressions for these coefficients in the classical gases [$\beta \gg 1$ in (17.42)] are $v\alpha_1 = \frac{1}{5}m(pk_\text{B}T)^{-1}$, $v\alpha_2 = \frac{1}{4}p^{-1}$, and $\beta_2 = -\frac{2}{5}(pT)^{-1}$, which are nothing but Grad's results. From the other hand, $v\alpha_0 = \frac{3}{5}m^2(pk^2_\text{B}T)^{-1}$ and $\beta_0 = \frac{4}{5}m(pk_\text{B}T^2)^{-1}$, but these coefficients will play no role as they are multiplied by the bulk viscous pressure, which is zero in this limit. In the ultrarelativistic case ($\beta \ll 1$), one obtains $v\alpha_1 = \frac{5}{8}p^{-1}$, $v\alpha_2 = \frac{3}{8}p^{-1}$, $\beta_2 = -\frac{1}{4}(pT)^{-1}$, $v\alpha_0 = 108(p\beta^4)^{-1}$, and $\beta_0 = 6(pT\beta^2)^{-1}$.

The knowledge of the coefficients (17.44) allows one to write λ, ζ, and η in terms of the relaxation times τ_0, τ_1, and τ_2. Such relaxation times depend themselves on the collision term of the Boltzmann equation, and their derivation is an extremely laborious task. For the present purpose, it suffices to say that the kinetic theory corroborates the form of the evolution equations for the fluxes (17.10–17.12) and provides explicit values for the coefficients (17.44).

17.4 Nuclear Matter and Relativistic Ion Collisions

Relativistic hydrodynamics is the root of the theory of collisions of heavy ions, and the analysis of these collisions is helpful to determine the nuclear equations of state and, to search for the phase transition from the hadronic matter to the quark-gluon plasma (Griffin 1976; Stocker 1987). It must be noted, however, that generally the duration of the collisions between heavy nuclei is only one order of magnitude higher than the mean free time of nucleons collisions inside the nuclei. As a consequence, relaxational effects are important in describing the dynamics of such phenomena. Furthermore, during collisions the nuclei are far from equilibrium, so that the non-equilibrium corrections of the equations of state may considerably affect the energy required for the phase transition in nuclear matter.

To formulate the state equations, we need an explicit expression of the Gibbs equation which means that we must know the expressions for the transport coefficients and the relaxation times. They have been derived by Danielewicz (1984) from the kinetic theory by expanding the Uhlenbeck–Uehling equation, the quantum version of the Boltzmann equation: the following expressions for the shear viscosity η and the thermal conductivity λ have been obtained

$$\eta = \frac{1700}{(k_B T)^2}\left(\frac{n}{n_0}\right)^2 + \frac{22}{1+10^{-3}(k_B T)^2}\left(\frac{n}{n_0}\right)^{0.7}, + \frac{5.8(k_B T)^{1/2}}{1+160(k_B T)^{-2}} \tag{17.45}$$

$$\lambda = \frac{0.15}{k_B}T\left(\frac{n}{n_0}\right)^{1.4} + \frac{0.02}{1+10^{-6}(k_B T)^4/7}\left(\frac{n}{n_0}\right)^{0.4} + \frac{0.225(k_B T)^{1/2}}{1+160(k_B T)^{-2}}, \tag{17.46}$$

where $k_B T$ is expressed in MeV, η in $\mathrm{MeV}/(\mathrm{fm})^2\mathrm{c}$, λ in $\mathrm{c}/(\mathrm{fm})^2$, the nucleon number n in fm^{-3} and where $n_0 = 0.145\,\mathrm{fm}^{-3}$ (here, fm stands for fermi, with $1\,\mathrm{fm} = 10^{-15}$ m and c for the speed of light). The corresponding relaxation times for the viscous pressure tensor $\mathbf{P}^v$ and the heat flux $\boldsymbol{q}$ are (Danielewicz 1984; Fai and Danielewicz 1996)

$$\tau_2 = \left[\frac{850}{(k_B T)^2}\right]\left(\frac{n}{n_0}\right)^{1/3}\left(1+0.04k_B T\frac{n}{n_0}\right) + \frac{38(k_B T)^{-1/2}}{1+160(k_B T)^{-2}}\left(\frac{n}{n_0}\right), \tag{17.47}$$

$$\tau_1 = \left[\frac{310}{(k_B T)^2}\right]\left(\frac{n}{n_0}\right)^{0.4}\left(1+0.1k_B T\frac{n}{n_0}\right) + \frac{57(k_B T)^{-1/2}}{1+160(k_B T)^{-2}}\left(\frac{n}{n_0}\right), \tag{17.48}$$

where τ_i $(i = 1, 2)$ is expressed in fm/c. The last terms in the right-hand side correspond to binary colllisions amongst nucleons, whereas the first terms describe collisions of nucleons with the surface of the nuclei. For $k_B T > 6$MeV, binary collisions are more frequent whereas at lower temperatures, a ballistic regime with collisions against the boundaries of the nucleus is observed.

The generalised non-equilibrium entropy up to the second-order contributions in the fluxes is given by

$$s(u, v, \boldsymbol{q}, \mathbf{P}^v) = s_{\mathrm{eq}}(u, v) - \frac{\tau_1}{2\lambda\rho T^2}\boldsymbol{q}\cdot\boldsymbol{q} - \frac{\tau_2}{4\eta\rho T}\mathbf{P}^v : \mathbf{P}^v. \tag{17.49}$$

Combining (17.47–17.48) with (17.49) results in an explicit expression for the non-equilibrium entropy. Since the general expression is very cumbersome, we particularize the results for high temperature, which is the regime of interest in the analysis of high-energy collisions. In this case, the expression of entropy which will serve as a basis to determine the non-equilibrium nuclear equations of state is

$$s = s_{\mathrm{eq}} - \frac{1.26}{mT^3} 10^3 \frac{n_0}{n^2} \boldsymbol{q} \cdot \boldsymbol{q} - \frac{1.64}{mT^2} \frac{n_0}{n^2} \mathbf{P}^v : \mathbf{P}^v. \tag{17.50}$$

Another subject of interest is the problem of the energy transfer, which is also affected by the relaxational effects. Supplementary applications are concerned with thermodynamic stability requirements on the nuclear equations of state (Kozlowski 1989; Olson and Hiscock 1989). The dynamical aspects of the collisions are very relevant, as for instance the propagation of shockwaves in the hot quark-gluon plasma at the initial stages of the collision taking into account viscosity, relaxation, and finite-size effects. These aspects have been considered in the framework of a relaxational dissipative thermodynamics by Bidar and Jou (1998), Koide et al. (2007), and Denicol et al. (2007, 2008), with a single relaxation time, for the sake of simplicity. It can thus be concluded that a promising field of application of relativistic EIT in the near future will be nuclear physics, where rather exciting topics are currently developed.

17.5 Problems

17.1 In the steady state and in the absence of viscous effects, the evolution equation (17.10) for the heat flux is written as

$$q^\mu = -\lambda \Delta^{\mu\nu} (\nabla T + T a_\nu),$$

with a_ν being the acceleration four-vector. In the local instantaneous rest frame, $\Delta^{\mu\nu}$ is diag (0,1,1,1), and the spatial components of the equation for the heat flux take the form

$$\boldsymbol{q} = -\lambda (\nabla T + T c^{-2} \boldsymbol{a}).$$

Here λ is the thermal conductivity, $\boldsymbol{q}$ the three-dimensional heat flux, c the speed of light in vacuo, and $\boldsymbol{a}$ the acceleration. In the presence of a gravitational field ϕ, one has $\boldsymbol{a} = -\nabla\phi$. (a) Show that in the presence of a gravitational field the equilibrium condition is not T uniform but T^* uniform, with $T^* = T(1 + c^{-2}\phi)$ up to the first order in ϕ. (b) Calculate the difference in the temperature T between a point located on the earth surface, at 300 K, and another one 100 m above. Determine the value of $\boldsymbol{a}$ so that the difference is 1 K. (See Pavón et al. (1980))

17.2. In general relativity, the conditions of thermal and material equilibrium are

$$T\sqrt{g_{00}} = \text{constant}, \quad \mu\sqrt{g_{00}} = \text{constant},$$

with g_{00} the temporal component of the metric tensor (Landau LD, Lifshitz EM (1980) Statistical Physics 3rd ed. Part 1, Pergamon, Oxford). In a weak gravitational field, $g_{00} = 1 + (2\phi/c^2)$, with ϕ being the gravitational potential. (a) Show the result of the Problem 17.1 for thermal equilibrium in terms of the temperature T^* introduced there. (b) Taking into account that in the classical limit the relativistic chemical potential μ tends to $\mu_0 + mc^2$, where μ_0 is the usual equilibrium chemical potential and m the mass of the particles, show that the condition of material equilibrium reduces in the classical limit to $\mu_0 + m\phi = \text{constant}$.

17.3. In relativistic transformations, it is generally assumed that entropy remains constant, $S = S_0$, while volume V changes as $V = \gamma^{-1}V_0$. Here, the subscript 0 denotes the values measured by an observer at rest, the quantities without the subscript correspond to those measured by an observer moving at speed v with respect to the system, and $\gamma = [1 - (v/c)^2]^{-1/2}$, with c the speed of light in vacuo. Show that the non-equilibrium entropy density (per unit volume) for radiation with energy density e and energy flux J obtained in (6.64) in the context of information theory, which may be rewritten as

$$s(e, J) = \tfrac{1}{2}s_{\text{eq}}(e)(2 + x)^{1/2}(x - 1)^{1/4},$$

with $x = [4 - 3(J/ce)^2]^{1/2}$, may be alternatively obtained from the equilibrium entropy density of radiation at rest, with energy density e_0 and $J = 0$, i.e. $s_{\text{eq}}(e_0) = \frac{4}{3}a^{1/4}e_0^{3/4}$ through a Lorentz transformation corresponding to the average speed of the photons in the direction of the energy flux, which is given by

$$v = c\left(3\frac{2 - x}{2 + x}\right)^{1/2}.$$

(*Hints*: The internal energy density transforms as $e = \gamma^2(e_0 + p_0) - p_0$, and $p_0 = \frac{1}{3}e_0$.) (Dominguez-Cascante R 1997) J Phys A: Gen Math 30:7707.)

17.4. There has been a debate about the relativistic transformation of temperature (see, for instance, Landsberg PT (1966) Nature 212:571; 214 (1967) 903; Callen HB, Horwitz G (1971) Am J Phys 39:938). The initial proposals by Einstein and Planck were that $T = T_0\gamma^{-1}$, with γ given in Problem 17.3, while in the 1960s Ott claimed that $T = T_0\gamma$. Show that the expression for the non-equilibrium temperature of radiation with energy density e and energy flux J obtained in (6.62), namely

$$T(e) = T_{\text{eq}}(e) \times \frac{2(x - 1)^{3/4}}{(2 + x)^{1/2}}$$

may be obtained by the mentioned Einstein–Planck criterion from the Lorentz transformation discussed in Problem 17.3.

17.5. Assume that a black body at rest temperature T_0 is orbiting around a planet, and assume that an observer in the planet measures its temperature by using Wien's law for the wavelength of the radiation corresponding to the maximum emitted power. Show that using the Doppler relativistic effect, the temperature T measured by the planetary observed is related to the rest temperature T_0 of the blackbody as $T = T_0\gamma^{-1}$, as in the Einstein-Planck proposal (neglect the gravitational effects on temperature predicted by general relativity).

17.6. A relevant parameter in the equations of state for nuclear matter is the compressibility K, defined as $K \equiv 9\,(\partial p/\partial\rho)_T$, with p the pressure and ρ the mass density.

(a) Starting from (17.49) with $\boldsymbol{q} = 0$ and neglecting (for the sake of simplicity in this problem) the non-equilibrium contributions to temperature, show that the non-equilibrium pressure p_{neq} may be written as

$$p_{\text{neq}} = p_{\text{eq}} + \rho^2 \frac{\partial}{\partial\rho}\left(\frac{\tau_2}{4\eta\rho}\right)\mathbf{P}^v : \mathbf{P}^v.$$

(b) Assume that η and τ_2 are given by the first terms in the right-hand side of (17.45) and (17.47), respectively. Using this approximation, estimate the non-equilibrium contribution to the pressure.

(c) Use the non-equilibrium pressure to find how the compressibility coefficient K is modified in the presence of a viscous pressure $\mathbf{P}^v$.

17.7. To estimate the order of magnitude of the non-equilibrium contributions to the compressibility K in a typical relativistic nuclear collision, consider a collision Au + Au at 400 MeV/nucleon. Consider $n = 0.30\,\text{fm}^{-3}$, $k_\text{B}T = 45\,\text{MeV}$, $\eta = 55\,\text{MeV}/\text{fm}^2\cdot c$, the value of the shear rate is $\gamma = 0.07\,c\cdot\text{fm}^{-1}$, and the viscous pressure P^v is of the order of $\eta\gamma$. (Here, fm stands for $1\,\text{fermi} = 1\,\text{femtometer} = 10^{-15}\,\text{m}$, and c for the speed of light.) (a) Estimate the value of P^v. (b) Using the data of this problem, estimate the value of $K_{\text{neq}} - K_{\text{eq}}$, the non-equilibrium contribution to the compressibility using the results obtained in Problem 17.6. (c) The observed order of magnitude of K_{eq} is 200 MeV; compare with $K_{\text{neq}} - K_{\text{eq}}$.

Chapter 18
Viscous Cosmological Models and Cosmological Horizons

Thermodynamics plays an important role in cosmological models because the energy–momentum tensor appearing in the equations of general relativity must be specified according to the contents of the Universe. The earlier classical cosmological models do not include dissipation, as they postulate a reversible adiabatic expansion of the Universe. However, the attention paid to dissipative phenomena in cosmology and astrophysics is growing up rapidly. The interaction between matter and radiation, and other phenomena, discussed later in this chapter, depend on dissipative effects mainly due to bulk viscosity.

Bulk viscous effects play a determinant role as entropy-producing processes in the early universe; as an example, let us mention galaxy formation, wherein the typical galactic mass is the mass of the smallest density fluctuation which could grow against dissipative effects during the period just prior to hydrogen recombination; another illustration is its possible driving role in inflationary periods (i.e. periods with exponential expansion) independently of the details of the phase transitions of the grand unified theories. Furthermore, relaxational effects have to be included when the relaxation time of some components of the contents of the Universe become very long, as a consequence of cooling and expansion of the Universe, as for instance in the decoupling between matter and radiation, a period in which the radiation behaviour changes from diffusive to ballistic.

At a first stage, the bulk viscous effects were described by the classical Newton–Stokes equation relating the bulk viscous pressure and the rate of change of volume. However, this equation is inconsistent with the postulates of relativity theory, as it yields infinite speed of propagation for viscous signals. Therefore, relaxational effects granting upper bounds to such speed must be taken into account, as postulated in extended irreversible thermodynamics. In this chapter we give an overview of this active topic of research. The interest on these subjects has been reinforced with the cosmological picture that 95% of the energy contents of the universe are contributed by dark matter and dark energy. The detailed physical nature of these majoritary constituents is still unknown, but their respective macroscopic effects have been the subject of a careful scrutiny since the last years of the twentieth century by means of a number of independent observations.

D. Jou et al., *Extended Irreversible Thermodynamics*,
DOI 10.1007/978-90-481-3074-0_18,

18.1 Viscous Cosmological Models and Accelerated Expansion

Thermodynamics enters in cosmological problems through the energy–momentum tensor $T_{\mu\nu}$ which appears in the right-hand side of the Einstein equation of general relativity governing the spacetime metric tensor $g_{\mu\nu}$ (Schultz 1985; Wald 1984; Weinberg 2008):

$$R_{\mu\nu} - \frac{1}{2} g_{\mu\nu} \mathcal{R} = 8\pi G T_{\mu\nu}, \tag{18.1}$$

where $R_{\mu\nu}$ is the Ricci tensor associated to $g_{\mu\nu}$, $\mathcal{R}$ the scalar curvature, and G the Newtonian gravitational constant. In some occasions, a further term proportional to $g_{\mu\nu}$ is added to the right-hand side: it is related to the so-called gravitational constant (see Problem 18.9), but we will ignore it for the sake of simplicity.

These equations are extremely intricate, but they may be simplified by assuming isotropy and homogeneity at large scales. These properties follow from cosmic observations, which have revealed the isotropy properties of our group of galaxies, and the cosmological principle, which states that, on the average, any two sufficiently large and otherwise arbitrary portions of the Universe look very similar. The hypothesis of isotropy is strongly supported by the 2.7 K cosmic microwave background radiation whose spectrum deviates from the Planckian one by less than one in ten thousand. These hypotheses are also confirmed by the observed abundances of light elements and redshifts of distant galaxies (Peebles 1993). Accordingly, one may adopt the Friedmann–Robertson–Walker (FRW) metric

$$\mathrm{d}s^2 = -c^2 \mathrm{d}t^2 + R^2(t) \left[(1 - \kappa r^2)^{-1} \mathrm{d}r^2 + r^2 (\mathrm{d}\theta^2 + \sin^2\theta \mathrm{d}\phi^2) \right], \tag{18.2}$$

which is the most general representation of the spacetime separation between two arbitrary events in a homogeneous and isotropic space. Here r, θ and ϕ are comoving coordinates and $R(t)$ is the cosmic scale factor, whose determination is one of the main aims of the model. The parameter κ is a constant related to the spatial curvature of the hyper-surfaces of homogeneity. An appropriate scaling restricts κ to only three possible values: $\kappa = 0$ (flat space sections), $\kappa = -1$ (negative spatial curvature, spatial sections are 3-dimensional hyperboloids) and $\kappa = +1$ (positive spatial curvature, spatial sections are 3-dimensional spheres).

To calculate $R(t)$ from the Einstein equations, an expression for the energy–momentum tensor is needed. Its most general form compatible with homogeneity and isotropy is

$$T_{\mu\nu} = \varepsilon u_\mu u_\nu + (p + \Pi)\Delta_{\mu\nu},$$

where p and Π are the equilibrium pressure and the bulk viscous pressure respectively, the four-velocity vector u^μ and the symmetric spatial projector $\Delta_{\mu\nu}$ have been defined in Sect. 17.1. In the reference frame attached to a comoving observer, the components of the energy–momentum tensor $T_{\mu\nu}$ may be written explicitly as

$$T^{\mu\nu} = \begin{pmatrix} -\varepsilon & 0 & 0 & 0 \\ 0 & p+\Pi & 0 & 0 \\ 0 & 0 & p+\Pi & 0 \\ 0 & 0 & 0 & p+\Pi \end{pmatrix}.$$

Unlike the perfect fluid hypothesis, which states that viscous pressure Π vanishes, here it is assumed that Π does not necessarily vanish. In this chapter, as in the preceding one, we use Π instead of p^v to denote the viscous pressure, because this is a more usual notation in cosmology.

