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GILBERTO MEDEIROS KREMER

An Introduction to the Boltzmann Equation and Transport Processes in Gases

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To Maria Rachel, Laura and Carla

Ludwig Eduard Boltzmann (1844–1906)

Preface

This book deals with the classical kinetic theory of gases. Its aim is to present the basic principles of this theory within an elementary framework and from a more rigorous approach based on the Boltzmann equation. The subjects are presented in a self-contained manner such that the readers can understand and learn some methods used in the kinetic theory of gases in order to investigate the Boltzmann equation.

In Chapter 1, a sketch on the evolution of the ideas of the kinetic theory is presented. Afterwards, the basic principles of an elementary kinetic theory are introduced, which are based on the concepts of mean free path, molecular mean velocity and mean free time. The Maxwellian distribution function is determined from statistical arguments, and the transport coefficients of shear viscosity, thermal conductivity and self-diffusion are obtained from the elementary theory. The most common interaction potentials used in the kinetic theory of gases are also introduced in this chapter, and the dynamics of a binary collision is analyzed.

Chapter 2 is dedicated to the study of the Boltzmann equation. First, the Boltzmann equation is derived and the equations of the BBGKY hierarchy are determined. From the knowledge of the transfer equation—which follows from the Boltzmann equation—the macroscopic balance equations for the moments of the distribution function are derived. The equilibrium distribution function is determined from the Boltzmann equation and the equilibrium states of a rarefied gas are also analyzed. In this chapter, the $\mathcal{H}$-theorem and the paradoxes of Loschmidt and Zermelo are discussed. The chapter ends with an analysis of the different forms of the entropy which are used in statistical mechanics to describe the canonical and microcanonical ensembles.

The Chapman–Enskog method is the subject of Chapter 3. First, a phenomenological theory based on the thermodynamic theory of irreversible processes is used to determine the laws of Navier–Stokes and Fourier of a single fluid. Afterwards, a simplified version of the Chapman–Enskog method is developed in order to derive these laws and to determine the transport coefficients of shear viscosity and thermal conductivity of a monatomic gas.

A more formal version of the method and the so-called BGK model of the Boltzmann equation are also presented in this chapter.

In Chapter 4, the moment methods are analyzed, which consist of the Grad's method, Maxwell and Ikenberry–Truesdell method and the Chapman–Enskog–Grad combined method. The Boltzmann equation in non-inertial frames of reference and the frame dependence of the heat flux vector are also discussed in that chapter.

Polyatomic gases are studied in Chapter 5 within the framework of a semiclassical model and of a classical model. The case of a polyatomic gas of rough spherical molecules is also discussed and the transport coefficients for this simple classical model are determined.

Chapter 6 is devoted to the analysis of moderately dense gases. First, the van der Waals equation of state is derived from the virial theorem and afterwards the Enskog equation for moderately dense gases is presented. From the knowledge of the distribution, the coefficients of shear and bulk viscosity and thermal conductivity are determined for a moderately dense gas. This chapter ends with a discussion on the modified Enskog equation.

Granular gases are examined in Chapter 7 where the cooling rate and the corrections to the transport coefficients due to inelastic collisions are determined. A sketch on the theory of granular gases of rough spherical molecules is also presented in this chapter.

In Chapter 8, mixtures of monatomic gases are analyzed. The Navier–Stokes, Fourier and Fick laws are determined from the knowledge of the distribution functions of the constituents, and the transport coefficients are obtained for mixtures of arbitrary number of constituents. The case of a binary mixture is likewise discussed in this chapter.

The last chapter is dedicated to the study of chemically reacting gas mixtures. It begins with a thermodynamic description of chemically reacting systems and the determination of the Boltzmann equations which take into account the bimolecular reactions of the type $A_1 + A_2 \rightleftharpoons A_3 + A_4$. The $\mathcal{H}$-theorem is analyzed, and for the chemical reaction $H_2 + Cl \rightleftharpoons HCl + H$, the transport coefficients are determined and the trend to equilibrium is discussed. Symmetric reactions of the type $A + A \rightleftharpoons B + B$ are also studied in that chapter and the influence of the heat reaction on slow reactions is determined. Furthermore, the symmetric reaction which proceeds without a barrier and the influence of the molecular geometry on chemically reacting systems are, in addition, discussed.

In almost all sections of the book exercises are proposed directly related with the text.

It is expected that this book could be useful as a textbook for students and researchers who are interested in the foundations of the Boltzmann equation and in the classical methods used in the kinetic theory for the determination of the transport coefficients of the gases.

Parts of this manuscript refer to several courses I have been teaching since 1986 at my Department and other Departments at Universidade Federal do

Rio de Janeiro, Universidade de São Paulo, Universidade Estadual de Ponta Grossa and Universidade do Minho (Portugal). I would like to thank all my students, collaborators and colleagues for comments and remarks on parts of the present manuscript, especially Professor Ingo Müller, Dr. Giselle Munhoz Alves and Dr. Wilson Marques Junior. I thank Gislaini Jacomini for reading the manuscript and helping with the English wording.

Curitiba, Brazil
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Contents

Chapter 1
Basic Principles of the Kinetic Theory

1.1 Introduction

One of the main objectives of the kinetic theory is to describe the macroscopic properties of gases—such as pressure, temperature, thermal conductivity, viscosity, diffusion, etc.—from microscopic quantities that are associated with the molecules which compose the gases—such as mass, velocity, kinetic energy, internal degrees of freedom and interaction forces between the molecules.

The concept of the atomic theory of the matter was formulated—according to Aristotle (384 BC–322 BC) and his pupil Theophrastus (ca. 372 BC–287 BC)–by Leucippus of Miletus (ca. 480 BC–ca. 420 BC) and his disciple Democritus of Abdera (about 460 BC to about 370 BC). The only statement of Leucippus known today is *"Nothing happens in vain, but everything from reason and of necessity"*, while one attributed to Democritus and related with atoms is *"By convention sweet, by convention bitter, by convention hot, by convention cold, by convention color: but in reality atoms and void."*

Whereas Aristotle did not agree with the ideas of atomism, Theophrastus had another point of view concerning the composition of matter: *"Both matter and void have real existence. The constituents of matter are elements infinite in number and always in motion, with an infinite variety of shapes, completely solid in composition."*

The ideas of atomism of Leucippus and Democritus were supported by Epicurus (341 BC–270 BC), who in a letter to Herodotus wrote *"Again, of bodies some are composite, others the elements of which these composite bodies are made. These elements are indivisible and unchangeable, and necessarily so, if things are not all to be destroyed and pass into non-existence, but are to be strong enough to endure when the composite bodies are broken up, because they possess, a solid nature and are incapable of being anywhere or anyhow dissolved. It follows that the first beginnings must be indivisible, corporeal entities."*

The concept of atoms was passed from the Greeks to the Romans, and the poet Titus Lucretius Carus (ca. 99 BC–ca. 55 BC) wrote in his book “De Rerum Natura”:

> *“So, any atom has a singleness*
> *Solid, coherent, not compound, but strong*
> *In its eternal singleness and nature*
> *Which keeps it as a seed of things, allows*
> *No diminution nor subtraction from it.”*

The ideas of atomic theory passed from the Romans to the Renaissance period where Pierre Gassendi (1592–1655), a French philosopher, scientist and mathematician, attempted to reconcile the atomism with Christianity. Robert Boyle (1627–1691), best known for the law which bears its name and gives the relation between pressure and volume of a gas, proposed a qualitative atomic theory in order to explain the elasticity ($\acute{\varepsilon}\lambda\alpha\tau\eta\rho$) of the air. Isaac Newton (1643–1727) in his “Philosophiae Naturalis Principia Mathematica” (1687) discussed also the elasticity of air and wrote *“... particles fleeing from each other, with forces that are inversely proportional to the distances of their centres, compose an elastic fluid, whose density is as the compression”.*

The main founders of the theory known nowadays as “Elementary Kinetic Theory” were the scientists: Daniel Bernoulli (1700–1782), John Herapath (1790–1868), John James Waterston (1811–1883), James Prescott Joule (1818–1889), Karl Krönig (1822–1879), Rudolf Clausius (1822–1888) and James Clerk Maxwell (1831–1879).

Bernoulli in his book “Hydrodynamica” (1738) explained the compressibility of elastic fluids (gases) by considering the gases constituted of very small particles in very rapid motion. He succeeded to deduce Boyle’s law from his model and a correction to it when the relationship between the diameter of the molecules and their mean distance was not negligible. Furthermore, he obtained a relationship connecting the pressure with the mean square of the molecular velocities.

In 1821, Herapath developed a kinetic theory and obtained almost the same results as Bernoulli but in a more systematic way. He introduced the concept of particle number density which he called “numeratom”, but related the temperature to the momentum of the molecules of the gas and not to its energy. Unfortunately, his works were rejected by the Royal Society of London, the referees claiming that his investigations were too speculative.

The next development of the kinetic theory came with Waterston, who in 1846 succeeded to obtain from a kinetic theory the correct expression for the dependence of the pressure on the particle number density of the gas and the mean square of the molecular velocities. In his report to the British Association, in 1851, it is stated *“... He (the author) shows that the result of this state of motion must be to give the gas an elasticity proportional to the mean square of the molecular motions, and to the total mass of the atoms contained in unit of bulk; that is to say, to the density of the medium. This* *elasticity, in a given gas, is a measure of temperature..."* He also showed that the temperature of a gas was proportional to its energy and introduced the energy equipartition principle. The fate of the works of Waterston was the same as that of Herapath; they were rejected for publication by the Royal Society of London.

Herapath's kinetic theory was restored by Joule in 1848 who using this theory calculated the velocity of a hydrogen molecule and estimated the heat capacity of a gas by considering only the translational motion of its molecules.

Krönig in 1856 published a paper that has called the attention of other scientists to the field of kinetic theory of gases, since he was a well-known scientist at that time and editor of the prestigious journal "Die Fortschritte der Physik". In his paper, there were no significant advances with respect to the previous works but it was considered as an independent research.