Under the above assumptions, the non-trivial components of the Einstein equation (18.1) take the simple form

$$\left(\frac{\dot{R}}{R}\right)^2 + \frac{\kappa}{R^2} = \frac{8\pi G}{3}\varepsilon, \tag{18.3a}$$

$$\frac{\ddot{R}}{R} = -\frac{4\pi G}{3}\left[\varepsilon + 3(p + \Pi)\right]. \tag{18.3b}$$

The first of these is known as Friedmann's equation. Note, from (18.3b), that the rate of change of the expansion, $\ddot{R}$, does not depend on the energy density ε alone but on the combination $\varepsilon + 3(p + \Pi)$. If the total pressure is negative enough in such a way that $3(p + \Pi) < -\varepsilon/3$, the cosmic expansion will accelerate, instead of becoming slower, as it could be expected from the usual Newtonian gravitational attraction.

To complement the set of equations (18.3) one needs an equation of state for p and a constitutive equation for Π, and for this we select

$$p = (\gamma_0 - 1)\varepsilon\,,\ \tau_0\dot{\Pi} + \Pi = -3\zeta\frac{\dot{R}}{R}. \tag{18.4}$$

The first relation (18.4) is standard, the second one is nothing but a simplified version of the EIT equation (17.11), in which use is made of $u^{\mu}{}_{;\mu} = 3(\dot{R}/R)$ and $\nabla\cdot\boldsymbol{v} = 3H$, that follows from the observational result $\boldsymbol{v} = \mathrm{d}\boldsymbol{r}/\mathrm{d}t = H\boldsymbol{r}$, with $\boldsymbol{r}$ being the position vector of the particles and H (Hubble factor) independent of position. The value $\gamma_0 = \frac{4}{3}$ corresponds to radiation $\left(p = \frac{1}{3}\varepsilon\right)$ and $\gamma_0 = 1$ to an ideal non-relativistic gas $\left(k_{\mathrm{B}}T \ll mc^2\right)$; recalling that the pressure is proportional to T, one may put $p = 0$. The bulk viscosity ζ and the relaxation time τ are assumed to depend on ε through the following relations (Belinskii et al. 1979):

$$\zeta = \alpha\varepsilon^{\nu}\,,\ \tau = \zeta/\varepsilon = a\varepsilon^{\nu-1}. \tag{18.5}$$

With this choice, the viscous signals propagate with speed equal to c, since the speed of propagation of viscous signals is $v = [\zeta/(\varepsilon\tau)]^{1/2}$. If they propagated more slowly, τ should be higher than the value given by the second of equations in (18.5). By setting $\nu = 1$, (18.5) describes a radiative fluid, whereas the choice

$\nu = \frac{3}{2}$ corresponds to a string-dominated universe (Lima et al. 1988; Oliveira and Salim 1988; Barrow 1988; Pavón et al. 1991).

Elimination of ε in (18.3) yields, for a flat spacetime ($\kappa = 0$),

$$\frac{\ddot{R}}{R} + \frac{3\gamma_0 - 2}{2}\left(\frac{\dot{R}}{R}\right)^2 = -4\pi G \Pi. \tag{18.6}$$

In the standard cosmological model, viscous effects are ignored ($\Pi = 0$), and one is led to $R \sim t^{1/2}$ and $R \sim t^{2/3}$ for radiation and matter-dominated universes, respectively (see Problem 18.1). The presence of bulk viscosity may have several consequences, depending on the relation between ζ and ε. If ζ is proportional to ε, the big-bang singularity with infinite spacetime curvature would not occur (Murphy 1973). However, more realistic models are based on $\zeta \sim \varepsilon^{\nu}$, with $0 \leq \nu \leq \frac{1}{2}$, in which case the big-bang singularity still persists (Pavón et al. 1991).

The initial motivations behind the introduction of bulk viscous effects were, for instance (e.g. Lima et al. 1988; Calvão et al. 1992 and references therein): (1) to study the action of the entropy-producing processes in the early universe; (2) to analyse the initial density fluctuations, which are of pivotal importance in galaxy formation; (3) shear viscosity could provide a mechanism to eliminate initial anisotropies in the universe, and transform them in heat (Schultz 1985); (4) bulk viscous effects could drive an inflationary period independently of the details of the phase transitions of grand unified theories (Hiscock and Salmonson 1991; Zakari and Jou 1993).

Viscous dissipation finds its origin in several phenomena. Following a chronological order, let us first mention the appearance of 4-dimensional superstrings right after the compactification of the extra spatial dimensions (around the Planck time $t_{\mathrm{P}} = hG/(2\pi c^5) \approx 10^{-44}$s) (Turok 1988). Another possibility is the quantum creation of particles by the intense gravitational field (Hu 1982). Likewise, mini black holes could spontaneously condense from the radiation at very high temperature (Turok 1988; Calvão et al. 1992) . These black holes behave as non-relativistic particles [$k_{\mathrm{B}}T/(mc^2) \ll 1$], whereby the mixture might result in a radiative fluid of non-vanishing viscosity. However, a careful study (Hayward and Pavón 1989; Calvão and Salim 1992) has revealed that this is not the case, for at that stage of the Universe evolution the interaction time between these mini black holes and the surrounding radiation is greater than the expansion time of the Universe. In the context of grand unified theories (GUT), bulk viscosity may arise from the production of superheavy gauge bosons and magnetic monopoles in the broken phase of the GUT phase transition, or from the existence of a primordial bosonic charge (the difference between boson and antiboson numbers) initially confined to the Bose–Einstein condensed ground state (Lima et al. 1988; Barrow 1988; Pavón et al. 1991). Neutrinos (whether massless or massive) interacting with matter represent an efficient mechanism of dissipation owing to their long mean free path (Calvão et al. 1992). Likewise, photons in contact with matter, e.g. electrons, constitute a radiative fluid able to generate dissipation (Weinberg 2008).

In most of these models, bulk viscosity is introduced by means of classical transport equations, i.e. $\Pi = -3\zeta \dot{R}/R$, but this is inconsistent, since it leads to infinite speeds and unstable solutions. Belinskii et al. (1979) studied several consequences of the introduction of the relaxation term in (18.4), which are important when the product of the relaxation time and the Hubble parameter is higher or comparable to unity. This may happen at several stages of the expansion of the Universe, because different components of the cosmic fluid may have different collision times. Indeed, there are several decoupling stages in which some components decouple from the others, because their collision time becomes comparable to the inverse of the expansion rate of the Universe.

We analyse here the simple model based on (18.3b) (Lima et al. 1988; Oliveira and Salim 1988; Barrow 1988; Pavón et al. 1991). This equation may be written in terms of the Hubble parameter $H = \dot{R}/R$ and for a flat spacetime $\kappa = 0$ adopts the form

$$\dot{H} + \frac{3}{2}\gamma_0 H^2 = -4\pi G \Pi. \tag{18.7}$$

After combining this relation with (18.4) one has

$$\tau \ddot{H} + \dot{H}(3\tau\gamma_0 H + 1) + H\left(\frac{3}{2}\gamma_0 H - 12\pi G\zeta\right) = 0. \tag{18.8}$$

Resolution of (18.8) implies the knowledge of two initial conditions for H and $\dot{H}$. In the standard theory, only one initial condition for H is required and is usually taken to be $H(0) = \infty$. In the present case, the initial value of H can be finite, even negative. Therefore the analysis of the first moments of the Universe needs not only a unified theory of the basic interactions, but also a thermodynamic description of the collective effects, which are usually ignored in standard approaches.

Inserting into (18.8) the relationships (18.5) for ζ and τ and using (18.3a) (with $\kappa = 0$), one obtains

$$\alpha\beta^n H^{2n}\ddot{H} + \dot{H}\left(3\alpha\beta^n\gamma_0 H^{2n+1} + 1\right) + H^2\left(\frac{3}{2}\gamma_0 - \frac{12\pi G\alpha}{\beta^\nu}H^{2n+1}\right) = 0, \tag{18.9}$$

with $n = \nu - 1$ and β a shorthand for $\frac{3}{8}(\pi G)^{-1}\frac{3}{8}$. Upon introducing the quantities

$$h = \frac{H}{H_0}, \quad H_0 = \left[\frac{\gamma_0}{3\alpha}\left(\frac{8\pi G}{3}\right)^n\right]^{1/(2n+1)}, \quad \nu \neq \frac{1}{2}, \tag{18.10}$$

and rescaling the time as $t^* = H_0 t$, (18.9) may be cast into the simpler form

$$\gamma_0 h^{2n}\ddot{h} + 3\dot{h}(\gamma_0 h^{2n+1} + 1) + \frac{9}{2}\gamma_0 h^2(1 - h^{2n+1}) = 0. \tag{18.11}$$

From now on an upper dot will denote derivation with respect to t^*; the asterisks will be dropped whenever no confusion arises. The second-order differential equation

(18.11) which governs the evolution of the reduced Hubble parameter h has two different stationary trivial solutions $h = 1$ and $h = 0$. The first implies inflationary expansion with a constant rate given by H_0.

One may study the behaviour of h near the steady solutions analytically. Setting $h = 1 + \chi$, with $|\chi| \ll 1$, one obtains after linearization

$$\gamma_0 \ddot{\chi} + 3\dot{\chi}(\gamma_0^2 + 1) - \frac{3}{2}\gamma_0(2n + 1)\chi = 0. \tag{18.12}$$

Its solution reads as

$$\chi(t) = \chi_+ \exp(\lambda_+ t) + \chi_- \exp(\lambda_t), \tag{18.13}$$

where χ_+ and χ_- are constants which depend on $h(0)$ and $\dot{h}(0)$, while λ_+ and λ_- are the roots

$$\lambda_\pm = \frac{3(1 + \gamma_0^2)}{2\gamma_0} \left[-1 \pm \sqrt{1 + 2\gamma_0^2 \frac{2n + 1}{(1 + \gamma_0^2)^2}} \right]. \tag{18.14}$$

Note that for $n + 1 < -(1 + \gamma_0^4)/(4\gamma_0^2)$ the quantity under the square root of the right-hand side of (18.14) is negative, so that h shows an oscillatory damped behaviour of frequency

$$\omega = \frac{3}{2}\gamma_0^{-1} \sqrt{(1 + \gamma_0^2)^2 + 2\gamma_0^2(2n + 1)} \tag{18.15}$$

around $h = 1$. This kind of behaviour has not been explored in the literature. Note also that if $\nu > \frac{1}{2}$, one of the roots of (18.14) will be positive, and therefore the state with $h = 1$ will be unstable.

Non-stationary solutions of (18.11) are obtained via numerical integration. The most significant results are shown in Fig. 18.1 and compared with the behaviour corresponding to a zero relaxation time. Some comments are in order.

1. At short times, the solutions depend strongly on the initial conditions $h = 0$ and $\dot{h} = 0$.
2. At short times, there are quantitative and qualitative differences between the solutions, leading to changes in the chronology of the successive eras of the primordial Universe. At long times, both sets of solutions attain the same stationary value.
3. For $0 < \nu < \frac{1}{2}$, and an initial value of $|\dot{h}|$ not very high, the solutions tend to the constant value $h = 1$, whether or not the initial value of h is greater or lower than unity.
4. For $\nu > \frac{1}{2}$ and $h(0) > 1$, the solutions diverge if $|\dot{h}|$ is large enough; otherwise they tend to. For $h(0) > 1$, they also tend to $h(0) = 0$.
5. If $\nu > 0$ and the initial value $|\dot{h}(0)|$ is large enough, the solutions of (18.11) diverge, irrespective of the value of $h(0)$.

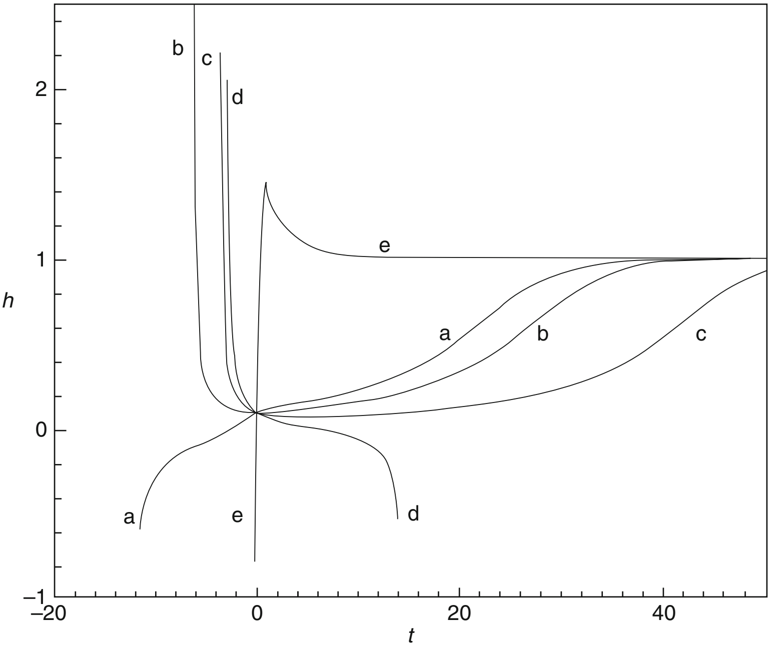


Fig. 18.1 Behaviour of the reduced Hubble factor h as a function of the reduced time t^* for a fluid with $\gamma_0 = 1.5$ and $\nu = 0.3$ according to (18.11). The initial value $h(0)$ is 0.1. The different curves correspond to initial conditions for $\dot{h}$: (a) $\dot{h}(0) = 0.02$; (b) $\dot{h}(0) = 0$; (c) $\dot{h}(0) = -0.02$; (d) $\dot{h}(0) = -0.04$; (e) $\dot{h}(0) = 9.0$. Curves (a) and (e) start with a contracting phase ($h < 0$) and evolve to a de Sitter expansion. Curves (b) and (c) begin with a Friedmann-like behaviour and tend to a de Sitter one for long times. Curve (d) starts with a Friedmann-like expansion and evolves towards a contracting phase (Reprinted with permission from Pavón et al. D (1991) Class Quantum Grav 8:347)

It was also shown by Belinskii et al. (1979) that, in the relaxed model, the effect of matter creation near the initial singularity is preserved, just as in the absence of relaxation, but that the tendency towards isotropy during the contraction disappears. The cosmological singularity still persists, but it may belong to a new type connected to the accumulation of elastic energy. Furthermore, the Friedmann solutions are shown to be unstable in the vicinity of the singularity.

The analysis of viscous fluid models with time-varying cosmological constant has been fostered by the discovery of the accelerating cosmic expansion. (For bibliographical references of the causal viscous effects in these models see Pradhan 2007; Bali and Singh 2008). Since bulk viscous pressure may be negative, it could provide an alternative to dark energy in yielding an accelerated expansion, when $\zeta(\varepsilon)$ is conveniently chosen, providing some unification between dark matter and dark energy. A viscous pressure given by $\zeta(\varepsilon) = 0.236\varepsilon^{-0.4}$ has been found to give a reasonably accurate description of the known behaviour, but it is not enough accurate to describe some aspects of gravitational lensing or the spectrum of the cosmic microwave radiation (Li and Barrow 2009).

Note that (18.4b) for $\dot{\Pi}$ is not the most general evolution equation obtained from EIT. Indeed, if in expression (17.6) for the entropy four-vector one assumes $q^\mu = P^{\mu\nu} = 0$, it is found that

$$S^\mu = \left(s_{\mathrm{eq}} - \frac{\tau \Pi^2}{2\zeta T} \right) u^\mu. \tag{18.16}$$

Taking the full derivative of this expression, one obtains for the entropy production

$$S^\mu{}_{;\mu} = -\frac{\Pi}{T} \left(u^\mu{}_{;\mu} + \frac{\tau}{\zeta}\dot{\Pi} + \Pi T \frac{\tau}{\zeta T} u^\mu{}_{;\mu} \right), \tag{18.17}$$

which implies, instead of (18.4b), the non-truncated equation

$$\Pi + \tau\dot{\Pi} = -3\zeta H - \frac{1}{2}\Pi\tau \left(3H + \frac{\dot{\tau}}{\tau} - \frac{\dot{\zeta}}{\zeta} - \frac{\dot{T}}{T} \right) \tag{18.18}$$

where we have used the result $u^\mu{}_{;\mu} = 3H$ from the FRW model. The influence of the non-linear terms has been studied by several authors (Zakari and Jou 1993; Romano and Pavón 1994; Maartens and Mendez 1997; van den Hoogen 1995). The behaviour of the cosmological models depends both on the equations of state for p, T, τ, and ζ and on the transport equation being used. For instance, Hiscock and Salmonson, starting from (18.18) together with the equations of state for the Boltzmann gas, found no inflationary phase. With the simpler equations of state $\Pi = \lambda\rho$, $\tau = \alpha\rho^m$, $\zeta = \tau\rho$ other authors have found that an inflationary phase remains possible, but with a different expansion rate than in the truncated version (18.4). Both the values of H_0 and the behaviour of the temperature during this inflationary period have been the subject of recent analyses (Zakari and Jou 1993; Romano and Pavón 1994; Maartens and Mendez 1997; van den Hoogen 1995).

To summarize, when viscous effects are introduced in cosmological models, it is imperative to include relaxational equations compatible with causality. This is a new topic of research in cosmology, whose importance has only been recognized recently.

18.2 Particle Production and Effective Bulk Viscosity

Another subject of interest related to bulk viscosity concerns particle production, which in some situations may be described by means of an apparent or effective bulk viscosity (Zimdahl and Pavón 1993, 1994). Such a decay or production of particles finds its origin in several effects, as for instance the decay of scalar particles, production of relativistic particles in the re-heating phase of inflationary eras, electron–positron annihilation after neutrino decoupling, decay of heavy bosons to quarks and leptons, or creation of particles by the gravitational field. Prigogine et al. (1989) were able to frame these effects in a thermodynamic description by formulating a balance equation for the number density of created particles in addition to the Einstein field equations. Another way out is to model the loss and source terms by an effective viscous pressure (Sudharan and Johri 1994; Sussman 1994; Triginer and Pavón 1994; Gariel and Le Denmat 1994; Abramo and Lima 1996).