A new impulse to the kinetic theory of gases came in 1858 with the answer of Clausius to the question formulated by the Dutch chemist and meteorologist C.H.D. Buys-Ballot (1817–1890), who argued that: if according to the kinetic theory, the molecules of a gas have a large mean velocity—about 1,800 m/s for hydrogen molecules—they should diffuse and mix more rapidly than it is observed in the experiments. For the answer, Clausius introduced the concept of mean free path—which is the length traveled by a molecule of a gas between successive collisions—and stated that the molecules undergo encounters with other molecules which change their direction after a very short time of flight, the so-called mean free time. Clausius also recognized the importance of a link between the kinetic theory and thermodynamics. Furthermore, he calculated the velocity of the molecules of some gases and considered—apart from the translational—the rotational motion of the molecules of a gas. Aside from the formulation of the second law of thermodynamics, Clausius gave also another important contribution to the physical sciences by proposing the so-called "virial theorem", which can be used for the determination of an equation of state for a dense gas (see Section 6.1.1).

The last great scientist who developed the elementary kinetic theory was Maxwell, who in 1860 deduced the velocity distribution law which nowadays is known as the Maxwellian distribution function. He succeeded in determining the shear viscosity coefficient of an ideal gas and showed that it depends on the temperature but not on the particle number density, a fact which was unknown at that time.

The main scientists who developed the modern kinetic theory of gases were James Clerk Maxwell (1831–1879) and Ludwig Eduard Boltzmann (1844–1906).

The foundations of the modern kinetic theory of gases were established in 1867 by Maxwell, who proposed a general transport equation for arbitrary macroscopic quantities associated with mean values of microscopic quantities. This equation of transport relates the time evolution of a macroscopic quantity with the motion of the molecules, collision between the molecules and action of external forces. Although the theory was valid for any molecular interaction potential, Maxwell could only determine the transport coefficients of shear viscosity, thermal conductivity and diffusion by assuming that the interaction potential was derived from a repulsive force which was inversely proportional to the fifth power of the relative distance between the molecules. Nowadays, this type of potential is known as Maxwellian potential. About the kinetic theory proposed by Maxwell, Boltzmann wrote the following remark: *"... First the variations in velocity develop majestically, then the equations of state enter on one side, the equations of the central motion on the other; ever higher surges the chaos of formulae. Suddenly, four words sound out: 'Put $n = 5$'. The evil demon V (velocity) disappears..."*

The kinetic theory of gases gained a new impulse in 1872 with the work by Boltzmann, who proposed an integro-differential equation—the Boltzmann equation—which represents the evolution of the velocity distribution function in the phase space spanned by the coordinates and velocities of the molecules. In the Boltzmann equation, the temporal change of the distribution function has two terms, one of them is a drift term due to the motion of the molecules, while the other one is a collision term related to encounters of the molecules. Based on this equation, Boltzmann proposed the so-called $\mathcal{H}$-function which decreases with time or remains constant. The identification of this function as the negative of the gas entropy gave a molecular interpretation of the increase of the entropy for irreversible processes. Furthermore, Boltzmann in the same work presented a rigorous deduction of the Maxwellian distribution function.

The determination of the entropy from a molecular theory turned out to be one of the cornerstones of a new physical theory: statistical mechanics, a name which was coined by another founder of this science, the great American scientist Josiah Willard Gibbs (1839–1903). However, the explanation of the second law of thermodynamics by a molecular model was not yet in consensus among the scientists in Boltzmann time. Indeed, two paradoxes were discussed at that time, which are connected with the molecular interpretation of the entropy increase, namely:

(a) The proof is based on Newtonian mechanics where time is considered reversible, hence under time reversal the entropy should decrease. This is known as the "time-reversal paradox" formulated by the Austrian physicist Josef Loschmidt (1821–1895) and

(b) According to a theorem of the French mathematician Jules Henri Poincaré (1854–1912), any isolated, finite and conservative system of particles should return to an arbitrary small neighborhood of its initial state after a sufficient large time interval, the so-called Poincaré recurrence time. Hence, the entropy—according to its molecular interpretation—should approach its initial value after a finite time which could be attained only by decreasing its value. This is the "recurrence paradox" formulated by the German mathematician Ernst Zermelo (1871–1953) who at that time was an assistant of the German physicist Max Planck (1858–1947).

The above paradoxes will be discussed in Section 2.8.4.

From the Boltzmann equation, one could determine the velocity distribution function and hence the transport coefficients of rarefied gases; however, this task was not so easy. Indeed, it took almost 40 years after the proposition of Boltzmann equation for David Hilbert (1862–1943) to show how one could get an approximate solution of the integro-differential equation from a power series expansion of a parameter which is proportional to the mean free path. Further advances were due to Sydney Chapman (1888–1970) and David Enskog (1884–1947) who—in the years 1916 and 1917—calculated independently and by different methods the transport coefficients for gases whose molecules interact according to any kind of spherically symmetric potential function.

Although the kinetic theory of gases is nowadays an important theory in science, in Boltzmann time, there were scientists who were against the use of “hypothetical concepts” such as “atoms” in natural sciences. The principal opponents were: Ernst Mach (1838–1916), Wilhelm Ostwald (1853–1932) and Ernst Zermelo (1871–1953). The criticism was so severe that Boltzmann wrote in the preface of his book on kinetic theory of gases: *“...It was just at this time that attacks on the theory of gases began to increase. I am convinced that these attacks are merely based on a misunderstanding, and that the role of gas theory in science has not played out. ...In my opinion it would be a great tragedy for science if the theory of gases were temporarily thrown into oblivion because of a momentary hostile attitude toward it, as was for example the wave theory because of Newton’s authority.”*

Boltzmann committed suicide on September 5, 1906 in the village of Duino in Italy and in the years following his death, the atomic theory of matter was recognized as a well-established physical theory, thanks mainly to the theoretical explanation of the Brownian motion and the experimental determination of the Avogadro’s number from this theory (see Section 1.3).

This book deals with the classical kinetic theory of gases and its aim is to present the main ideas behind the Boltzmann equation and the methods used for the determination of the transport coefficients in gases, including shear viscosity, thermal conductivity, diffusion and thermal diffusion, which are related to the classical laws of Navier-Stokes, Fourier and Fick. The particle systems analyzed here are restricted to ideal monatomic and polyatomic gases, dense gases, granular gases, mixtures of monatomic gases and chemically reacting gases. The transport coefficients are obtained here by using the classical methods of the kinetic theory and the question of various higher order corrections is not addressed here. Furthermore, in this book it is not discussed neither exact nor numerical solutions of the Boltzmann equation and of the field equations derived from it. The analysis of the Boltzmann equation is restricted to small Knudsen numbers where the collision term is important for the determination of the transport coefficients. The calculation of the transport coefficients from the Boltzmann equation for realistic potential functions is a very difficult problem which can be solved only through numerical calculations. In order to have explicit expressions for the transport coefficients only very simple potentials (hard-sphere potentials, purely repulsive potentials, etc.) were analyzed. In view of the schematic nature of these potentials, no comparison with the available experimental data has been attempted in this book. The book is intended to be an introductory textbook on the Boltzmann equation and not a compendium of recent results. Therefore up to date references are not given in each section and modern developments are not discussed. The reader who is interested in the contemporary developments in the theory of the Boltzmann equation and the rigorous mathematical methods of kinetic theory of gases should consult the books:

- G. A. Bird, *Molecular Gas Dynamics and the Direct Simulation of Gas Flows* (Oxford University Press, Oxford, 1994).
- C. Cercignani, R. Illner and M. Pulvirenti, *The Mathematical Theory of Dilute Gases* (Springer, New York, 1994).
- C. Cercignani, *Rarefied Gas Dynamics: From Basic Concepts to Actual Calculations* (Cambridge University Press, Cambridge, 2000).
- Y. Sone, *Kinetic Theory and Fluid Dynamics* (Birkhäuser, Boston, 2002).
- C. Cercignani, *Slow Rarefied Flows: Theory and Application to Micro-Electro-Mechanical Systems* (Birkhäuser, Basel, 2006).
- Y. Sone, *Molecular Gas Dynamics: Theory, Techniques, and Applications* (Birkhäuser, Boston, 2006).

It is hoped that the book could be useful to the beginners in the field who are interested in the historical development of various approaches to the Boltzmann equation and in the classical tools of the kinetic theory of gases which are still widely used for the determination of the transport coefficients.

The notation used throughout this book is the following:

(a) Cartesian notation for tensors is used with Latin indexes $i, j, k, \ldots$—which may range from 1 to 3—denoting the three-dimensional system of spatial coordinates x, y, z;

(b) Einstein's summation convention over repeated indexes is used, for example, $T_{ij}v_j \equiv \sum_{j=1}^{3} T_{ij}v_j$;

(c) Parentheses around the indexes denote the symmetric part of a tensor, brackets its antisymmetric part, while angular parentheses refer to its traceless symmetric part, for example,

$$T_{(ij)} = \frac{1}{2}(T_{ij} + T_{ji}), \quad T_{[ij]} = \frac{1}{2}(T_{ij} - T_{ji}), \quad T_{\langle ij\rangle} = T_{(ij)} - \frac{1}{3}T_{rr}\delta_{ij}.$$

where δ_{ij} is Kronecker's symbol, defined by

$$\delta_{ij} = \begin{cases} 1, & \text{if} \quad i = j, \\ 0, & \text{if} \quad i \neq j. \end{cases}$$

The traceless tensor $T_{\langle ij\rangle}$ is also called tensor deviator;

(d) The permutation symbol is defined by

$$\varepsilon_{ijk} = \begin{cases} 1 & \text{if } (i,j,k) \text{ is an even permutation of } (1,2,3), \\ -1 & \text{if } (i,j,k) \text{ is an odd permutation of } (1,2,3), \\ 0 & \text{otherwise.} \end{cases}$$

The following identities for the permutation symbol hold:

$$\varepsilon_{ijk}\varepsilon_{imn} = \delta_{jm}\delta_{kn} - \delta_{jn}\delta_{km}, \qquad \varepsilon_{ijk}\varepsilon_{ijn} = 2\delta_{kn}, \qquad \varepsilon_{ijk}\varepsilon_{ijk} = 6.$$

1.2 Molecular Structure of a Gas

1.2.1 Basic Principles

The kinetic theory considers the gases composed by a large number of molecules, which in the major part of time intervals are moving independently towards each other across the volume they are restricted. In the absence of external body forces, the molecules move in straight lines and their motion is briefly interrupted when they collide either with themselves or with the walls of the recipient. If the potential energies of the molecules are negligible in comparison to their kinetic energies, the gas is called ideal or rarefied; otherwise, it is known as dense or real gas.