To be explicit, assume that the number of particles in the Universe is not constant, but that there is a particle production with a rate per unit volume $\dot{\xi}$. The evolution equation for the particle number density n is then

$$\dot{n} = -3n\frac{\dot{R}}{R} + \dot{\xi}. \tag{18.19}$$

This is a particular case of the general mass balance equation

$$\dot{n} = -n\nabla \cdot \boldsymbol{v} + \dot{\xi}, \tag{18.20}$$

where $n\nabla \cdot \boldsymbol{v}$ describes the change of density due to the variation in volume and $\dot{\xi}$ expresses the particle production rate per unit volume. In the situation of expanding universe, one has $\boldsymbol{v} = H\boldsymbol{R}$ and therefore $\nabla \cdot \boldsymbol{v} = 3H = 3(\dot{R}/R)$. Introduction of this result into (18.20) yields (18.19).

Let us now assume that each created particle carries an entropy s. To obtain the entropy production, we start from the classical Gibbs equation

$$T\mathrm{d}s = \mathrm{d}e + p\mathrm{d}v = \mathrm{d}e + p\mathrm{d}(1/n) \tag{18.21}$$

where s is the entropy per particle and e the energy per particle (i.e. $e = \varepsilon/n$, since ε is the energy density per unit volume). Taking the time derivative of (18.21) yields

$$nT\dot{s} = (\varepsilon/n) + p(1/n) = (1/n)\dot{\varepsilon} - (\varepsilon + p)(\dot{n}/n^2). \tag{18.22}$$

Since the non-trivial components of Einstein's equations (18.3a–b) are

$$3H^2 = 8\pi G\varepsilon, \tag{18.23a}$$

$$2\dot{H} = -8\pi G(\varepsilon + p - 3\zeta H), \tag{18.23b}$$

the energy balance equation will be written as

$$\dot{\varepsilon} = -3H(\varepsilon + p)\left(1 - \frac{3\zeta}{\varepsilon + p}H\right). \tag{18.24}$$

Introducing into (18.22) the balance equations (18.19) and (18.24) leads to

$$\dot{s} = -\frac{\varepsilon + p}{n^2T}\left(-\frac{9\zeta}{\varepsilon + p}H^2 + \frac{\dot{\xi}}{n}\right). \tag{18.25}$$

Two particular cases are worth to be discussed: (a) non-vanishing bulk viscosity ($\zeta \neq 0$) but vanishing particle production ($\dot{\xi} = 0$); in this example one has simply

$$\dot{s}_1 = \frac{9\zeta}{n^2 T} H^2; \tag{18.26}$$

(b) vanishing bulk viscosity ($\zeta = 0$ but non-vanishing particle production ($\dot{\xi} \neq 0$), then

$$\dot{s}_2 = -\frac{\varepsilon + p}{n^2 T} \frac{\dot{\xi}}{n}. \tag{18.27}$$

Comparison of (18.26) and (18.27) shows that one can modelize the entropy production due to the particle production in terms of an effective bulk viscosity ζ_{eff} by writing

$$\dot{s}_2 = -\frac{\varepsilon + p}{n^2 T} \frac{\dot{\xi}}{n} \equiv \frac{9\zeta_{\text{eff}}}{n^2 T} H^2. \tag{18.28}$$

This yields for the effective bulk viscosity the result

$$\zeta_{\text{eff}} = \frac{\varepsilon + p}{9} \frac{\dot{\xi}}{n} \left(\frac{\dot{R}}{R} \right)^{-2}. \tag{18.29}$$

Spacetime geometries more complicated than the FRW model have been studied, for instance, Bianchi I and II universes include bulk and shear viscous stresses, both in the truncated and the non-truncated models, and other descriptions include peculiar velocities of the galaxies with respect to the global cosmic motion. Several of these macroscopic results have been confirmed by the kinetic theory of gases in an expanding universe (Romano and Pavón 1994; Triginer and Pavón 1994; Triginer et al. 1996; Zimdahl et al. 1996).

18.3 Extended Thermodynamics and Cosmological Horizons

The cosmological horizon is the boundary of the observable universe. Since we can not observe beyond it, this horizon plays a role analogous to the event horizon of a black hole. In the Hawking-Bekenstein thermodynamics of black holes it is known that the entropy of a black hole of radius R is given by $S_{\text{BH}} = \pi\, (R/l_{\text{P}})^2$, l_{P} being the Planck length. The black hole has then a temperature $T_{\text{BH}} = \partial E/\partial S$, E being its energy $E = Mc^2$, in such a way that $T_{\text{BH}} \sim R^{-1}$. These ideas have been applied to the cosmological horizon, which contributes in this way to the total entropy of the observable universe in a non negligible way. In this section, we briefly comment on this aspect of cosmological thermodynamics

The qualitative differences between Eckart's version of relativistic thermodynamics and extended relativistic thermodynamics also appear in the context of the de Sitter model of the Universe. The latter possesses an event horizon endowed with an entropy and a temperature of quantum origin (Gibbons and Hawking 1977) given by

$$S_h = \frac{8\pi^2}{H^2}, \quad T_h = \frac{H}{2\pi}, \tag{18.30}$$

where the subscript h refers to horizon. (In this section we use units in which $8\pi G = h/(2\pi) = c = k_B = 1$ and the size of the visible universe is of the order of cH^{-1}.) The horizon is a closed spherical surface purely geometrical in nature such that events at one side of it cannot enter into causal contact with events at the other side. This follows from the spacetime metric of this model, which can be found in the specialized literature (Peebles 1993).

It is currently thought that, at some very early epoch, our Universe undergoes a de Sitter phase of exponential inflation (i.e. $R \sim \exp(Ht)$, with H being a positive constant) driven by the energy density ε_v and pressure p_v of the quantum vacuum, which dominates at that time all other forms of energy (subscript v stands for vacuum). Roughly speaking, a de Sitter universe should contain no other forms of energy than that of the vacuum. However, in the case of our Universe one can take for certain that other forms of energy may contaminate the mentioned vacuum. As a consequence, the Hubble parameter deviates slightly from its otherwise steady value.

In virtue of (18.30), the horizon entropy change is

$$\dot{S}_h = -16\pi^2 \frac{\dot{H}}{H^3}, \tag{18.31}$$

and will increase or decrease depending on the sign of $\dot{H}$. By using Eckart's theory, Davies (1987) has shown that, if the fluid (let us say matter plus radiation) perturbing the vacuum obeys a reasonable equation of state of the form of the first of equations (18.4), then the time derivative of the total entropy of the fluid plus the horizon $\dot{S}_h$, will be positive or zero so long as $\gamma_0 > 0$, a relationship not violated by any known kind of fluid. Note that the first of equations (18.4) implies that the fluid fulfils the dominant energy condition (Schultz 1985)

$$\varepsilon_f + p_f \geq 0, \tag{18.32}$$

with subscript f referring to the fluid. Moreover, if the fluid has a bulk viscosity of the form $\zeta = \alpha\varepsilon_f$ with α being a positive constant, it was shown Davies (1987) that the entropy of the fluid plus the horizon satisfies

$$\dot{S} = \dot{S}_f + \dot{S}_h = \frac{8\pi^2}{H^3}\gamma_0\varepsilon_f, \tag{18.33}$$

which is positive, provided that $\gamma_0 \geq 0$. It is worth noting that (18.33) is met whether the dominant energy condition, which for a viscous fluid in standard thermodynamics reads

$$(\gamma_0 - 3\alpha H)\varepsilon_f \geq 0, \tag{18.34}$$

is satisfied or not.

The rate of variation of total entropy S by using relativistic EIT instead of the traditional one was calculated by Pavón (1990). The relevant relations are the Friedmann equation, the first of equations (18.3) with $\kappa = 0$ and the energy conservation equation

$$\dot{\varepsilon} + 3(\rho + p) = 0, \tag{18.35}$$

with $\varepsilon = \varepsilon_v + \varepsilon_f$ and $p = p_v + p_f$ where units have been chosen so that $8\pi G = 1$. These have to be supplemented by appropriate equations of state for the vacuum $p_v = -\varepsilon_v$ and for the material fluid $p_f = (\gamma_0 - 1)\varepsilon_v + \Pi_f$, where the bulk viscous pressure obeys a relaxational equation, the second of equations (18.4), with $\zeta = \alpha\varepsilon_f$. Combining these equations results in

$$\dot{\varepsilon} = -3\left[(\gamma_0 - 3\alpha H)\varepsilon_f - \tau\dot{\Pi}_f\right]H. \tag{18.36}$$

Substituting in the rate of entropy variation associated with the evolution of the horizon,

$$\dot{S}_h = -\frac{8}{3}\pi^2\dot{\varepsilon}H^4, \tag{18.37}$$

leads to

$$\dot{S}_h = \frac{8\pi^2}{H^3}\left[(\gamma_0 - 3\alpha H)\varepsilon_f - \tau\dot{\Pi}_f\right]H. \tag{18.38}$$

On the other hand, the rate of entropy variation associated to the material fluid

$$\dot{S}_f = \frac{R^3}{T_f\zeta}\Pi_f^2, \tag{18.39}$$

becomes

$$\dot{S}_f = \frac{R^3}{\alpha\varepsilon_f T_f}\left(3\alpha\rho_f H + \tau\dot{H}_f\right)^2. \tag{18.40}$$

The term $\tau\dot{\Pi}_f$ in (18.40) may bear either sign. For decreasing bulk viscous pressure rate, $\dot{\Pi}_f < 0$, since causality demands $\tau > 0$, hence $\dot{S}_h > 0$, and the rate of variation of total entropy is positive. However, if $\dot{\Pi}_f$ is increasing, $\dot{S}_f$ could be negative, which implies that $\dot{S}_f + \dot{S}_h$ could become negative, in clear contradiction with the second law of thermodynamics.

The total rate of entropy production, with $T_f = T_h$, is given by

$$\dot{S} = \frac{8\pi^2}{H^3}\left(\gamma_0\varepsilon_f + \frac{\tau^2\dot{H}_f^2}{3\alpha\varepsilon_f H} + \tau\dot{\Pi}_f\right). \tag{18.41}$$

This is a positive quantity unless the last term on the right-hand side becomes dominantly negative. Although ordinary fluids are not expected to present very large values for $\tau\dot{\Pi}_f$, this cannot be ruled out in principle, especially at the very early stages of cosmic expansion where exotic quantum fields may play a crucial role.

Nevertheless, if the dominant energy condition holds, which in the formalism of EIT reads as

$$\gamma_0\varepsilon_f \geq \tau\dot{\Pi}_f + 3\alpha\varepsilon_f H, \tag{18.42}$$

then combination of (18.41) and (18.42) implies that

$$\dot{S} \geq \frac{8\pi^2}{3\alpha\varepsilon_f H^4}\left(\tau\dot{\Pi}_f + 3\alpha\varepsilon_f H\right)^2 \geq 0. \tag{18.43}$$

In other terms, it can be stated that the second law ($\dot{S} \geq 0$) is guaranteed if and only if the dominant energy condition (18.42) is satisfied. This contrasts with the result of Davies, according to which the second law holds irrespectively of the dominant energy condition (18.34).

18.4 Astrophysical Problems: Gravitational Collapse

The relaxational terms in the transport laws have been exploited to interpret fast explosions or implosions in astrophysics (Martínez and Pavón 1994; Herrera and Falcón 1995; Martínez 1996; Herrera et al. 1997). In rapid processes, as in the fast collapse phase preceding neutron star formation, the relaxational effects are important and the fluid is far from hydrostatic equilibrium. Such effects cannot be accounted for in classical models wherein the evolution of the star is regarded as a sequence of hydrostatic states. In contrast with cosmological problems, two different metrics must be introduced, one for the interior and the other for the exterior of the star. Furthermore, the inhomogeneity generates a heat flux, which plays a decisive role. Among other results, it turns out that the behaviour of the system depends strongly on the observers: for an observer at rest at infinity, the total mass loss of the star is the same but with greater speed (i.e. higher luminosity) than in the nonviscous case, whereas the comoving observer perceives a larger mass loss. Another result is that the energy of the neutrinos at the surface of the star is not correlated with that at the interior. In (Martínez and Pavón 1994; Herrera and Falcón 1995; Martínez 1996; Herrera et al. 1997) it was shown that when the heat flux relaxes, the evolution of the star depends critically on the thermal relaxation time, thermal conductivity, proper energy density and pressure.

Starting from a Maxwell–Cattaneo equation, Herrera and Falcón (1995) have studied the secular stability of nuclear burning in accreting neutron star envelopes, which is at the basis of X-ray bursters models, for times shorter than the effective relaxation time of the heat flux. The characteristic time scales for the growth of the nuclear burning instability spans a wide period, from milliseconds to minutes. The relaxational effects of the heat flux (its relaxation time is of the order of milliseconds for a highly degenerate matter) produce a fast oscillation in the luminosity as a precursor of the X-ray burst.

18.5 Problems

18.1. From (18.3a) show that for a plane universe ($\kappa = 0$) dominated by matter (namely $\varepsilon \sim R^{-3}$), $R(t)$ behaves as $R \sim t^{2/3}$. Show that for an universe dominated by radiation, for which $\varepsilon \sim T^4 \sim R^{-4}$, $R(t)$ behaves as $R \sim t^{1/2}$.

18.2. Compare the entropy in the 2.7 K microwave background radiation with the entropy in the baryons to conclude that the ratio between the number of photons and baryons in the Universe is about 10^8. Assume that the expansion of the Universe is adiabatic and that the present number density of baryons is roughly 1 m^{-3} and that the entropy per baryon is the Boltzmann constant.

18.3. Using the data of Problems 5.4 and 5.5, find the bulk viscosity of a gas composed of photons, electrons, and protons at 3,000 K, with $n = 4,000$ electrons/m^3. Neglect the collisions between photons and protons, and between the particles themselves. See Appendix C for numerical values of the physical constants.

18.4. (a) Starting from (18.7) and assuming that $\Pi = -3\zeta H$, show that a constant bulk viscosity leads to inflationary behaviour of the universe (i.e. behaviour with $H = \text{const}$ and therefore an exponential increase of R with time). (b) Study the stability of the solutions in terms of the dimensionless quantity $c^2 H/(G\zeta)$. (c) Compare the results with those obtained under the assumption that the bulk viscosity is of the form $\zeta = \alpha\varepsilon$ with α a constant. (See Murphy (1973))

18.5. Show that, for a viscous fluid with $p = \lambda\varepsilon$ and with a bulk viscosity $\zeta = a\varepsilon^{1/2}$, the Einstein equations yield a behaviour for the scale factor of the Universe of the form $R \sim t^a$, with $a^{-1} = \frac{3}{2}[1 + \lambda - 2a(6\pi G)^{1/2}]$.

18.6. The mixture of neutrino and electrons is especially relevant at the so-called leptonic era, which lasted between 10^{-3} and 10 s, with temperatures ranging from 10^{12} to 10^{10} K. The cross-section of the neutrino–electron collisions due to weak interactions is

$$\sigma_{\text{wk}} = \left[2\pi G_{\text{F}} k_{\text{B}} T/(hc)^2\right]^2,$$

with the Fermi constant $G_{\text{F}} = 1.4 \times 10^{-62}\,\text{kg}\,\text{m}^5\,\text{s}^{-2}$ (a) Evaluate the neutrino mean free path at the initial and final stages of the leptonic era, for an electron density given by $n = [2\pi k_{\text{B}} T/(hc)]^3$. (b) Determine the neutrino collision time τ and τH, i.e. the ratio of τ to the characteristic expansion time of the universe H^{-1}. (c) The neutrinos are said to decouple from the electrons when $\tau H = 1$; find the decoupling temperature of neutrinos (remember that in a radiation-dominated era, $R \propto t^{1/2}$ and $T \propto t^{-1/2}$).

18.7. The bulk viscosity of a mixture of neutrinos and nuclei in a collapsing stellar core has been estimated to be of the order of $10^{23}\,\mathrm{kg\,m^{-1}\,s^{-1}}$. The compression rate $\nabla \cdot \boldsymbol{v}$ is of the order of $10^3\,\mathrm{s}^{-1}$. Evaluate the entropy production per unit time per baryon for a temperature of 1 MeV and a density of $10^{15}\,\mathrm{kg\,m^{-3}}$. If the time interval during which the bulk viscosity is effective is 1 s, what is the total entropy production per particle?

18.8. The classical entropy production has the form

$$\sigma_{\mathrm{CIT}} = -T^{-1}\Pi\nabla \cdot \boldsymbol{v},$$

whereas the entropy production found in EIT is given by

$$\sigma_{\mathrm{EIT}} = -T^{-1}\Pi[\nabla \cdot \boldsymbol{v} - (\tau/\zeta)\dot{\Pi}].$$

This expression suggests writing $\tau\dot{\Pi} + \Pi = -3\zeta H$. (a) Show that for constant ζ and up to the first order in τ one may write $\Pi = -3\zeta(H - \tau\dot{\Pi})$ for $\nabla \cdot \boldsymbol{v} = 3H$. (b) Evaluate the ratio $\sigma_{\mathrm{EIT}}/\sigma_{\mathrm{CIT}}$ at the beginning of the leptonic era and at the neutrino decoupling time, by using the data of Problem 18.5 (recall that in a radiation-dominated era $R \propto t^{1/2}$).

18.9. Show that if one uses the non-truncated transport equation (18.18) instead of the truncated equation (18.4b), one obtains (for $0 < \nu < \frac{1}{2}$) a de Sitter expansion with constant reduced Hubble factor $h = H/H_0 = [2/(2-\gamma_0)]^{1/(2\nu-1)}$ instead of $h = 1$, with H_0 and ν defined in (18.10) and (18.5) respectively (see Romano, Pavón (1994)).

18.10. Einstein introduced a ‘cosmological constant’ Λ by writing instead of (18.1)

$$R_{\mu\nu} - \frac{1}{2}g_{\mu\nu}R = 8\pi G T_{\mu\nu} - \Lambda g_{\mu\nu}.$$

A possible solution to the puzzle of the cosmological constant (i.e. to understand its low present value in contrast with its possibly high values in the past) has been to introduce a variable cosmological ‘constant’ in the Einstein equations. (a) Show that in the presence of a time-dependent cosmological constant, the entropy production reads as

$$S^{\alpha}{}_{;\alpha} = \frac{9\zeta H^2}{T} - \frac{c^5}{8\pi G}\frac{\dot{\Lambda}}{T}$$

(Méndez, Pavón (1996)). (b) Show that if Λ depends on t as $\sim t^{-2}$, its effects are similar to those of a bulk viscosity in a fluid with null cosmological constant in the radiation era (Beesham (1993)).

18.11. Assume that instead of the classical equation $\Pi = -3\zeta H$ one has a nonlinear relation yielding a saturation behaviour as the flux limiters used in Sect. 10.6, i.e.

$$\Pi = -\frac{3\zeta H}{\sqrt{1 + (aH)^2}}.$$

Find which requirements should obey the parameter a in order that the fluid fulfils the dominant energy condition (18.21) at high values of H (see Maartens, Méndez 1997), for the use of a slightly different model of flux limiter).

18.12. From the arguments of Sect. 18.3, estimate the entropy of the current cosmological horizon, by taking for the Hubble parameter H the approximate value $H \approx 72\ \mathrm{Km\,s^{-1}}\ /\mathrm{Mpc}$, pc standing for parsec $\approx$ 3.26 light years.

Appendix A
Summary of Vector and Tensor Notation

In general, we have used tensorial notation throughout the book. Tensors of rank 0 (scalars) are denoted by means of italic type letters a; tensors of order 1 (vectors) by means of boldface italic letters $\boldsymbol{a}$ and tensors of rank two and higher orders by capital boldface letters **A**. In some special circumstances, three-dimensional Cartesian coordinates are used:

$\boldsymbol{a}(a_i)$	vector,
$\mathrm{A}(A_{ij})$	tensor of rank 2,
$\mathrm{U}(\delta_{ij})$	unit tensor (δ_{ij} is Kronecker's symbol),
$\mathrm{J}(J_{ijk})$	tensor of rank 3.

A.1 Symmetric and Antisymmetric Tensors

Denoting by superscript T the transpose, the symmetric and antisymmetric tensors are respectively defined as

$$\text{symmetric } \mathbf{A} = \mathbf{A}^T \ (A_{ij} = A_{ji}), \quad \text{antisymmetric } \mathbf{A} = -\mathbf{A}^T \ (A_{ij} = A_{ji}). \tag{A.1}$$

The trace of a tensor is defined as the sum of its diagonal components, namely

$$\text{trace of a tensor Tr } \mathbf{A} = \sum_i A_{ii}\,. \tag{A.2}$$

A.2 Decomposition of a Tensor

It is customary to decompose second-order tensors into a scalar (invariant) part A, a symmetric traceless part $\overset{0}{\mathbf{A}}$, and an antisymmetric part $\mathbf{A}^a$ as follows

$$\mathbf{A} = \tfrac{1}{3}(\mathrm{Tr}\,\mathbf{A})\mathbf{U} + \overset{0}{\mathbf{A}} + \mathbf{A}^a = \tfrac{1}{3}A\delta_{ij} + \overset{0}{A}_{ij} + A^a_{ij}. \tag{A.3}$$

Note that this decomposition implies $\mathbf{Tr}\ \overset{0}{\mathbf{A}} = 0$ $(\sum_i \overset{0}{A}_{ii} = 0)$.

The antisymmetric part of the tensor is often written in terms of an axial vector $\boldsymbol{a}^a$ whose components are defined as

$$a^a_i = \sum_{j,k} \varepsilon_{ijk} A^a_{jk}, \tag{A.4}$$

where the permutation symbol ε_{ijk} has the values

$$\varepsilon_{ijk} = \begin{cases} +1 & \text{for even permutations of indices (i.e. } 123,\ 231,\ 312) \\ -1 & \text{for odd permutations of indices (i.e. } 321,\ 132,\ 213) \\ 0 & \text{for repeated indices.} \end{cases} \tag{A.5}$$

A.3 Scalar (or Dot) and Tensorial (Inner) Products

We have used for the more common products the following notation:

Dot product between

$$\begin{aligned} &\text{two vectors} && \boldsymbol{a}\cdot\boldsymbol{b} = \sum_i a_i b_i \ \text{(scalar)}, \\ &\text{a vector and a tensor} && \mathbf{A}\cdot\boldsymbol{b} = \sum_j a_{ij} b_i \ \text{(vector)}, \\ &\text{a tensor and a vector} && \boldsymbol{b}\cdot\mathbf{A} = \sum_j b_j a_{jk} \ \text{(vector)}, \\ &\text{two tensors} && \mathbf{A}\cdot\mathbf{B} = \sum_k a_{ik} b_{kj} \ \text{(tensor)}. \end{aligned} \tag{A.6}$$

Double scalar product between tensors

$$\mathbf{A}:\mathbf{B} = \sum_{i,k} a_{ik} b_{kj} \ \text{(scalar)}. \tag{A.7}$$

The trace of a tensor may also be written in terms of its double scalar product with the unit matrix as $\mathrm{Tr}\mathbf{A} = \mathbf{A}:\mathbf{U}$.

A.4 (Inner) Tensorial Product (also Named Dyadic Product)

$$\begin{aligned}
&\text{between two vectors } (\boldsymbol{ab})_{ij} = a_i b_j && \text{(tensor of rank 2)},\\
&\text{a vector and a tensor } (\boldsymbol{a}\mathbf{B})_{ijk} = a_i B_{jk} && \text{(tensor of rank 3)},\\
&\text{a tensor and a vector } (\mathbf{B}\boldsymbol{a})_{ijk} = B_{ij} a_k && \text{(tensor of rank 3)},\\
&\text{two tensors } (\mathbf{AB})_{ijkl} = A_{ij} B_{kl} && \text{(tensor of rank 4)}.
\end{aligned} \tag{A.8}$$

A.5 Cross Multiplication Between Two Vectors and Between a Tensor and a Vector

$$\begin{aligned}
(\boldsymbol{a} \times \boldsymbol{b})_k &= \varepsilon_{ijk} a_i b_j && \text{(vector)},\\
(\mathbf{B} \times \boldsymbol{a})_{ik} &= \sum_{j,l} \varepsilon_{jkl} B_{ij} b_l && \text{(tensor)}.
\end{aligned} \tag{A.9}$$

A.6 Differentiation

The most usual differential operators acting on tensorial fields may be expressed in terms of the so-called nabla operator, defined in Cartesian coordinates as

$$\nabla = \left(\frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \frac{\partial}{\partial x_3} \right). \tag{A.10}$$

Gradient (defined as dyadic product)

$$(\nabla a)_i = \frac{\partial a}{\partial x_i} \quad \text{(vector)}, \qquad (\nabla \boldsymbol{a})_{ij} = \frac{\partial a_j}{\partial x_i} \quad \text{(tensor of rank 2)},$$

$$(\nabla \mathbf{A})_{jki} = \frac{\partial A_{jk}}{\partial x_i} \quad \text{(tensor of rank 3)}.$$

Divergence (defined as the scalar product)

$$\nabla \cdot \boldsymbol{a} = \sum_i \frac{\partial a_i}{\partial x_i} \quad \text{(scalar)}, \qquad (\nabla \cdot \mathbf{A})_i = \sum_j \frac{\partial A_{ji}}{\partial x_j} \quad \text{(vector)}. \tag{A.11}$$

Rotational or curl (defined as the cross product)

$$(\nabla \times \boldsymbol{a})_i = \sum_{j,k} \varepsilon_{ijk} \frac{\partial a_k}{\partial x_j} \quad \text{(vector)}, \quad (\nabla \times \mathbf{A})_{ik} = \sum_{j,l} \varepsilon_{ijk} \frac{\partial A_{ij}}{\partial x_l} \quad \text{(tensor of rank 2)}.$$

The most usual second-order differential operator in tensorial analysis is the Laplacian, defined as

$$\nabla \cdot \nabla = \sum_i \frac{\partial^2}{\partial x_i \partial x_i} \,. \tag{A.12}$$

A.7 Tensor Invariants

Some combinations of the elements of a tensor remain invariant under changes of coordinates. Such invariant combinations are

$$\begin{aligned} I_1 &= \mathrm{Tr}\mathbf{A} = \mathbf{A} : \mathbf{U} = \sum_i A_{ii}, \\ I_2 &= \mathrm{Tr}\mathbf{A} \cdot \mathbf{A} = \mathbf{A} : \mathbf{A} = \sum_{i,j} A_{ij} A_{ji}, \\ I_3 &= \mathrm{Tr}\mathbf{A} \cdot \mathbf{A} \cdot \mathbf{A} = \sum_{i,j,k} A_{ij} A_{jk} A_{ki}. \end{aligned} \tag{A.13}$$

Other invariant combinations may also be formed, but they are combinations of I_1, I_2 and I_3; for instance, one often finds the invariants I, II and III defined as

$$I = I_1, \qquad II = \tfrac{1}{2}(I_1^2 - I_2), \qquad III = \tfrac{1}{6}(I_1^3 - 3I_1 I_2 + 2I_3) = \det \mathbf{A}. \tag{A.14}$$

The invariants I, II and III appear as coefficients in the "characteristic equation" $\det(\lambda \mathbf{U} - \mathbf{A}) = 0$.

It is also possible to form joint invariants of two tensors **A** and **B** as

$$I_{11} = \mathrm{Tr}\,\mathbf{A} \cdot \mathbf{B}, \quad I_{21} = \mathrm{Tr}\,\mathbf{A} \cdot \mathbf{A} \cdot \mathbf{B}, \quad I_{12} = \mathrm{Tr}\,\mathbf{A} \cdot \mathbf{B} \cdot \mathbf{B}, \quad I_{22} = \mathrm{Tr}\,\mathbf{A} \cdot \mathbf{A} \cdot \mathbf{B} \cdot \mathbf{B}. \tag{A.15}$$

Appendix B
Useful Integrals in the Kinetic Theory of Gases

We present here some useful integrals appearing in several calculations based on the kinetic theory of gases. Let $F(\boldsymbol{C})$ be any scalar function of the peculiar velocity $\boldsymbol{C}$ such that the integrals appearing below converge, and let C_x and C_y be two components of $\boldsymbol{C}$. Then

$$\int F(\boldsymbol{C}) C_x^2 \mathrm{d}\boldsymbol{C} = \frac{1}{3} \int F(\boldsymbol{C})\, \boldsymbol{C}^2 \mathrm{d}\boldsymbol{C}, \tag{B.1}$$

$$\int F(\boldsymbol{C}) C_x^4 \mathrm{d}\boldsymbol{C} = \frac{1}{5} \int F(\boldsymbol{C})\, \boldsymbol{C}^4 d\boldsymbol{C}, \tag{B.2}$$

$$\int F(\boldsymbol{C}) C_x^2 C_y^2 \mathrm{d}\boldsymbol{C} = \frac{1}{15} \int F(\boldsymbol{C})\, \boldsymbol{C}^4 \mathrm{d}\boldsymbol{C}. \tag{B.3}$$

The following definite integrals are also useful

$$\int_0^\infty \exp(-\alpha C^2) C^r \mathrm{d}C = \frac{\sqrt{\pi}}{2} \frac{1}{2} \frac{3}{2} \frac{5}{2} \cdots \frac{r-1}{2} \alpha^{-(r+1)/2} \qquad (r \text{ even}), \tag{B.4}$$

$$\int_0^\infty \exp(-\alpha C^2) C^r \mathrm{d}C = \frac{1}{2} \left[(r-1)/2\right]! \alpha^{-(r+1)/2} \quad (r \text{ odd}). \tag{B.5}$$

Appendix C
Some Physical Constants

Boltzmann's constant	k_B	1.38×10^{-23} J K^{-1} $= 8.62 \times 10^{-5}$ eV K^{-1}
Stefan-Boltzmann's constant	σ_0	5.67×10^{-8} W m^{-2} K^{-4}
Radiation constant	$a = 4\sigma_0/c$	7.56×10^{-16} J m^{-3} K^{-4}
Atomic mass unit	amu	1.66×10^{-27} kg
Electron charge	e	1.60×10^{-19} C
Electron mass	m_e	9.11×10^{-31} kg
Proton mass	m_p	1.673×10^{-27} kg
Planck's constant	h	6.63×10^{-34} J s $= 4.14 \times 10^{-15}$ eV s

References

Abramo LRW, Lima JAS (1996) Inflationary models driven by adiabatic matter creation. Class Quant Grav 13:2953–2964

Ackerson BJ, Clark NA (1981) Shear-induced melting. Phys Rev Lett 46:123–127

Akcasu AZ, Daniels E (1970) Fluctuation analysis in simple fluids. Phys Rev A 2:962–975

Alley WE, Alder BJ (1983) Generalized transport coefficients for hard spheres. Phys Rev A 27:3158–3173

Alsemeyer H (1976) Density profiles in argon and nitrogen shock waves measured by absorption of an electron beam. J Fluid Mech 74:497–513

Alvarez FX, Jou D (2007) Memory and the non-local effects in heat transport from diffusive and ballistic regimes. Appl Phys Lett 90:083109 (3p)

Alvarez FX, Jou D, Sellitto A (2009) Phonon hydrodynamics and phonon-boundary scattering in nanosystems. J Appl Phys 105:014317 (5p)

Andreev NS, Boiko GG, Bokov NA (1970) Small-angle scattering and scattering of visible light sodium-silicate glasses of phase separation. J Non-Cryst Solids 5:41–54

Anile AM, Majorana A (1981) Shock structure for heat conducting and viscid fluids. Meccanica 16:149–156

Anile AM, Muscato O (1995) An improved thermodynamic model for carrier transport in semiconductors. Phys Rev B 51:16728–16740

Anile AM, Pennisi S (1992) Extended thermodynamics of the Blotekjaer hydrodynamical model for semiconductors. Continuum Mech Thermodyn 4:187–197

Anile AM, Pennisi S, Sammartino M (1991) A thermodynamic approach to Eddington factors. J Math Phys 32:544–550

Anile AM, Pluchino S (1984) Linear wave modes for dissipative fluids with rate type constitutive equations. Meccanica 19:104–110

Anile AM, Allegretto W, Ringhofer C (2003) Mathematical problems in semiconductor physics. Lecture Notes in Mathematics, vol 1823. Springer, Berlin

Anile AM, Marrocco A, Romano V, Sellier JM (2005) 2D numerical simulation of the MEP energy-transport model with a mixed finite elements scheme. J Comp Electron 4:231–259

Antaki PJ (1998) Importance on non-Fourier heat conduction in solid-phase reactions. Combust Flame 112:329–334

Astarita G, Marucci G (1974) Principles of non-Newtonian Fluid Mechanics. McGraw-Hill, New York

Aziz MJ, Kaplan T (1988) Continuous growth model for interface motion during alloy solidification. Acta Metall 36:2335–2347

Baccarani G, Wordemann MR (1985) An investigation of steady state velocity over shoot in silicon. Solid State Electron 28:407–416

Bali R, Singh JP (2008) Bulk viscous Bianchi type I cosmological models with time-dependent cosmological term Λ. Int J Theor Phys 47:3288–3297

Bampi F, Morro A (1984) Non-equilibrium thermodynamics: a hidden variable approach. In: Casas-Vázquez J, Jou D, Lebon G (eds) Recent Developments in Non-equilibrium Thermodynamics. Lecture Notes in Physics, vol 199. Springer, Berlin

Banach Z (1987) On the mathematical structure of Eu's modified moment method. Physica A 159:343–368

Banach Z (2000) An extended Gibbs relation for the relativistic Boltzmann entropy: classical and quantum gases. Physica A 275:405–428

Banach Z and Pierarski (1993) On the concept of temperature for systems not infinitesimally near to equilibrium. Mater Sci Forum 123–125:69–78

Baranyai A (2000) Numerical temperature measurements in far from equilibrium systems. Phys Rev E 61:R3306–3309

Baranyai A, Cummings PT (1995) Fluctuations close to equilibrium. Phys. Rev. E 52:2198–2203

Baranyai A, Evans DJ (1989) Direct entropy calculation from computer simulation of liquids. Phys Rev A 40:3817–3822

Baranyai A, Evans DJ, Daivis PJ (1992) Isothermal shear-induced flow. Phys Rev A 46:7593–7600

Barrow JD (1988) String-driven inflationary and deflationary cosmological models. Nucl Phys B 310:743–763

Barton G (1979) Some surface effects in the hydrodynamic model of metals. Rep Prog Phys 42:963–1016

Bataille J, Kestin J (1975) L'interprétation physique de la thermodynamique rationelle. J Mécanique 14:365–384

Bauer H-J (1965) Phenomenological theories of the relaxation phenomena in gases. In: Mason WP (ed) Physical Acoustics, vol 2A. Academic, New York

Beck C, Schlögl F (1993) Thermodynamics of Chaotic Systems. Cambridge University Press, Cambridge

Bedeaux D, Albano AM, Mazur P (1976) Boundary conditions and thermodynamics. Physica A 147:438–462

Beenakker CWJ (1997) Random-matrix theory of quantum transport. Rev Mod Phys 69:731–808

Beesham A (1993) Cosmological models with constant deceleration parameter and bulk viscosity. Gen Rel Grav 25:561–565

Belinskii VA, Nikomarov S, Khalatnikov IS (1979) Investigation of the cosmological evolution of a viscoelastic matter with causal thermodynamics. Sov Phys JETP 50:213–221

Berdichevsky VL (1997) Thermodynamics of Chaos and Order. Longman, Essex

Beris AN (2003) Simple non-equilibrium thermodynamics to polymer rheology. In: Binding DM, Walters K (eds) Rheology Reviews 2003. The British Society of Rheology, Aberystwyth, pp 33–75

Beris AN, Edwards BJ (1994) Thermodynamics of Flowing Systems with Internal Microstructure. Oxford University Press, Oxford

Beris AN, Mavrantzas (1994) Te compatibility between various macroscopic formulations for the concentration and flow of dilute polymer solutions. J Rheol 38:1235–1250

Berne BJ (ed) (1977) Statistical Mechanics (Part B: Time-dependent Processes). Plenum, New York

Berne BJ, Pecora R (1976) Dynamic Light Scattering with Application to Chemistry, Biology and Physics. Wiley, New York

Bidar H (1997) Non-equilibrium free energy under shear flow. J Non-Equilib Thermodyn 22: 156–161