In order to have an idea of the characteristic dimensions valid for an ideal gas, suppose the molecules as hard spheres of diameter d. As is well known in physical-chemistry, a mole of an ideal gas at a temperature of 273.15 K and pressure of 1 atmosphere (102,325 Pa) occupies a volume of $V_M = 2.24 \times 10^{-2}$ m^3 and has a number of molecules equal to Avogadro's number $N_A = 6.022 \times 10^{23}$ molecules/mol. In this case, the particle number density is of order of $n = N_A/V_M \approx 2.68 \times 10^{25}$ molecules/m^3, and by supposing the molar volume divided into small cubic cells with one molecule per cell, the volume of each cell is approximately $V_C = 1/n \approx 3.72 \times 10^{-26}$ m^3. Hence, the length of the edge of each cell is $D = \sqrt[3]{V_C} \approx 3.34 \times 10^{-9}$ m, which represents a mean distance between the molecules.

Consider now one test molecule which moves with a mean relative velocity $\bar{g}$ in a gas where the particle number density is n. From Figure 1.1 one can conclude that per unit of time the test molecule will collide with all molecules whose centers are within the cylinder of basis $\pi\mathsf{d}^2$ and height $\bar{g}$. Hence, the collision frequency ν is given by

$$\nu = n\pi\mathsf{d}^2\bar{g}, \tag{1.1}$$

while the mean free time τ, which is the inverse of the collision frequency, reads

$$\tau = \frac{1}{\nu} = \frac{1}{n\pi \mathsf{d}^2 \bar{g}}. \tag{1.2}$$

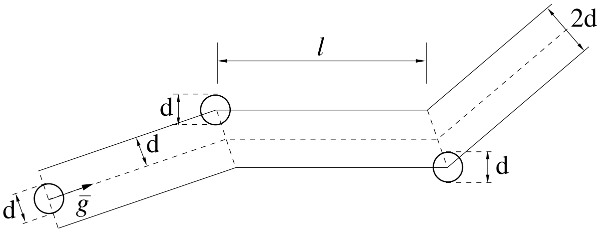

Fig. 1.1 Collision cylinder generated by the test molecule.

The mean free path l is defined as the mean distance traveled by a molecule between two successive collisions. Since the molecule moves with a velocity equal to the mean thermal velocity $\bar{c}$, the mean free path becomes

$$l = \bar{c}\tau = \frac{\bar{c}}{n\pi \mathsf{d}^2 \bar{g}}. \tag{1.3}$$

The mean collision time τ_c represents the time interval of interaction between molecules and it is considered to be proportional to the range of the intermolecular forces and inversely proportional to the mean relative velocity of the test molecule. The range of the intermolecular forces are of the same order of the molecular diameter, which implies that the collision time is proportional to the ratio

$$\tau_c \propto \frac{\mathsf{d}}{\bar{g}}. \tag{1.4}$$

Exercise

1.1 Estimate the collision frequency ν, the mean free time τ, the mean free path l and the mean collision time τ_c of an ideal gas with: (i) particle number density $n = 2.68 \times 10^{25}$ molecules/m^3, (ii) molecular diameter $\mathsf{d} = 2 \times 10^{-10}$ m and (iii) mean relative velocity of order of the mean thermal velocity $\bar{g} \approx \bar{c} = 10^3$ m/s.

1.2.2 The Maxwellian Distribution Function

In this section, the velocity distribution function of a gas in equilibrium—also known as the Maxwellian distribution function—will be deduced on the basis of the work by Maxwell.[1] The question is to know the probability of finding a molecule which is moving with velocity components within the range c_1 and c_1+dc_1 according to the x_1-axis, c_2 and c_2+dc_2 according to the x_2-axis and c_3 and c_3+dc_3 according to the x_3-axis. In this case, it is considered that for equilibrium processes without external forces, the following hypothesis are valid:

(i) the number of velocities which can be found within the range c_i and $c_i + dc_i$ is proportional to dc_i $(i = 1, 2, 3)$. Hence, $\phi(c_i)\ dc_i$ represents the probability to find a molecule with a velocity component within the range c_i and $c_i + dc_i$ for $i = 1, 2, 3$;

(ii) the three events are independent from each other, so that

$$\phi(c_1)dc_1\phi(c_2)dc_2\phi(c_3)dc_3$$

represents the probability to find the molecule with velocity components within the range c_1 and $c_1 + dc_1$, c_2 and $c_2 + dc_2$, c_3 and $c_3 + dc_3$. Instead of probabilities, one can define a distribution function $f(c_1, c_2, c_3)$ such that

$$f(c_1, c_2, c_3)dc_1dc_2dc_3 \equiv f(c_1, c_2, c_3)d\mathbf{c}$$

gives the particle number density of the molecules whose velocity components are at the intervals dc_1, dc_2 and dc_3. Therefore, the distribution function $f(c_1, c_2, c_3)$ can be written in terms of the probabilities as

$$f(c_1, c_2, c_3)dc_1dc_2dc_3 = n\phi(c_1)dc_1\phi(c_2)dc_2\phi(c_3)dc_3, \tag{1.5}$$

where n denotes the particle number density;