Bidar H, Jou D (1998) A generalized Gibbs equation for nuclear matter out of equilibrium. Phys Rev C 57:2068–2070

Bidar H, Jou D, Criado-Sancho M (1997) Thermodynamics of ideal gases under shear: a maximum-entropy approach. Physica A 233:163–174

Binder K, Fratzl P (2001) Spinodal decomposition. In: Kostorz G (ed) Phase Transformations in Materials. Wiley-VCH, Wienheim

Biot MA (1970) Variational Principles in Heat Transfer. Oxford University Press, Oxford

Bird RB, De Gennes PG (1983) Discussion about the principle of objectivity. Physica A 118:43–47

Bird RB, Armstrong RC, Hassager O (1987a) Dynamics of polymeric liquids. Fluid Mechanics, 2nd edn, vol 1. Wiley, New York

Bird RB, Curtiss CF, Armstrong RC, Hassager O (1987b) Dynamics of polymeric liquids. Kinetic Theory, 2nd edn, vol. 2. Wiley, New York

Blotekjaer K (1970) Transport equations for electrons in two-valley semiconductors. IEEE Trans Electron Devices 17:38–47

Bodenshatz E, Pech W, Ahlers G (2000) Recent developments in Rayleigh-Bénard convection. Ann Rev Fluid Mech 32:851–919

Boillat G, Ruggeri T (1996) Relativistic gas: moment equations and maximum wave velocity. J Math Phys 40:6399–6406

Boillat G, Strumia A (1988) Limitation des vitesses d'onde et de choc quand la densité relativiste d'entropie ou d'energie est convexe, C R Acad Sci Paris 307:111–114

Boon JP, Yip S (1980) Molecular Hydrodynamics. McGraw-Hill, New York

Brenner H (1970) Rheology of two-phase systems, Ann Rev Fluid Mech 2:137–176

Bressan A (1978) Relativistic Theories of Materials. Springer, Berlin

Brey JJ and Santos A (1992) Nonequilibrium entropy of a gas. Phys. Rev A 45:8566–8572

Bridgman PW (1943) The Nature of Thermodynamics. Harvard University Press, Cambridge

Cahn JW, Hilliard JE (1958) Free energy of a nonuniform system. I. Interfacial free energy. J Chem Phys 28:258–267

Callen HB (1985) Thermodynamics and an Introduction to Thermostatistics, 2 edn. Wiley, New York

Calvão MO, Salim JM (1992) Extended thermodynamics of Friedmann–Robertson–Walker models in the Landau-Lifshitz frame. Class Quant Grav 9:127–135

Calvão MO, Lima JAS, Waga I (1992) On the thermodynamics of matter creation in cosmology. Phys Lett A 162:223–226

Camacho J (1995) Third law of thermodynamics in the presence of a heat flux. Phys Rev E 51: 220–225

Camacho J, Jou D (1990) On the thermodynamics of dilute dumbbell solutions under shear. J Chem Phys 92:1339–1344

Camacho J, Jou D (1992) H theorem and the telegrapher type kinetic equations. Phys Lett A 171:26–30

Camacho J, Zakari M (1994) Irreversible thermodynamic analysis of a two-layer system. Phys Rev E 50:4233–4236

Caplan SR, Essig A (1983) Bioenergetics and Linear Non-equilibrium Thermodynamics. The Steady State. Harvard University Press, Cambridge

Carrassi M, Morro A (1972) A modified Navier–Stokes equations and its consequences on sound dispersion. Nuovo Cimento B 9:321–343; (1984), 13:281–289

Carreau PJ (1972) Rheological equations from molecular network theories. Trans Soc Rheol 16:99–127

Casas-Vázquez J, Jou D (2003) Temperature in non-equilibrium states: a review of open problems and current proposals. Rep Prog Phys 66:1937–2023

Casas-Vázquez J, Jou D, Lebon G (eds) (1984) Recent Developments in Non-equilibrium Thermodynamics. Lecture Notes in Physics, vol. 199. Springer, Berlin

Casimir HBG (1945) On Onsager's principle of microscopic irreversibility. Rev Mod Phys 17: 343–350

Castillo VM, Hoover WM (1988) Comment on Maximum of the local entropy production becomes minimal in stationary processes. Phys Rev Lett 81:5700 (1p)

Cattaneo C (1948) Sulla conduzione del calore, Atti Seminario Mat. Fis. Univ. Modena 3:83–101

Cavalli-Sforza LL, Menozzi P, Piazza A (1993) Demic expansions and human evolution. Science 259:639–646

Chapman S, Cowling TG (1970) The Mathematical Theory of Non-uniform Gases. Cambridge University Press, Cambridge

Chen G (2001) Ballistic-diffusion heat conduction equation. Phys Rev Lett 86:2297–2300

Chen G (2002) Ballistic-diffusive equations for transient heat conduction from nano-to macroscales. J Heat Transf 124:320–329

Chen G (2004) Nanoscale Energy Transport and Conversion. Oxford University Press, Oxford

Chen M (1999) On the geometric structure of thermodynamics. J Math Phys 40:830–837

Chester M (1963) Second sound in solids. Phys Rev 131:2013–2015

Chester M (1966) High-frequency thermometry. Phys Rev 145:76–80

Chiu HY, Desphbande VV, Postma HWC, Lau CN, Miko C, Forro L, Bockrath M (2005) Ballistic phonon thermal transport in multiwalled carbon nanotubes. Phys Rev Lett 95:226101 (4p)

Christiansen RF, Leppard WR (1974) Steady-state and oscillatory flow properties of polymer solutions. Trans Soc Rheol 18:65–86

Chung C-H, Yip S (1969) Generalized hydrodynamics and time correlation functions. Phys Rev 182:323–339

Ciancio V, Verhas J (1991) A thermodynamic theory for heat radiation through the atmosphere. J Non-Equilib Thermodyn 16:57–65

Ciancio V, Restuccia L, Kluitenberg GA (1990) A thermodynamic derivation of equation for dielectric relaxation phenomena in anisotropic polarisable media. J Non-Equilib Thermodyn 15:157–172

Cimmelli VA (2002) Boundary conditions in the presence of internal variables. J Non-Equilib Thermodyn 27:327–348

Cimmelli VA, Frischmuth K (2005) Nonlinear effects in thermal wave propagation near zero absolute temperature. Physica B 355:147–157

Cimmelli VA, Kosinsky W (1991) Nonequilibrium semiempirical temperature in materials with thermal relaxation Arch Mech 43:753–767

Clause PJ and Balescu R (1982) A non-linear approach to the kinetic theory of heat conductivity in a plasma. Plasma Phys 24:1429–1450

Coleman BD (1964) Thermodynamics of materials with memory. Arch Rat Mech Anal 17:1–46

Coleman BD, Newman D (1988) Implications of a nonlinearity in the theory of second sound in solids. Phys Rev B 37:1492–1498

Coleman BD, Noll W (1963) The thermodynamics of elastic materials with heat conduction and viscosity. Arch Rat Mech Anal 13:167–178

Coleman BD, Truesdell C (1960) On the reciprocal relations of Onsager. J Chem Phys 33:28–31

Coleman BD and Owen DR (1974) A mathematical foundation for thermodynamics, Arch Rat Mech Anal 54:1

Coleman BD, Markowitz H, Noll W (1966) Viscometric Flows of Non-Newtonian Fluids. Springer, New York

Conforto F, Giambò S (1996) An extended thermodynamics description of thermal, viscous and dielectric phenomena in fluid systems. J Non-Equilib Thermodyn 21:260–269

Corbet AB (1974) New thermodynamic variables for a nonequilibrium system. Phys Rev A 9:1371–1384

Crank J (1975) The Mathematics of Diffusion. Clarendon, Oxford

Criado-Sancho M, Casas-Vázquez J (2004) Termodinámica Química y de los Processos Irreversibles, 2nd edn. Pearson/Addison-Wesley, Madrid

Criado-Sancho M, Llebot JE (1993) Behaviour of entropy in hyperbolic heat transport. Phys Rev E 47:4104–4108

Criado-Sancho M, Jou D, Casas-Vázquez J (1999) Ginzburg-Landau expression for the free energy of polymer solutions under flow. Physica A 274:466–475

Criado-Sancho M, Llebot JE (1993b) On the admissible values of the heat flux in hyperbolic heat transport. Phys Lett A 177:323–326

Criado-Sancho M, Jou D, Casas-Vázquez J (2006) Nonequilibrium kinetic temperatures in flowing gases. Phys Lett A 350:339–341

Criminale WO, Ericksen JL, Filbey GL (1957) Steady shear flow of non-Newtonian fluids. Arch Rat Mech Anal 1:410–417

Crisanti A, Ritort F (2003) Violation of the fluctuation-dissipation theorem in glassy systems: basic notions and the numerical evidence. J Phys A: Math Gen 36:R181–R290

Crochet MJ, Davies A, Walters K (1984) Numerical Simulations of Non-Newtonian Flow. Elsevier, Amsterdam

Curzon FL, Ahlborn B (1975) Efficiency of a Carnot engine at maximum power output Am J Phys 43:22–24

Daivis PJ (2008) Thermodynamic relationships for shearing linear viscoelastic fluids. Non-Newtonian Fluid Mech 152:120–128

Danielewicz P (1984) Transport properties of excited nuclear matter and the shock-wave profile. Phys Lett B 146:168–175

D'Anna G, Mayor P, Barrat A, Loreto V, Nori F (2003) Observing Brownian motion in vibration-fluidized granular matter. Nature 424:909–912

Datta S (2002) Electronic Transport in Mesoscopic Systems. Cambridge University Press, Cambridge, UK

Dauby PC, Lebon G (1990) Constitutive equations of rheological materials: towards a thermodynamic unified approach. Appl Math Lett 3:45–48

Davies PCW (1987) Cosmological horizons and the generalised second law of thermodynamics. Class Quantum Grav 4:L225–L228

Day W (1977) An objection against using entropy as a primitive concept in continuum thermodynamics. Acta Mech 27:251–255

De Groot SR, Mazur P (1962) Non-equilibrium Thermodynamics. North-Holland, Amsterdam

De Felice LJ (1981) Introduction to Membrane Noise. Plenum, New York

Dedeurwaerdere T, Casas-Vázquez J, Jou D, Lebon G (1996) Foundations and applications of a mesoscopic thermodynamic theory of fast phenomena. Phys Rev E 53:498–506

Del Castillo LF, Dávalos-Orozco LA (1990) Dielectric relaxation in polar and viscoelastic fluids. J Chem Phys 93:5147–5155

Del Castillo LF, Rodríguez RF (1989) Extended thermodynamics and membrane transport. J Non-Equilib Thermodyn 14:127–142

Del Castillo LF, Dávalos-Orozco LA, García-Colín LS (1997) Ultrafast dielectric relaxation response of polar liquids. J Chem Phys 106:2348–2354

Dempsey J, Halperin BI (1992) Magnetoplasma excitations in parabolic quantum wells: Hydrodynamic model. Phys Rev B 45:1719–1735

Denbigh RG (1950) The Thermodynamics of the Steady State. Wiley, New York

Denicol GS, Kodama T, Koide T, Mota Ph (2007) Effects of finite size and viscosity in relativistic hydrodynamics. Nucl Phys A 787:60c–67c

Denicol GS, Kodama T, Koide T, Mota Ph (2008) Shock propagation and stability in causal dissipative hydrodynamics. Phys Rev C 78:034901 (12p)

Doi M, Edwards SF (1986) The Theory of Polymer Dynamics. Clarendon, Oxford

Domínguez R, Jou D (1995) Thermodynamic pressure in nonequilibrium gases. Phys Rev E 51:158–162

Domínguez-Cascante R, Faraudo J (1996) Non-equilibrium corrections to the pressure tensor due to an energy flux. Phys Rev E 54:6933–6935

Dreyer W, Struchtrup H (1993) Heat pulse experiments revisited. Continuum Mech Thermodyn 5:3–50

Dreyer W, Weiss W (1986) The classical limit of relativistic extended thermodynamics. Ann Inst Henri Poincaré 45:401–418

Drucker DC (1967) Introduction to Mechanics of Deformable Bodies. McGraw-Hill, New York

Dufty JW and McLennan JA (1974) Persistent correlation in diffusion. Phys Rev A 9:1266–1272

Duhem P (1911) Traité d'énergétique ou de thermodynamique générale. Gauthier-Villars, Paris

Dunn JE, Fosdick RL (1974) Thermodynamics, stability, and boundedness of fluids of complexity 2 and fluids of second grade. Arch Rat Mech Anal 56:191–252

Durning CJ, Tabor M (1986) Mutual diffusion in concentrated polymer solutions under a small driving force. Macromolecules 19:2220–2232

Eckart C (1940) The thermodynamics of irreversible processes. I–III. Phys Rev 58:267–269, 269–275, 919–924; IV, Phys. Rev. (1948), 73:373–382

Edelen DGD, McLennan JA (1973) Material indifference: a principle or a convenience. Int J Eng Sci 11:813–817

Eringen AC (1967) Mechanics of Continua. Wiley, New York

Ernst MH, Hauge EH, van Leeuwen JMJ (1976) Asymptotic time behaviour of correlation functions. III. Local equilibnrium and mode-coupling theory. J. Stat Phys. 15:23–58

Eu BC (1991) Revision of the modified moment method and a differential form for the compensated part of the entropy. Physica A 171:285–312

Eu BC (1992) Kinetic Theory and Irreversible Thermodynamics. Wiley, New York

Eu BC (1998) Nonequilibrium Statistical Mechanics: Ensemble Method. Kluwer, Dordrecht

Eu BC and Garcia-Colín LS (1996) Nonequilibrium thermodynamics and temperature. Phys Rev E 54:2510–2512

Evans DJ (1989) On the entropy of nonequilibrium states. J Stat Phys 57:745–758

Evans DJ, Hanley HJM (1980) A thermodynamics of steady homogeneous shear flows. Phys Lett A 80:175–179

Evans DJ, Morriss GP (1990) Statistical Mechanics of Non-equilibrium Liquids. Academic, London

Evans DJ, Searles DJ (2002) The fluctuation theorem. Adv Phys 51:1529–1585

Fai G, Danielewicz P (996) Non-equilibrium modifications of the nuclear equation of state. Phys Lett B 373(1):5–8

Fedotov S (1998) Traveling waves in a reaction-diffusion system: Diffusion with finite velocity and Kolmogorov–Petrovskii–Piskunov kinetics. Phys Rev E 58:5143–5145

Ferrer M, Jou D (1995) Information-theoretical analysis of a classical relativistic gas under a steady heat flow. Am J Phys 63:437–441

Finlayson B (1972) The Method of Weighted Residuals and Variational Principles. Academic, New York

Fort J, Jou D and Llebot JE (1998) Measurable temperatures in nonequilibrium radiative systems, Physica A 248:97–110

Fort J, Jou D and Llebot JE (1999) Temperature and measurement: comparison between two models of nonequilibrium radiation. Physica A 269:439–454

Fort J, Méndez V (2002) Wavefronts in time-delayed reaction-diffusion systems. Theory and comparison with experiments. Rep Prog Phys 65:895–954

Frankel NA, Acrivos A (1970) The constitutive equations for a dilute emulsion. J Fluid Mech 44:65–78

Friedrichs KO and Lax PD (1971) Systems of conservation equations with a convex extension. Proc. Natl. Acad Sci USA 68:1686

Frisch HL (1980) Sorption and transport in glassy polymers-a review. Polym Eng Sci 20:2–13

Fröhlich H, Kremer F (eds) (1983) Coherent Excitations in Biological Systems. Springer, Berlin

Galenko P (2004) Morphological transitions in crystal patterns at high solidification rates. In: Vincenzini, Faenza P (ed) Computational Modeling and Simulation of Materials III. Techna Group Publishers, Italy, pp 551–558

Galenko P (2007) Solute trapping and diffusionless solification in a binary system. Phys Rev E 76:031606 (9 p)

Galenko P, Danilov DA (2000) Selection of the dynamically stable regime of rapid solidification front motion in an isothermal binary alloy. J Cryst Growth 216:512–526

Galenko PK and Danilov DA (2000b) Steady-state shapes of growing crystals in the field of local nonequilibrium diffusion. Phys Lett A 272:207–217

Galenko P, Danilov DA (2004) Linear morphological stability analysis of the solid-liquid interface in rapid solidification of a binary system. Phys Rev E 69:051608 (14p)

Galenko P, Krivilyov MD (2000) Modelling of crystal pattern formation in isothermal undercooled alloys. Model Simul Mater Sci Eng 8:81–94

Galenko P, Lebedev V (2008) Nonequilibrium effects in spinodal decomposition of a binary system. Phys Lett A 372:985–989

García-Colín LS (1991) Extended irreversible thermodynamics beyond the linear regime: a critical overview. J Non-Equilib Thermodyn 16:89–128

García-Colín LS (1995) Extended irreversible thermodynamics: an unfinished task. Mol Phys 86:697–706

García-Colín LS, López de Haro M, Rodríguez RF, Casas-Vázquez J, Jou D (1984) On the foundations of extended irreversible thermodynamics. J Stat Phys 37:465–484

Gariel J, Le Denmat G (1994) Relationship between two theories of dissipative relativistic hydrodynamics applied to cosmology. Phys Rev D 50:2560–2566

Garrido PL, Hurtado P, Nadrowski B (2001) Simple one-dimensional model of heat conduction, which obeys Fourier's law. Phys Rev Lett 86:5486–5489

Garzó V, Santos A (2003) Kinetic Theory of Gases in Shear Flows. Nonlinear Transport. Kluwer, Dordrecht

Germain P (1973) Cours de mécanique des milieux continus, Masson, Paris

Ghosh K, Dill KA, Inamdar MM, Seitaridou E, Phillips R (2006) Teaching the principles of statistical dynamics. Am J Phys 74:123–133

Giannozzi P, Grosso G, Moroni S, Parravicini GP (1988) The ordinary and matrix continued fractions in the thermodynamic analysis of Hermitian and relaxation operators. Appl Numer Math 4:273–295

Giardina R, Livi R, Politi A, Vassalli M (2000) Finite thermal conductivity in 1-D lattices. Phys Rev Lett 84:4029–4032

Gibbons GW, Hawking SW (1977) Cosmological events horizons, thermodynamics, and particles creation. Phys Rev D 15:2738–2751

Gibbs JW (1948) The collected works of J.W. Gibbs. Thermodynamics, vol 1. Yale University Press, Yale

Giesekus H (1982) A simple constitutive equation for polymer fluids based on the concept of deformation dependent tensorial mobility. J Non-Newtonian Fluid Mech 11:69–109

Glansdorff P, Prigogine I (1964) On a general evolution criterion in macroscopic physics. Physica 30:351–374

Glansdorff P, Prigogine I (1971) Thermodynamics of Structure, Stability and Fluctuations. Wiley, New York

Godoy S, García-Colín LS (1999) Compatibility of the Landauer diffusion coefficient with classical transport theory. Physica A 268:65–74

Goldstein H (1975) Classical Mechanics, 2nd edn. Addison-Wesley, Reading, MA

Goldstein S (1951) On diffusion by discontinuous movements and on the telegraph equation. Quart J Mech Appl Math 4:129–156

Gollub JP, Langer JS (1999) Pattern formation in non-equilibrium physics. Rev Mod Phys 71:S396–S403

Gorban AN, Karlin IV (2005) Invariant Manifolds for Physical and Chemical Kinetics. Lectures Notes in Physics. Springer, Berlin

Gorban AN, Karlin IV, Zinovyev AY (2004) Constructive methods of invariant manifolds for kinetic problems. Phys Rep 396:197–403

Grabert H (1981) Projection Operator Techniques in Non-equilibrium Statistical Mechanics, Springer, Berlin

Grad H (1958) Principles of the kinetic theory of gases. In: Flugge S (ed) Hd. der Physik, vol XII. Springer, Berlín

Grandy WT (1987–1988) Foundations of Statistical Mechanics, 2 vol. D. Riedel, Dordrecht

Greco A, Müller I (1983) Extended thermodynamics and superfluidity. Arch Rat Mech Anal. 83:279–301

Green AE, Rivlin RS (1957) The mechanics of non-linear materials with memory. Arch Rat Mech Anal 1:410–417

Green HS (1969) The molecular theory of fluids. Dover, New York

Greenspan M (1965) Transmission of sound waves in gases at very low pressures. In: Mason WP (ed) Physical Acoustics, vol 2A. Academic, New York

Griffin JJ, Kan KK (1976) Colliding heavy ions: nuclei as dynamical fluids. Rev Mod Phys 48:467–477

Grmela M (1984) Bracket formulation of dissipative fluid mechanics equations. Phys Lett A 102:355–358

Grmela M (1993) Thermodynamics of driven systems. Phys. Rev E 48:919–930

Grmela M (2001) Complex fluids subjected to external influences. J Non-Newtonian Fluid Mech 96:221–254

Grmela M, Lebon G (1990) Hamiltonian extended thermodynamics. J Phys A: Math Gen 23: 3341–3351

Grmela M, Öttinger HC (1997) Dynamics and thermodynamics of complex fluids. I. Development of a general formalism. Phys Rev E 56:6620–6632

Grmela M, Elafif A, Lebon G (1998) Isothermal nonstandard diffusion in a two-component fluid mixture: a Hamiltonian approach. J Non-Equilib Thermodyn 23:312–327

Grmela M, Karlin IV, Zmievski (2002) Boundary layer variational principles: a case study. Phys Rev E 65:011201–011213

Grmela M, Lebon G, Lhuillier D (2003) A comparative study of the coupling of flow with non-Fickean thermodiffusion. Part II: GENERIC. J Non-Equilib Thermodyn 28:23–50

Grmela M, Lebon G, Dauby PC, Bousmina M (2005) Ballistic-diffusive heat conduction at nanoscale: a GENERIC approach. Phys Lett A 339:237–245

Guyer RA, Krumhansl JA (1966) Solution of the linearized Boltzmann phonon equation. Phys Rev 148:766–778, 778–788

Gyarmati I (1970) Non-equilibrium Thermodynamics. Springer, Berlin

Haase R (1969) Thermodynamics of Irreversible Processes. Addison-Wesley, Reading, MA

Hafskold B, Kjelstrup S (1995) Criteria for local equilibrium in a system with transport of heat and mass. J Stat Phys 78:463–494

Haken H (ed) (1977) Synergetics, a workshop. Springer, Berlin

Hanley HJM, Evans DJ (1982) A thermodynamics for a system under shear. J Chem Phys 76: 3225–3232

Hanley HJM, Rainwater JC, Clark NA, Ackerson BJ (1983) Liquid structure under shear: Comparison between computer simulation and colloidal suspensions. J Chem Phys 79: 4448–4458

Hänsch W (1991) The Drift-diffusion Equation and its Application in MOSFET Modeling. Springer, Berlin

Harris S (1971) An introduction to the theory of the Boltzmann equation. Holt, Rinehart and Winston, New York

Hatano T and Jou D (2003), Measuring temperature of forced oscillators. Phys Rev E 67:026121 (6p)

Hayward G, Pavón D (1989) Primordial black holes in the very early Universe. Phys Rev D 40:1748–1752

Herlach D, Galenko P, Holland-Moritz D (2007) Metastable Solids from Undercooled Melts. Pergamon Materials Series, Elsevier, Amsterdam

Herrera L, Falcón N (1995) Convection theory before relaxation. Astrophys Space Sci 234: 139–152

Herrera L, di Prisco A, Hernández-Pastora JL, Martín J, Martínez J (1997) Thermal conduction in systems out of hydrostatic equilibrium. Class Quantum Grav 14:2239–2247

Hess S (1977) On nonlocal constitutive relations, continued fraction expansion for the wave vector dependent diffusion coefficient. Z Naturforsch 32a:678–684

Hiscock WA, Lindblom L (1983) Stability and causality in dissipative relativistic fluids. Ann Phys (NY) 151:466–496

Hiscock WA, Lindblom L (1985) Generic instabilities in first-order dissipative relativistc fluids theories. Phys Rev D 31:725–733

Hiscock WA, Salmonson T (1991) Dissipative Boltzmann-Robertson-Walker cosmologies. Phys Rev D 43:3249–3258

Holway LH (1964) Existence of kinetic theory solutions to the shock structure problem. Phys Fluids 7:911–913

Hoover WH (1999) Time Reversibility, Computer Simulations and Chaos. World Scientific, Singapore

Hoover WG, Holian BL, Posch HA (1992) Comments to A possible experiment to check the reality of a nonequilibrium temperature. Phys. Rev 48:3196–3198

Hoover W, Moran B, More R, Ladd A (1981) Heat conduction in a rotating disk via non-equilibrium molecular dynamics. Phys Rev A 24:2109–2115

Hopfenberg HB, Stannett V (1973) In: Haward RN (ed) The Physics of Glassy Polymers. Applied Science, London

Hopfenberg HB, Holley RH, Stannett V (1969) The effect of penetrant activity and temperature on the anomalous diffusion of hydrocarbons and solvent crazing in polystyrene part I: Biaxially oriented polystyrene. Polym Eng Sci 9:242–249

Hu BL (1982) Vacuum viscosity description of quantum processes in the early universe. Phys Lett A 90:375–380

Hutter K, Jöhnk K (2004) Continuum Methods of Physical Modelling. Springer, Berlin

Ichiyanagi M (1990) A contribution to the theory of non-equilibrium statistical mechanics. V. A microscopic foundation of extended irreversible thermodynamics. J Phys Soc Japan 59: 1970–1980

Ichiyanagi M (1991) A projection-operator approach to extended irreversible thermodynamics. Prog Theor Phys 84:810–823

Ichiyanagi M (1994) Variational principles in irreversible processes. Phys Rep 243:125–182

Ilg P, Öttinger HC (1999) Non-equilibrium relativistic thermodynamics in bulk viscous cosmology. Phys Rev D 61:023510 (10p)

Israel W (1976) Nonstationay irreversible thermodynamics: a causal relativistic theory. Ann Phys (NY) 100:310–331

Israel W (1981) Thermodynamics of relativistic systems. Physica A 106:204–214

Israel W, Stewart JM (1979) Transient relativistic thermodynamics and kinetic theory. Ann Phys (NY) 118:341–372

Jackson H, Walker C, McNelly T (1976) Second sound in NaF. Phys Rev Lett 25:26–28

Jähnig E, Richter PH (1976) Fluctuations in spatially homogeneous chemical steady states. J Chem Phys 64:4645

Jaynes ET (1963) Information theory and statistical mechanics. In: Ford WK (ed) Statistical Physics. Benjamin, New York

Jaynes ET (1963) In: Ford WK (ed) Statistical Physics. Benjamin, New York

Jeffrey A, Taniuti T (1964) Nonlinear Wave Propagation. Academic, New York

Joseph DD, Preziosi L (1989) Heat waves. Rev Mod Phys 61:41–74; (1990) 62:375–392

Joshi AA, Majumdar A (1993) Transient ballistic and diffusive phonon heat transport in thin films. J Appl Phys74:31–39

Jou D, Camacho J (1990) On the non-equilibrium thermodynamics of some complex dynamical behaviours. J Phys A 23:4603–4617

Jou D, Llebot JE (1990) Introduction to the Thermodynamics of Biological Processes. Prentice-Hall, Englewood Cliffs, NJ

Jou D, Pavón D (1991) Non local and nonlinear effects in shock waves. Phys Rev. A 44:496–6502

Jou D, Zakari M (1995) Information theory and heat transport in relativistic gases. J Phys A: Math Gen 28:1585–1592

Jou D, Casas-Vázquez J, Lebon G (1979) A dynamical interpretation of second-order constitutive equations of hydrodynamics. J Non-Equilib Thermodyn 4:349–362

Jou D, Bampi F, Morro A (1982) Thermodynamic description of ultrasonic attenuation in metals. J Non-Equilib Thermodyn 7:201–212

Jou D and Casas-Vázquez J (1983), Equilibrium third moments and nonequilibrium second moments of fluctuations of dissipative fluxes. J Non-EquilibThermodyn 8:127–142

Jou D, Pérez-García C, Casas-Vázquez J (1984) On a non-equilibrium partition function for heat conduction. J Phys A: Math Gen 17:2799–2805

Jou D, Pérez-García C, García-Colín LS, López de Haro M, Rodríguez RF (1985) Phys Rev A 31:2502

Jou D, Ferrer-Suquet F, Pérez-Vicente C (1986) On the nonequilibrium chemical potential of open pores in a membrane. J Chem Phys 85:5314–5316

Jou D, Casas-Vázquez J, Lebon G (1988) Extended irreversible thermodynamics. Rep Prog Phys 51:1105–1179

Jou D, Zakari M (1995) Information theory and heat transport in a relativistic gas. J Phys A: Math Gen 28:1585–1592

Jou D, Casas-Vázquez J, Lebon G (1999) Extended irreversible thermodynamics revisited (1988–1998). Rep Prog Phys 62:1035–1142

Jou D, Casas-Vázquez J, Criado-Sancho M (2001) Thermodynamics of Fluids under Flow. Springer, Berlin, Heidelberg

Jou D, Casas-Vázquez J, Lebon G (2001) Extended Irreversible Thermodynamics, 3rd edn. Springer, Berlin

Jou D, Casas-Vázquez J, Lebon G, Grmela M (2005) A phenomenological scaling approach for heat transport in nanosystems. Appl Math Lett 18:963–967

Jou D, Criado-Sancho M, del Castillo LF, Casas-Vázquez J (2001) A simple thermodynamic model of shear-induced polymer banding and separation. Polymer 46:6239–6245

Junk M, Romano V (2005) Maximum entropy moment system of the semiconductor Boltzmann equation using Kane's dispersion relation. Cont Mech Thermodyn 17:247–267

Kaplan SR and Essig A (1983) Bioenergetics and linear non-equilibrium Thermodynamics. The steady state, Harvard University Press, Cambridge MA

Karlin IV (2000) Exact summation of the Chapman-Enskog expansion from moment equations. J Phys A Math Gen 33:8037–8046

Kestin J (1968) A Course in Thermodynamics. Blaisdell, Waltham

Keizer J (1983) On the relationship between fluctuating irreversible thermodynamics and 'extended' irreversible thermodynamics. J Stat Phys 31:485–497

Keizer J (1987) Statistical Thermodynamics of Nonequilibrium Processes. Springer, Berlín

Kestin J (1990) A note on the relation between the hypothesis of local equilibrium and the Clausius-Duhem inequality. J Non-Equilib Thermodyn 15:193–212

Kestin J (1992) Local-equilibrium formalism applied to mechanics of solids. Int J Solids Struct 29:1827–1836

Kestin J, Bataille J (1980) Thermodynamics of solids. In: Continuum Models of Discrete Systems. University of Waterloo Press, Waterloo

Khalatnikov IM (1965) An introduction to the Theory of Superfluidity. W.A. Benjamin, New York

Kivelson D, Keyes T (1972) A unified theory of orientational relaxation. J Chem Phys 57:4599

Kjelstrup S, Bedeaux D (2008) Non-equilibrium Thermodynamics of Heterogeneous Systems. World Scientific, Singapore

Kleidon A, Lorenz RD (eds) (2005) Non-equilibrium Thermodynamics and the Production of Entropy. Life, Earth and Beyond. Springer, Berlin

Kluitenberg G (1962) Thermodynamical theory of elasticity and plasticity. Physica 28: 217–232

Kluitenberg G (1984) Plasticity and Non-equilibrium Thermodynamics (CISM Course 281). Springer, Wien

Knesser HO (1965) Relaxation processes in gases. In: Mason WP (ed) Physical Acoustics. vol. 2A. Academic, New York

Koide T, Denicol GS, Mota Ph, Kodama T (2007) Relativistic dissipative hydrodynamics: a minimal causal theory. Phys Rev C 75:034909 (5p)

Kondepudi D, Prigogine I (1998) Modern Thermodynamics: From Heat Engines to Dissipative Structures. Wiley, New York

Kozlowski M (1989) The temperature pulse propagation in interacting nuclear slabs. Nucl Phys A 492:285–293

Krall AN, Trivelpiece AW (1973) Principles of Plasma Physics. McGraw-Hill, New York

Kranys M (1967) General relativistic thermodynamics with finite transport velocity of interaction in matter. Nuovo Cimento B 50: 48–64

Kranys M (1972) Kinetic derivation of non-stationary general relativistic thermodynamics. Nuovo Cimento B 8:417–441

Kranys M (1977) Hyperbolic elasticity of dissipative media and its wave propagation modes. J Phys A 10:689–709

Kreuzer H. J (1981) Non-Equilibrium Thermodynamics and Its Statistical Foundations, Clarendon, Oxford

Kröner E (1963) Dislocation: a new concept in the continuum theory of plasticity. J Math Phys 42:27–37

Kurz W, Fisher DJ (1992) Fundamentals of Solidification, 3rd edn. Trans Tech Publications, Aedermannsdorf

Lambermont J (1974) On the unification of the mathematical theory of plasticity and dislocation theory by using thermodynamics. Int J Eng Sci 12:937–952, 953–965

Lambermont J, Lebon G (1973) On a generalization of the Gibbs equation for heat conduction. Phys Lett A 42:499–500

Lambermont J, Lebon G (1974) On the derivation of the Gibbs equation for a class of rheological bodies. Int J Non-Linear Mech 9:55–74

Landau LD (1965) On the theory of superconductivity. In: Ter Haar (ed) Collected papers. Pergamon, Oxford

Landau LD, Lifshitz EM (1980) Statistical Physics, 3rd edn. Pergamon, Oxford

Landau LD, Lifshitz EM (1985) Mechanics of Fluids. Pergamon, Oxford

Landsberg PT, Tonge G (1980) Thermodynamic energy conversion efficiencies. J Appl Phys 51:R1–R18

Larecki W (1993) Symmetric conservative form of low-temperature phonon-gas hydrodynamics II. Equations of heat transport and thermal equations of state. Nuovo Cimento D 14:141–176

Larson BC, Tischler JZ, Mills DM (1986) Nanosecond resolution time-resolved x-ray study of silicon during pulsed-laser irradiation. J Mater Res 1:144–154

Lavenda B (1979) *Thermodynamics of Irreversible Processes*. McMillan, London

Lax PD (1957) Hyperbolic systems of conservation laws II. Comm Pure Appl Math 10: 537–566

Lebon G (1980) Variational Principles in Thermomechanics. In CISME Courses and Lecture Notes, vol 262. Springer, Wien

Lebon G (1992) Extended Thermodynamics. In CISME Courses and Lecture Notes, vol 336. Springer, Wien, pp 139–204

Lebon G, Boukary MS (1988) Objectivity, kinetic theory, and extended irreversible thermodynamics. Ing J Eng Sci 26:471–483

Lebon G, Cloot A (1989) Propagation of ultrasonic sound waves in dissipative dilute gases and extended irreversible thermodynamics. Wave Motion 11:23–32

Lebon G, Dauby PC (1990) Heat transport in dielectric crystals at low temperature: a variational formulation based on extended irreversible thermodynamics. Phys Rev A 42:4710–4715

Lebon G, Jou D (1979) A continuum theory of liquid helium II based on the classical theory of irreversible processes. J Non-Equilib Thermodyn 4:259–276

Lebon G, Jou D (1983) Linear irreversible thermodynamics and the phenomenological theory of liquid helium II. J Phys C 16:L199–L204

Lebon G, Jou D, Casas-Vázquez J (1980) An extension of the local equilibrium hypothesis. J Phys A: Math Gen 13:275–290

Lebon G, Dauby PC, Palumbo A, Valenti G (1990) Rheological properties of dilute polymer solutions: an extended thermodynamic approach. Rheol Acta 29:127–136

Lebon G, Casas-Vázquez J, Jou D (1992) Questions and answers about a thermodynamic theory of the third type. Contemp Phys 33:41–51

Lebon G, Jou D, Casas-Vázquez J, Muschik W (1998) Weakly nonlocal and nonlinear heat transport in rigid solids. J Non-Equil Thermodyn 23:176–191

Lebon G, Depireux N, Lhuillier D (2001) An extended thermodynamic description of colloidal suspensions. Proc 9th Natl Cong Theor Appl Mech 1:205

Lebon G, Grmela M, Lhuillier D (2003) A comparative study of the coupling of flow with non-Fickian thermodiffusion. Part I: Extended irreversible thermodynamics. J Non-Equilib Thermodyn 28:1–22

Lebon G, Baltov A, Grmela M (2004) Extended thermodynamics of thermoelasticity, viscoelasticity and viscoplasticity. J Theor Appl Mech 34:3–20

Lebon G, Desaive Th, Dauby PC (2006) Two-fluid diffusion as a model for heat transport at micro and nanoscales. In Proceedings of 7th International Meeting on Thermodiffussion. San Sebastian