(iii) hypothesis of isotropy: for equilibrium processes in the absence of external forces there is no distinction between the three directions, so that $f(c_1, c_2, c_3)$ depends on c_1, c_2 and c_3 only through the invariant $c = \sqrt{c_1^2 + c_2^2 + c_3^2}$, i.e.,

$$f(c_1, c_2, c_3) = n\phi(c_1)\phi(c_2)\phi(c_3) = \varPhi\left(c = \sqrt{c_1^2 + c_2^2 + c_3^2}\right). \tag{1.6}$$

The determination of the distribution function f from the functional equation (1.6) proceeds by taking its logarithm, i.e.,

$$\ln\varPhi(c) = \ln n + \ln\phi(c_1) + \ln\phi(c_2) + \ln\phi(c_3), \tag{1.7}$$

and afterwards by differentiating the resulting equation successively with respect to c_1, c_2 and c_3, yielding

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[1] J.C. Maxwell, "Illustrations of the dynamical theory of gases", *Phil. Mag.*, **19** 19-32; **20** 21-37 (1860).

$$\frac{1}{c}\frac{d\ln\varPhi(c)}{dc}=\frac{1}{c_1}\frac{d\ln\phi(c_1)}{dc_1}=\frac{1}{c_2}\frac{d\ln\phi(c_2)}{dc_2}=\frac{1}{c_3}\frac{d\ln\phi(c_3)}{dc_3}. \tag{1.8}$$

The only possibility to fulfill (1.8) is that all terms must be equal to a constant which is taken equal to $-2b^\star$. Therefore, one obtains through integration

$$\phi(c_i)=a^\star e^{-b^\star c_i^2}, \qquad (i=1,2,3), \qquad \varPhi(c)=f(c_1,c_2,c_3)=na^{\star 3}e^{-b^\star c^2}, \tag{1.9}$$

where $a^\star$ is an integration constant. Since f is a bounded positive function, it follows that the constants $a^\star$ and $b^\star$ must be positive.

The determination of the constants $a^\star$ and $b^\star$ is based on the premises that the thermodynamic equilibrium of a gas is characterized by two state variables, namely, its mass density ϱ and its internal energy density $\varrho\varepsilon$. In kinetic theory of monatomic gases, these two state variables are defined in terms of the mass of a molecule[2] m and its kinetic energy $mc^2/2$ by

$$\varrho=mn=\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} mf\,dc_1dc_2dc_3, \tag{1.10}$$

$$\varrho\varepsilon=\frac{3}{2}nkT=\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{1}{2}mc^2f\,dc_1dc_2dc_3. \tag{1.11}$$

Equation (1.11) expresses the condition that the mean kinetic translational energy per molecule of a monatomic rarefied gas is equal to $3kT/2$, where T denotes the temperature of the gas and $k=1.38\times10^{-23}$ J/K is the Boltzmann constant. This last relationship is a consequence of the energy equipartition principle which states: to each molecule a mean energy of $kT/2$ is associated per degree of freedom.

Now inserting $(1.9)_2$ into (1.10), the subsequent transformation of the Cartesian coordinates (c_1,c_2,c_3) into spherical coordinates (c,θ,φ) and the integration of the resulting equation leads to

$$\begin{aligned}\varrho&=\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} mna^{\star 3}e^{-b^\star c^2}dc_1dc_2dc_3\\&=\int_0^\infty\int_0^\pi\int_0^{2\pi} mna^{\star 3}e^{-b^\star c^2}c^2\sin\theta\,d\varphi\,d\theta\,dc=\varrho a^{\star 3}\left(\frac{\pi}{b^\star}\right)^{\frac{3}{2}},\end{aligned} \tag{1.12}$$

thanks to (1.123) in the Appendix to this chapter.

By following the same procedure, the substitution of $(1.9)_2$ into (1.11) and subsequent integration of the resulting equation yields

$$\frac{3}{2}nkT=\frac{3}{4}mna^{\star 3}\left(\frac{\pi}{b^\star}\right)^{\frac{3}{2}}\frac{1}{b^\star}. \tag{1.13}$$

---

[2] Note that the mass of a molecule $m=M/N_A$, defined as the ratio of its molecular weight M and Avogadro's number N_A, is given in grams.

The constants $a^\star$ and $b^\star$ can be determined from (1.12) and (1.13), resulting in

$$a^\star = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}}, \qquad b^\star = \frac{m}{2kT}. \tag{1.14}$$

Hence, $(1.9)_2$ can be written as

$$f(c_1, c_2, c_3) = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mc^2/(2kT)}, \tag{1.15}$$

which represents the velocity distribution function, the so-called Maxwellian distribution function.