Lebon G, Desaive Th, Dauby PC (2006) A unified extended thermodynamic description of diffusion, thermo-diffusion, suspensions, and porous media. J Appl Mech 73:16–20

Lebon G, Lhuillier D, Palumbo A (2007) A thermodynamic description of thermo-diffusion in suspensions of rigid particles. Eur Phys J ST 146:3–12

Lebon G, Ruggieri M, Valenti A (2008a) Extended thermodynamics revisited: renormalized flux variables and second sound in rigid solids. J Phys C 20:025223 (11p)

Lebon G, Jou D, Casas-Vázquez J (2008b) Understanding Non-equilibrium Thermodynamics, Foundations, Applications, Frontiers. Springer, Berlin, Heidelberg

Lebon G, Grmela M, Dubois Ch. (2010) From ballistic to diffusive regimes in heat transport a nano-scales, in Proceedings of IMT 9 meeting, Toulouse, June 2010

Lebowitz JL (1999) Microscopic origins of irreversible macroscopic behaviour. Physica A 263:516–527

Lepri S, Livi R, Politi A (2003) Thermal conduction in classical low-dimensional lattice. Phys Rep 377:1–80

Levermore;D (1984) Relating Eddington factors to flux limiters. J Quant Spec Rad Transfer 31:149–160

Levermore CD (1996) Moment closure hierarchies for kinetic theories. J Stat Phys 83:1021–1065

Levermore CD, Pomraning GC (1981) A flux-limited diffusion theory. Astrophys J 348:321–334

Levine RD, Tribus M (eds) (1979) The Maximum Entropy Formalism. MIT Press, Cambridge, MA

Lhuillier D (1995) From molecular mixtures to suspensions of particles. J Phys II France 5:19–36

Lhuillier D (2001) Internal variables and the non-equilibrium thermodynamics of colloidal suspensions. J Non-Newtonian Fluid Mech 96:19–30

Lhuillier D, Ouibrahim A (1980) A thermodynamic model for solutions of deformable molecules. J Mécanique 19:725–741

Lhuillier D, Grmela M, Lebon G (2003) A comparative study of the coupling of flow with non-Fickian thermodiffusion. Part III: internal variables. J Non-Equilib Thermodyn 28:51–68

Li B, Barrow JD (2009) Does bulk viscosity create a viable unified dark matter model? Phys Rev D 79:103521 (9p)

Lima JAS, Portugal R, Waga I (1988) Bulk-viscosity-driven asymmetric inflationary universe. Phys Rev D 37:2755–2760

Liu I-S (1972) Method of Lagrange multipliers for exploitation of the entropy principle. Arch Rat Mech Anal 46:131–148

Liu W, Asheghi M (2004) Phonon-boundary scattering in ultrathin single-crystal silicon layers Appl Phys Lett 84:3819–3821

Liu I-S, Müller I, Ruggeri T (1986) Relativistic thermodynamics of gases. Ann Phys (NY) 169:191–219

Liu I-S, Rincon MA, Müller I (2002) Iterative approximation of stationary heat conduction in extended thermodynamics. Cont Mech Thermodyn 14:483–493

Llebot JE, Jou D, Casas-Vázquez J (1983), A thermodynamic approach to heat and electrical conduction in solids. Physica A 121:552–562

Lodge AS (1989) An attempt to measure the first normal-stress difference N_1 in shear flow for a polyisobutylene/decalin solution “D2b” at shear rates up to $10^8\ \mathrm{s}^{-1}$. J Rheol 33:821–841

Loose W, Hess S (1989) Rheology of dense model fluids via nonequilibrium molecular dynamics: Shear thinning and ordering transition. Rheol Acta 28:91–101

Luikov AV, Bubnov VA, Soloviev A (1976) On wave solutions of heat conduction equations. Int J Heat Mass Transf 19:175–245

Lumley J (1983) Turbulence modeling. J Appl Mech 50:1097–1103

Luzzi R, Vasconcellos AR, Casas-Vázquez J, Jou D (1997) Characterization and measurement of a nonequilibrium temperature-like variable in irreversible thermodynamics. Physica A 234: 699–714

Luzzi R, Vasconcellos AR, Casas-Vázquez J, Jou D (1998) On the selection of the state space in non-equilibrium thermodynamics. Physica A 248:111–137

Luzzi R, Vasconcellos AR, Ramos JG (2001) Statistical Foundations of Irreversible Thermodynamics. Teubner, Leipzig

Luzzi R, Vasconcellos AR, Ramos JG (2002) Predictive Statistical Mechanics: A Non-equilibrium Ensemble Formalism. Kluwer, Dordrecht

Lyapunov M (1966) Stability of Motion (English translation). Academic, New York

Maartens R (1995) Dissipative cosmology. Class Quant Grav 12:1455–1466

Maartens R, Mendez V (1997) Nonlinear bulk viscosity and inflation. Phys Rev D 55:1937–1942

MacDonald MJ, Muller SJ (1996) Experimental study of shear-induced migration of polymers in dilute solutions. J Rheol 40:259–283

Machlup S, Onsager L (1953) Fluctuations and irreversible process. II Systems with kinetic energy. Phys Rev 91:1512–1515

Madruga S, Pérez-García C, Lebon G (2003) Convective instabilities in two laterally superposed horizontal layers heated. Phys Rev E 68:041607, 1–12.

Madureira J, Vasconcellos AR, Luzzi R, Casas-Vázquez J, Jou D (1998) Evolution of dissipative processes via a statistical thermodynamical approach. II. Thermodynamic properties of a fluid of bosons. J Chem Phys 108:7580–7586

Magnasco MO (1994) Molecular combustion motors. Phys Rev Lett 72:2656–2659

Mahan G, Sales B, Sharp J (1997) Thermoelectric materials: new approaches to an old problem. Phys Today 50:42–47

Majumdar A (1993) Microscale heat conduction in dielectric thin films. J Heat Transf 115: 7–16

Mandel J (1978) Propriétés Mécaniques des Matériaux. Eyrolles, Paris

Martínez J (1996) Transport processes in the gravitational collapse of an anisotropic fluid. Phys Rev D 53:6921–6940

Martínez J, Pavón D (1994) Radiating gravitational collapse with bulk viscosity. Mon Not R Astron Soc 268:654–664

Masoliver J, Porrà JM, Weiss GH (1992) Solutions to the telegrapher's equation in the presence of traps. Phys Rev A 45:2222–2227

Matzner RA (1972) Dissipative effects in the expansion of the universe. II. A multicomponent model for neutrino dissipation of anisotropy in the early universe. Astrophys J 171:433–448

Matzner RA, Misner CW (1972) Dissipative effects in the expansion of the universe. I. Astrophys J 171:415–432

Maugin G (1999) The Thermodynamics of Nonlinear Irreversible Behaviours. World Scientific, Singapore

Maugin G (1992) The Thermodynamics of Plasticity and Fracture. Cambridge University Press, Cambridge

Maugin G, Muschik W (1994) Thermodynamics with internal variables. J Non-Equilib Thermodyn 19:217–249, 250–289

Maurer MJ, Thomson HA (1973) Non-Fourier effects at high heat flux. J Heat Transf 95: 284–286

Maxwell JC (1867) On the dynamical theory of gases. Philos Trans Roy Soc Lond 157:49–88

Mc Dougall JC, Turner JS (1982) Influence of cross-diffusion on 'finger' double-diffusive convection. Nature 299:812–814

Mc Quarrie DA (1976) Statistical Mechanics. Harper & Row, New York

Meixner J (1943) Zur thermodynamik der irreversiblen prozesse in gasen mit chemisch reagierenden, dissozierenden und anregbaren komponenten. Ann Phys (Leipzig) 43:244–269

Meixner J (1954) Thermodynamische Theorie der elastische Relaxation. Z Naturforsch 9a:654

Meixner J (1973) The entropy problem in thermodynamics of processes. Rheol Acta 12: 272–283

Meixner J (1973) On the foundations of thermodynamics of processes. In: Stuart E, Gal-Or B, Brainard A (eds) A Critical Review of Thermodynamics. Mono Book Corp., Baltimore, MD

Meixner J, Reik HG (1959) Thermodynamik der Irreversible Prozesse. in Handbuch der Physik, Bd 3/ II, Springer, Berlin

Méndez V, Compte A (1998) Wavefronts in bistable hyperbolic reaction-diffusion systems. Physica A 260:90–98

Méndez V, Fort J (1999) Irreversible thermodynamics of Poisson processes with reaction. Phys Rev E 60:6168–6171

Méndez V, Llebot JE (1997) Hyperbolic reaction-diffusion equations for a forest fire model. Phys Rev E 56:6557–6563

Méndez V, Fort J, Farjas J (1999) Speed of wave-front solutions to hyperbolic reaction-diffusion equations. Phys Rev E 60:5231–5243

Méndez V, Fedotov S, Horsthemke W (2009) Reaction-Transport Systems: Mesoscopic Foundations, Fronts, and Spatial Instabilities. Springer, Berlin

Mendez V, Pavón D (1996) Expanding models with a varying cosmological term and bulk stress. Gen Rel Grav 28:679–689

Metiu H, Freed KF (1977) Bulk viscosity of polymer solutions. J Chem Phys 67:3303–3315

Meyer E, Sessler G (1957) Schallausbreitung in Gasen bei hohen Frequenzen und sehr niedrigen Drucken. Z für Phys 149:15–39

Mihalas D, Mihalas BW (1984) Radiation hydrodynamics. Oxford University Press, Oxford

Miller DG (1960) Thermodynamics of irreversible processes: the experimental verification of the Onsager reciprocal relations. Chem Rev 60:15–37

Miller BN, Larson PM (1979) Heat flow in a linear harmonic chain: An information-theoretic approach to the nonequilibrium stationary state. Phys Rev A 20:1717–1727

Mises R von (1928) Mechanik der plastischen formänderung von kristallen. Z Angew Math Mech 8:161–185

Modest MF (1993) Radiative Heat Transfer. McGraw-Hill, New York

Mogilner A, Fisher JJ, Baskin RJ (2001) Structural changes in the neck linker of kinesin explain the load dependence of the motor's mechanical cycle. J Theor Biol 211:143–157

Mongiovì MS (1993) Extended irreversible thermodynamics of liquid helium II. Phys Rev B 48:6276–6283

Mongiovì MS (2001) Extended irreversible thermodynamics of liquid helium II: Boundary conditions and propagation of fourth sound. Physica A 292:55–74

Mongiovì MS, Jou D (2007) Thermodynamical derivation of a hydrodynamical model of inhomogeneous superfluid turbulence. Phys Rev B 75:024507 (12p)

Mori H (1965) A continued-fraction representation of the time-correlation functions. Prog Theoret Phys 34:399–416

Morse PM, Feshbach H (1953) Mathematical Methods of Theoretical Physics. McGraw-Hill, New York

Movchan A (1959) The direct method of Lyapunov in stability problems of elastic systems. J Appl Math Mech 23:686–700

Mróz Z, Oliferuk W (2002) Energy balance and identification of hardening moduli in plastic deformation processes. Int J Plasticity 18:379–397

Müller I (1967) Zum Paradoxon der Wärmetheorie. Z Phys 198:329–344

Müller I (1969) Toward relativistic thermodynamics. Arch Rat Mech Anal 34:259–282

Müller I (1971) The coldness, a universal function in thermoelastic bodies. Arch Rat Mech Anal 41:319

Müller I (1972) On the frame dependence of stress and heat flux. Arch Rat Mech Anal 45: 241–250

Müller I, Ruggeri T (1998) Rational Extended Thermodynamics, 2nd edn. Springer, New York

Müller I, Wilmanski K (1986) Extended thermodynamics of a non-Newtonian fluid. Rheol Acta 25:335–349

Murdoch AI (1983) On material frame-indifference, intrinsic spin and certain constitutive relations motivated by the kinetic theory of gases. Arch Rat Mech Anal 83:185–194

Murphy GL (1973) Big-bang model without singularities. Phys Rev D 8:4231–4233

Muscato O, Di Stefano V (2008) Modelling heat generation in a submicrometric $n^+ - n - n^+$ silicon diode. J Appl Phys 104:124501–124510

Muschik W (1977) Empirical foundation and axiomatic treatment of non-equilibrium temperature. Arch Rat Mech Anal 66:379–401

Muschik W (1990) Aspects of Non-equilibrium Thermodynamics. World Scientific, Singapore

Nagano K, Karasudani T, Okamoto H, Mori H (1980) Reduced equations of motion for generalized fluxes and forces in the continued-fraction expansion. Prog Theoret Phys 63:1904–1911

Naqvi KR, Waldenstrom A (2005) Brownian motion description of heat conduction by phonons. Phys Rev Lett 95:065901 (4p)

Narayanamurti V, Dynes RC (1972) Observation of second sound in bismuth. Phys Rev Lett 28:1461–1465

Neogi P (1983) Anomalous diffusion of vapors through solid polymers. Part I. Irreversible thermodynamics of diffusion and solution processes. AIChE J 29:829–833

Nettleton RE (1959) Thermodynamics of viscoelasticity in liquids. Phys Fluids 2:256–263

Nettleton RE (1960) Relaxation theory of thermal conduction in liquids. Phys Fluids 3: 216–225

Nettleton RE (1987) Shear-rate non-analicity in simple liquids. J Non-Equilib Thermodyn 12: 273–290

Nettleton RE (1988) Information-theoretic extended entropy for steady heat conduction in dense fluids. J Phys A 21:3939–3949

Nettleton RE (1990) The Gibbs equation for maximum entropy. J Chem Phys 93:8247–8253

Nettleton RE (1994) On the relation between thermodynamic temperature and kinetic energy per particle. Can J Phys 72:106–112

Nicolis G, Prigogine I (1977) Self-organization in Nonequilibrium Systems. Wiley, New York

Nicolis G, Prigogine I (1989) Exploring Complexity. Freeman, New York

Nigmatulin RY (1990) Dynamics of Multiphase Media. Hemisphere, New York

Nisbet RM, Gurney WSC (1974) Comment on the information-theoretic derivation of non-equilibrium velocity distributions. Phys Rev A 10:720–723

Noll W (1974) The Foundations of Mechanics and Thermodynamics. Springer, Berlin

Oldroyd JG (1958) Non-Newtonian effects in steady motion of some idealized elastico-viscous fluids. Proc Roy Soc London A 245:278–297

Oliveira HP, Salim JM (1988) Non-equilibrium Friedman cosmologies. Acta Phys Pol B 19: 649–657

Olson TS, Hiscock WA (1989) Relativistic dissipative hydrodynamics and the nuclear equation of state. Phys Rev C 39:1818–1826

Olson TS, Salim WA (1988) Relativistic dissipative hydrodynamics and the nuclear equation of state. Phys Rev C 39:1818–1826

Onsager L (1931) Reciprocal relations in irreversible processes. Phys Rev 37:405–426; 38: 2265–2279

Onuki A (1997) Phase transitions of fluids in shear flow. J Phys: Condens Mater 9:6119–6157

Onuki A (2002) Phase Transitions Dynamics. Cambridge University Press, Cambridge

Ortiz de Zárate JM, Sengers JV (2006) Hydrodynamic Fluctuations in Fluids and Fluid Mixtures. Elsevier, Amsterdam

Öttinger HC (1999a) A thermodynamically admissible reptation model for fast flows of entangled polymers. J Rheol 43:1461–1493

Öttinger HC (1999b) Thermodynamically admissible equations for causal dissipative cosmology, galaxy formation, and transport processes in gravitational collapse. Phys Rev D 60: 103507, 1–9

Öttinger HC (2000) Derivation of a two-generator framework on non-equilibrium thermodynamics for quantum systems. Phys Rev E 62:4720–4724

Öttinger HC (2005) Beyond Equilibrium Thermodynamics. Wiley, Hoboken

Öttinger HC, Grmela M (1997) Dynamics and thermodynamics of complex fluids. II. Illustrations of a general formalism. Phys Rev E 56:6633–6655

Ozawa H, Ohmura A, Lorenz RD, Pujol T (2003) The second law of thermodynamics and the global climate system: A review of the maximum entropy production principle. Rev Geophys 41:4/1018 (24p)

Ozisik MN, Tzou DY (1994) On the wave theory in heat conduction. J Heat Transf Trans ASME 116:526–535

Pavón D (1990) The generalized second law and extended thermodynamics. Class Quant Grav 7:487–491

Pavón D, Jou D and Casas-Vázquez J (1980) About the relativistic temperature gradient. Phys Lett A 78:317–318

Pavón D, Jou D, Casas-Vázquez J (1982) On a covariant description of dissipative phenomena. Ann Inst Henri Poincaré A 36:79–88

Pavón D, Bafaluy J, Jou D (1991) Causal Friedmann–Robertson–Walker cosmology. Class Quant Grav 8:347–360

Peebles PJE (1993) Principles of Physical Cosmology. Princeton University Press, Princeton

Pérez-García C, Jou D, López de Haro M, Rodríguez RF, García-Colín LS (1986) An extended thermodynamic approach for the longitudinal velocity correlation function. Physica A 135:251–260

Perez-García C, Casas-Vázquez J, Lebon G (1989) A nonequilibrium thermodynamic description of dilute polymer solutions. J Polym Sci Part B: Polym Phys 27:1807–1821

Perzyna P (1966) Fundamental problems in plasticity. Adv Appl Mech 9:243–377

Ponter ARS, Bataille J, Kestin J (1979) A thermodynamic model for the time dependent plastic deformation of solids. J Mécanique 18:511–539

Prager W (1955) Probleme des Plasticitatstheorie. Birkauser, Bale

Pradhan A, Pandey P, Jotania K, Yadav MK (2007) Plane symmetric viscous fluid cosmological models with varying Λ-term. Int J Theor Phys 46:2774–2787

Prakash JR, Mashelkar RA (1991) The diffusion tensor for a flowing dilute solution of Hookean dumbbells: anisotropy and flow rate dependence. J Chem Phys 95:3743

Prigogine I (1947) Etude Thermodynamique des Phénomènes Irréversibles. Desoer, Liège

Prigogine I (1949) Le domaine de validité de la thermodynamique des phénomènes irreversibles. Physica 15:272–284

Prigogine I (1961) Introduction to Thermodynamics of Irreversible Processes. Interscience, New York

Qiu TQ, Tien CL (1992) Short-pulse laser heating of metals. Int J Heat Mass Transfer 35:719–726

Qiu TQ, Tien CL (1993) Heat transfer mechanisms during short-pulse laser heating of metals. ASME J Heat Transfer 33:835–841

Rangel-Nafaile C, Metzner A, Wissbrun K (1984) Analysis of stress-induced phase separations in polymer solutions. Macromolecules 17:1187–1195

Reguera D (2004) Mesoscopic nonequilibrium kinetics of nucleation processes. J Non-Equilib Thermodyn 29:327–344

Reguera D, Rubí JM, Vilar JM (2005) The mesoscopic dynamics of thermodynamic systems. J Phys Chem B 109:21502–21515

Reichl LE (1980) A Modern Course in Statistical Physics. University Texas Press, Austin, TX

Reiner M (1945) A mathematical theory of dilatancy. Am J Math 67:350–362

Résibois P, De Leener M (1977) Classical Kinetic Theory of Fluids. Wiley, New York

Reynolds O (1885) On the dilatancy of media composed of rigid particles in contact. With experimental illustrations. Phil Mag 20:469–481

Rice SA and Gray P (1965) The statistical mechanics of simple liquids, Wiley-Interscience, New York

Rivlin RS (1948) The hydrodynamics of non-Newtonian fluids I. Proc Roy Soc A 193: 260–281

Rivlin RS, Ericksen JL (1955) Stress-deformation relations for isotropic materials. J Rat Mech Anal 4:323–425

Robertson B (1967) Equations of motion in nonequilibrium statistical mechanics. Phys Rev 160:175–183

Rodríguez RF, García-Colín LS, del Castillo LF (1987) Fluids with internal degrees of freedom. Extended thermodynamics approach. J. Chem. Phys. 86:4208–4215

Roldughin VI (1995) Non-equilibrium thermodynamics and the moment method. J Non-Equilib Thermodyn 20:230–244

Romano V (2001) Non parabolic band hydrodynamical model of silicon semiconductors and simulation of electron devices. Math Meth Appl Sci 24:439–471.