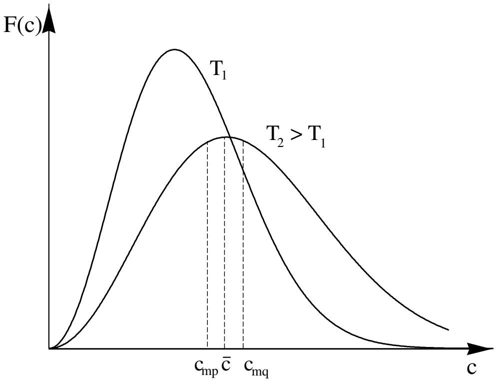

Fig. 1.2 $F(c)$ for two temperatures $T_2 > T_1$.

The distribution function for the velocity modulus $F(c)$ is defined in such a manner that $F(c)dc$ gives the number of molecules per unit volume with velocity modulus within the range of c and $c+dc$. In this case, it follows from (1.15) that

$$\begin{aligned} F(c)dc &= \int_0^{2\pi}\int_0^{\pi} n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mc^2/(2kT)} c^2 \sin\theta d\theta d\varphi dc \\ &= n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi c^2 e^{-mc^2/(2kT)} dc. \end{aligned} \tag{1.16}$$

Figure 1.2 shows the behavior of $F(c)$ for two different temperatures. Note that the maximum of the curve decreases and the curve becomes more flattened by the increase of the temperature.

Exercise

1.2 Perform the integrations and obtain the expressions on the right-hand sides of equations (1.12) and (1.13).

1.2.3 Determination of the Characteristic Velocities

From the distribution function for the velocity modulus (1.16), one can determine the mean thermal velocity of a molecule, which represents the mean value of the velocity modulus, i.e.,

$$\bar{c} = \frac{\int_0^\infty cF(c)dc}{\int_0^\infty F(c)dc} = \sqrt{\frac{8}{\pi}\frac{k}{m}T}. \tag{1.17}$$

The velocity modulus corresponding to the maximum value of $F(c)$ is called the most probable velocity and denoted by c_{mp}. By differentiating $F(c)$ with respect to c and equating the resulting equation to zero, it follows

$$c_{mp} = \sqrt{2\frac{k}{m}T}. \tag{1.18}$$

Another characteristic velocities is the mean quadratic velocity c_{mq}, defined as the square root of the mean value of the square of the velocity modulus:

$$c_{mq} = \sqrt{\overline{c^2}} = \sqrt{\frac{\int_0^\infty c^2F(c)dc}{\int_0^\infty F(c)dc}} = \sqrt{3\frac{k}{m}T}. \tag{1.19}$$

The three velocities $\bar{c}$, c_{mp} and c_{mq} are represented in Figure 1.2.

For the determination of the mean relative velocity, one has to consider molecules with velocity $\mathbf{c}$ whose particle number density in the velocity range $\mathbf{c}$ and $\mathbf{c}+d\mathbf{c}$ is given by $f(\mathbf{c})d\mathbf{c}$, and molecules with velocity $\mathbf{c}_1$ whose particle number density in the velocity range $\mathbf{c}_1$ and $\mathbf{c}_1+d\mathbf{c}_1$ corresponds to $f(\mathbf{c}_1)d\mathbf{c}_1$. If $g = |\mathbf{c}_1 - \mathbf{c}|$ denotes the relative velocity modulus and by considering a fixed value of the velocity $\mathbf{c}_1$, one may infer that the mean relative velocity modulus for a given velocity $\mathbf{c}_1$ with respect to all other molecules reads

$$\frac{\int gf(\mathbf{c})d\mathbf{c}}{\int f(\mathbf{c})d\mathbf{c}} = \frac{1}{n}\int gf(\mathbf{c})d\mathbf{c}. \tag{1.20}$$

The integral in (1.20) represents the three integrals for the components of the velocity $\mathbf{c}$ in the range $(-\infty,\infty)$ and this notation will be used henceforth. For the knowledge of the mean value of the relative velocity modulus referring to all velocities of the molecules—and not only to a fixed value $\mathbf{c}_1$—one has to integrate again the expression (1.20) with respect to all values of $\mathbf{c}_1$, yielding

$$\bar{g} = \frac{1}{n}\int f(\mathbf{c}_1)\Big[\frac{1}{n}\int g f(\mathbf{c}) d\mathbf{c}\Big] d\mathbf{c}_1. \tag{1.21}$$

For the integration of (1.21), new integration variables are introduced, namely, the relative velocity **g** and the center of mass velocity **G**, defined by

$$\mathbf{g} = \mathbf{c}_1 - \mathbf{c}, \qquad\qquad \mathbf{G} = \frac{\mathbf{c}_1 + \mathbf{c}}{2}. \tag{1.22}$$

The inverse transformations of the above equations read

$$\mathbf{c} = \mathbf{G} - \frac{1}{2}\mathbf{g}, \qquad\qquad \mathbf{c}_1 = \mathbf{G} + \frac{1}{2}\mathbf{g}, \tag{1.23}$$

which imply the following relationships

$$c^2 + c_1^2 = 2G^2 + \frac{1}{2}g^2, \tag{1.24}$$

$$J = \frac{\partial(c_1, c_2, c_3, c_1^1, c_2^1, c_3^1)}{\partial(g_1, g_2, g_3, G_1, G_2, G_3)} = \begin{vmatrix} -\frac{1}{2} & 0 & 0 & 1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 & 0 & 1 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 & 0 & 1 \\ \frac{1}{2} & 0 & 0 & 1 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 & 1 & 0 \\ 0 & 0 & \frac{1}{2} & 0 & 0 & 1 \end{vmatrix} = -1, \tag{1.25}$$

where J is the Jacobian of the transformation of the velocities $(\mathbf{c}, \mathbf{c}_1) \longmapsto (\mathbf{g}, \mathbf{G})$. Hence, the transformation of the velocity elements becomes

$$d\mathbf{c} d\mathbf{c}_1 = |J| d\mathbf{g} d\mathbf{G} = d\mathbf{g} d\mathbf{G}. \tag{1.26}$$