Romano V (2007) Quantum corrections to the semiclassical hydrodynamical model of semiconductors based on the maximum entropy approach. J Math Phys 48:123504 (24p)

Romano V, Pavón D (1994) Dissipative effects in Bianchi-III type cosmologies. Phys Rev D 50:2572–2580

Romano V, Russo G (2000) Numerical solutions for hydrodynamical models of semi-conductors. Math Models Meth Appl Sci 10:1099–1120

Rosenau P (1993) Random Walker and the telegrapher's equation: a paradigm of a generalized hydrodynamics. Phys Rev E 48:R655–R657

Rouse PE (1953) A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. J Chem Phys 21:1272–1280

Rubí JM (2004) The non-equilibrium thermodynamics approach to the dynamics of mesoscopic systems. J Non-Equilib Thermodyn 29:315–325

Rubí JM, Casas-Vázquez J (1980) Thermodynamical aspects of micropolar fluids. A non-linear approach. J Non-Equilib Thermodyn 5:155–164

Ruelle D (1991) Chance and Chaos. Princeton University Press, Princeton, NJ

Ruggeri T, Muracchini A, Seccia L (1994) Continuum approach to phonon gas and shape changes of second sound via shock wave theory. Nuovo Cimento D 16:15–44

Ruggeri T (1993) Breakdown of shock wave structure solutions. Phys Rev E 47:4135–4140

Ruggeri T Recent Results on Wave Propagation in Continuum Models. In CISM Courses and Lectures Notes, vol 344. Springer, Wien, New York, pp 105–154

Ruggeri T (2000) Maximum of entropy density in equilibrium and minimax principle for an hyperbolic system of balance laws. In: Albers B (ed) Contribution to Continuum Theories, vol 18. WIAS report

Ryskin G (1988) Brownian motion in a rotating fluid: diffusivity is a function of the rotating rate. Phys Rev Lett 61:1442–1445

Salamon P, Sieniutycz S (ed) (1991) Finite-time Thermodynamics and Optimization. Taylor & Francis, New York

Salamon P, Nitzan A, Andresen B, Berry RS (1980) Minimum entropy production and the optimization of heat engines. Phys Rev A 21:2115–2129

Santos A and Brey JJ (1991) Far from equilibrium velocity distribution of a dilute gas. Physica A 174:355–390

Schlesinger MF (1988) Fractal time in condensed matter. Ann Rev Phys Chem 39:269–290

Schlögl F (1980) Stochastic measures in nonequilibrium thermodynamics. Phys Rep 62: 267–380

Schmitz R (1988) Fluctuations in nonequilibrium fluids. Phys Rep 171:1–58

Schultz BE (1985) A First Course in General Relativity. Cambridge University Press, Cambridge

Schweizer MA (1985) Transient elastic photon diffusion. Astron Astrophys 151:79–89

Scriven LE, Sternling CV (1964) On cellular convection driven by surface tension gradients: effect of mean surface tension and viscosity. J Fluid Mech 19:321–340

Seeger A (1963) Electron Microscopy and Strength of Crystals. Wiley, New York

Seitaridou E, Inamdar MI, Phillips R, Ghosh K, Dill K (2007) Measuring flux distributions for diffusion in the small-numbers limit. J Phys Chem B 111:2288–2292

Shannon C (1948) A mathematical theory of communication. Bell System Tech J 27:379–423, 623–656

Shlüter A, Lortz D, Busse FH (1965) On the stability of steady finite amplitude convection. J Fluid Mech 23:129–144

Shvart D, Delettrez J, McCrory RL, Verdon CP (1981) Self-consistent reduction of the Spitzer-Härm electron thermal heal flux in steep temperature gradients in laser-produced plasmas. Phys Rev Lett 47:247–260

Sidoroff FJ (1975) Variables internes en viscoélasticité. J Mécanique 14:545–566, 571–595; (1976), 15:95–118

Sieniutycz S (1994) Conservation Laws in Variational Thermohydrodynamics. Kluwer, Dordrecht

Sieniutycz S, Farkas H (eds) (2004) Variational and Extremum Principles in Macroscopic Systems. Elsevier Science, Oxford

Sieniutycz S, Berry RS (1991) Field thermodynamic potentials and geometric thermodynamics with heat transfer and fluid flow. Phys Rev A 43:2807–2818

Sieniutycz S, Salamon P (eds) (1992) Extended Thermodynamic Systems. Taylor & Francis, New York

Silhavy M (1997) The Mechanics and Thermodynamics of Continuous Media. Springer, Berlín

Smith GF (1965) On isotropy integrity bases. Arch Rat Mech Anal 18:282–292

Snider RF, Lewchuk KS (1967) Irreversible thermodynamics of a fluid system with spin. J Chem Phys 46:3163–3172

Snyder GJ, Ursell TS (2003) Thermoelectric efficiency and compatibility. Phys Rev Lett 91:148301

Sobolev SL (1995) Two-temperature Stefan problem. Phys Lett A 197:243–246

Sparrow C (1982) The Lorenz Equations: Bifurcations, Chaos and Strange Attractors. Springer, New York

Spencer AJM, Rivlin RS (1959) Further results in the theory of matrix polynomials. Arch Rat Mech Anal 4:214–230

Spohn H, Lebowitz JL (1977) Stationary non-equilibrium states of infinite harmonic systems. Comm Math Phys 54:97–123

Stewart JM (1977) Non-transient relativistic thermodynamics and kinetic theory. Proc Roy Soc London A 357:59–75

Stöcker H, Greiner W (1986) High energy heavy ion collisions-probing the equation of state of highly excited hadronic matter. Phys Rep 137:277–392

Struchtrup H (1998) Projected moments in relativistic kinetic theory. Physica A 253:555–593

Struchtrup H, Torrilhon M (2007) H theorem, regularization, and boundary conditions for linearized 13-moment equations. Phys Rev Lett 99:014502–014504

Struchtrup H, Weiss W (1998) Maximum of the local entropy production in stationary processes. Phys Rev Lett 80:5048–505

Stuart JT (1958) O the non-linear mechanics of hydrodynamic instability. J Fluid Mech 4: 1–21

Sudharan P, Johri VB (1994) Cosmological models with particle production and bulk viscosity. Gen Relat Grav 26:41–51

Sussman RA (1994) Bulk viscosity and matter creation in inhomogeneous cosmologies with a shear free fluid source. Class Quant Grav 11:1445–1451

Tanner RI (1988) Engineering rheology, Clarendon Press, Oxford

Thom R (1972) Stabilité Structurelle et Morphogénèse. Benjamín, Reading, MA

Thomas NL, Windle AH (1982) A theory of case II diffusion. Polymer 23:529–542

Todd BB, Evans DJ, Daivis PJ (1965) Pressure tensor for inhomogeneous fluids. Phys Rev E 52:1627–1638

Todd BD, Evans DJ (1995) The heat flux vector for highly inhomogeneous nonequilibrium fluids in very narrow pores. J Chem Phys 103:9804–9809

Todd BD, Daivis PJ, Evans DJ (1995) Heat flux vector in highly inhomogeneous nonequilibrium fluids. Phys Rev E 51:4362–4368

Tokatly IV, Pankratov O (1999) Hydrodynamic theory of an electron gas. Phys Rev B 60:15550–15553

Tokatly IV, Pankratov O (2000) Hydrodynamics beyond local equilibrium: application to electron gas. Phys Rev B 62:2759–2772

Tremblay AMS (1984) Theories of fluctuations in nonequilibrium systems. In: Casas-Vázquez J, Jou D, Lebon G (eds) Recent Developments in Nonequilibrium Thermodynamics. Lecture Notes in Physics 199. Springer, Berlin

Tremblay AMS, Siggia ED, Arai, R (1981) Fluctuations about simple nonequilibrium steady states. Phys Rev 23:1451–1480

Tremblay A-MS, Vidal F (1982) Fluctuations in dissipative steady state of thin metallic films. Phys Rev B 25:7562–7576

Triginer J, Pavón D (1994) Particle production in a viscous cosmological fluid. Gen Relat Grav 26:513–524

Triginer J, Zimdahl W, Pavón D (1996) Kinetic theory for particle production. Class Quant Grav 13:403–416

Truesdell C (1968) Thermodynamics for beginners. In: Parkus H, Sedov L (eds) Irreversible Aspects of Continuum Mechanics. Springer, Wien

Truesdell C (1984) Rational Thermodynamics. 2nd edn. Springer, New York

Truesdell C, Noll W (1965) The Non-Linear Field Theories. In: Handbuch der Physik, Bd. III/3. Springer, Berlin

Truesdell C, Toupin R (1960) The Classical Field Theories. In: Handbuch der Physik, Bd. III/1. Springer, Berlin

Turok N (1988) String-driven inflation. Phys Rev Lett 60:549–552

Tzou DY (1997) Macro-to-Microscale Heat Transfer. The Lagging Behaviour. Taylor & Francis, New York

Udey N, Israel w (1982) General relativistic radiative transfer: the 14-moment approximation. Mon Not R Astr Soc 199:1137–1147

Valenti A, Torrisi M, Lebon G (1997) Heat pulse propagation by second sound in dielectric crystals. J Phys C 9:3117–3127

Valenti A, Torrisi M, Lebon G (2002) Shock waves in crystalline dielectrics at low temperature. J Phys Condens Matter 14:3553–3564

Van den Broeck C (1990) Taylor dispersion revisited. Physica A 168:677–696

Van den Hoogen RJ, Coley AA (1995) Qualitative analysis of causal anisotropic viscous-fluid cosmological models. Class Quant. Grav 12:2335–2354

Van Kampen NG (2000) Views of a physicist. World Scientific., Singapore

Van Weert CG (1982) Maximum entropy principle and relativistic hydrodynamics. Ann Phys (NY) 140:133–162

Vasconcellos AR Luzzi R, García-Colin LS (1991) A microscopic approach to irreversible thermodynamics (I): General theory. Phys Rev A 43:6622–6632

Vasconcellos AR, Luzzi R, García-Colin LS (1995) A microscopic approach to Irreversible Thermodynamics (VIII): Diffusion and mobility and generalized Einstein relation. Physica A 221:495–510

Velasco RM, García-Colín LS (1992) The kinetic foundations of extended irreversible thermodynamics revisited. J Stat Phys 69:217–229

Velasco RM, García-Colín LS (1993) The kinetic foundations of non-local nonequilibrium thermodynamics. J Non-Equilib Thermodyn 18:157–172

Velasco RM, García-Colín LS (1995) Generalized hydrodynamics in gases. J Non-Equilib Thermodyn 20:1–18

Vernott P (1958) La veritable équation de la chaleur. Compt Rend Acad Sci Paris 247: 2103–2107

Vidal C, Dewel G, Borckmans P (1994) Au delà de l'équilibre. Hermann, Paris

Villar JMG, Rubí JM (2001) Thermodynamics beyond local equilibrium. Proc Natl Acad Sci USA 98:11081–11084

Vlad MO, Ross J (1993) H theorem for telegrapher-type master equation. Phys Lett A 184:403–408

Wald RM (1984) General Relativity. University of Chicago Press, Chicago, IL

Waldmann L (1967) Non-equilibrium thermodynamics and boundary conditions. Z Naturforschung 22a:269–280

Waldman L and Vestner H (1975) On the theory of boundary condition. Physica A 80:528

Wang J, Wang J-S (2006) Carbon nanotube thermal transport: Ballistic to diffusive. Appl Phys Lett 88:111909

Weinberg S (2008) Cosmology. Oxford University Press, Oxford

Weiss W (1990) Hierarchie der Erweitereten Thermodynamik. Dissertation Tech. Univ. Berlin, Berlin

Weiss W (1996) Comments on “Existence of kinetic theory solutions to the shock structure problem” [PhysFluids 7:(1964)], Phys Fluids A 8:1689–1690

Wilhelm HE, Choi SH (1975) Nonlinear hyperbolic theory of thermal waves in metals. J Chem Phys 63:2119

Wilmanski K (1998) Thermodynamics of Continua. Springer, Berlín

Wolf BA (1984) Thermodynamic theory of flowing polymer solutions and its application to phase separation. Macromolecules 17:615–618

Wong CK, McLennan JA, Lindenfeld M, Dufty JW (1978) Theory of nonlinear transport in Burnett order. J Chem Phys 68:1563–1573

Woods LC (1975) The Thermodynamics of Fluid Systems. Clarendon, Oxford

Woods LC (1981/1982) The bogus axioms of continuum mechanics. Bull Inst Math Appl 17: 98–102; 18:64–67

Woods LC, Troughton H (1980) Transport processes in dilute gases over the whole range of Knudsen numbers. Part 2: ultrasonic sound waves. J Fluid Mech 100:321–331

Woods LC (1994) Kinetic theory of gases and magnetoplasmas, Oxford University Press, Oxford

Yang R, Chen G, Laroche M, Taur Y (2005) Simulation of nanoscales multidimensional transient heat conduction problems using ballistic-diffusive equations and phonon Boltzmann equation. J Heat Transf 127:298–306

Zakari M, Jou D (1993) Equations of state and transport equations in viscous cosmological model. Phys Rev D 48:1597–1601

Zemansky MW (1951) Heat and Thermodynamics. McGraw-Hill, New York

Zhang ZM (2007) Nano/Microscale Heat Transfer. McGraw-Hill, New York

Zhang H, Lü Z, Tian L, Tan Z, Liu L, Li Z (2006) Measurement of thermal conductivity of ultra-thin single crystal silicon film using symmetric structure. Chin J Semicond 27: 1961–1965

Zienkiewics OC, Morgan K (1983) Finite elements and approximation, Wiley, New York

Zimdahl W, Pavón D, Jou D (1993) Cosmological perturbations in a universe with particle production. Class Quant Grav 10:1775–1789

Zimdahl W, Pavón D (1993), Cosmology with adiabatic matter creation. Phys Lett A 176:57–61

Zimdahl W, Pavón D (1994), Cosmology with adiabatic matter creation, Int J Mod Phys D 3: 327–330

Zimdahl W, Triginer J, Pavón D (1996) Collisional equilibrium, particle production, and the inflationary universe. Phys Rev D 54:6101–6110

Zimm BH (1956) Dynamics of polymer molecules in dilute solution: viscoelasticity, flow birefringence and dielectric loss. J Chem Phys 24:269–278

Zubarev DN, Morozov V, Röpke G (1997) Statistical mechanics of nonequilibrium processes. Basic Concepts, Kinetic Theory, vol 1.;elaxation and Hydrodynamic Processes, vol 2. Akademie Verlag, Berlin

General Books and Popularizations

Atkins PW (2007) Four Laws that drive the Universe. Oxford University Press, Oxford

Bergé P, Pomeau Y, Vidal C (1984) L’ordre dans le chaos. Hermann, Paris

Coveney P, Highfield R (1990) The Arrow of Time. Flamingo, London

Davies PCW (1974) The Physics of Time Asymmetry. University of California Press, Berkeley
Denbigh K, Denbigh J (1985) Entropy in Relation with Incomplete Knowledge. Cambridge University Press, Cambridge
Landsberg PT (2001) Seeking Ultimates. An Intuitive Guide to Physics. Institute of Physics Publishing, Bristol/Philadelphia
Leggett AJ (1987) The Problems of Physics. Oxford University Press, Oxford
Prigogine I (1980) From Being to Becoming. Freeman, San Francisco
Prigogine I (1996) La fin des certitudes. O. Jacob, Paris
Prigogine I, Stengers I (1979) La nouvelle alliance, métamorphose de la science. Gallimard; Order out of Chaos: Man's new dialogue with nature. Bantam, New York, 1984
Prigogine I, Stengers I (1988) Entre le temps et l'éternité. Fayard, Paris
Segrè G (2002) Einstein's Refrigerator: Tales of the Hot and Cold. Penguin, London
Segrè G (2002) A Matter of Degrees: What Temperature Reveals about the Past and Future of our Species, Planet, and Universe. Penguin, London
Schneider ED, Sagan D (2005) Into the Cool: Energy Flow, Thermodynamics, and Life. Chicago University Press, Chicago, IL/London
Vidal Ch, Lemarchand H (1988) La réaction créatrice. Herman, Paris
Winfree A (1980) The Geometry of Biological Time. Springer, Heidelberg
Winfree A (1987) The Timing of Biological Clocks. Scientific American Library, Freeman, New York
Winfree A (1987) When Time Breaks Down. Princeton University Press, Princeton, NJ

Author Index

Subject Index