Now, the substitution of (1.15), (1.24) and (1.26) into the expression for the mean relative velocity modulus (1.21) leads to

$$\bar{g} = \Big(\frac{m}{2\pi kT}\Big)^3 \Big(\int e^{-mG^2/(kT)} d\mathbf{G}\Big)\Big(\int g e^{-mg^2/(4kT)} d\mathbf{g}\Big). \tag{1.27}$$

Finally, the integration of (1.27) by following the same procedure described above yields

$$\bar{g} = \sqrt{2}\sqrt{\frac{8kT}{\pi m}} = \sqrt{2}\bar{c}. \tag{1.28}$$

The mean free time (1.2) and the mean free path (1.3) can be rewritten, thanks to (1.28) as

$$\tau = \frac{1}{4n\mathsf{d}^2}\sqrt{\frac{m}{\pi kT}}, \qquad\qquad l = \frac{1}{\sqrt{2}\pi\mathsf{d}^2 n}, \tag{1.29}$$

showing that both are inversely proportional to the particle number density. Moreover, the mean free time is inversely proportional to the square root of the temperature.

Exercises

1.3 Show that the Jacobian of the transformation from $(\mathbf{c}, \mathbf{c}_1)$ to $(\mathbf{g}, \mathbf{G})$ is given by (1.25).

1.4 Obtain the expression (1.28) for the mean value of the relative velocity modulus.

1.5 Estimate the mean thermal velocity (1.17), the most probable velocity (1.18) and the mean quadratic velocity (1.19) for a helium gas at a temperature of 273 K. The molecular mass of helium is 4.00.

1.2.4 Molecular Flux

The number of molecules ΔN per time interval Δt which crosses a surface element ΔA perpendicular to the x_3-axis is given by

$$\Delta N = c_3 \Delta t \Delta A f(c_1, c_2, c_3) dc_1 dc_2 dc_3, \tag{1.30}$$

where $c_3 \Delta t \Delta A$ is the volume of the cylinder and $f(c_1, c_2, c_3) dc_1 dc_2 dc_3$ represents the number of molecules within the cylinder (see Figure 1.3). It is supposed that the molecules within the cylinder do not collide with themselves.

The molecular flux, defined as the number of molecules per unit of area and time, reads

$$\Delta \phi = \frac{\Delta N}{\Delta A \Delta t} = c_3 f(c_1, c_2, c_3) dc_1 dc_2 dc_3. \tag{1.31}$$

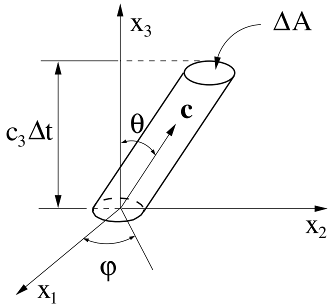

Fig. 1.3 Molecular flux across a surface ΔA.

The total flux is obtained from (1.31) by transforming the Cartesian coordinates (c_1, c_2, c_3) into spherical coordinates (c, θ, φ), by using the Maxwellian distribution function (1.15) and by integrating the resulting equation over the ranges of $0 \leqslant c < \infty$, $0 \leqslant \theta \leqslant \pi/2$ and $0 \leqslant \varphi \leqslant 2\pi$, yielding

$$\begin{aligned}\phi &= \int_0^\infty \int_0^{\frac{\pi}{2}} \int_0^{2\pi} n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mc^2/(2kT)} c^3 \cos\theta \sin\theta \, d\varphi \, d\theta \, dc \\ &= \frac{n}{4}\sqrt{\frac{8kT}{\pi m}} = \frac{n}{4}\bar{c}. \end{aligned} \tag{1.32}$$

The pressure exerted by a gas enclosed in a recipient upon its walls is caused by the transfer of the linear momentum of its molecules to the walls. By considering that the collisions of the molecules with the walls are elastic, the modulus of the velocity of a molecule before and after the collision remains unchanged. While the component of the velocity tangential to the walls remains also unchanged after collision, its normal component inverts its sign from c_3 to $-c_3$ (say). Hence, the change in the momentum of a molecule before and after its collision with the walls is $2mc_3$. The momentum transfer per unit of area and time of all molecules which are within a cylinder of basis ΔA and height $c_3 \Delta t$ is given by

$$\Delta p = 2mc_3 \frac{\Delta N}{\Delta A \Delta t} = 2mc_3^2 f(c_1, c_2, c_3) dc_1 dc_2 dc_3, \tag{1.33}$$

and is identified as the pressure Δp exerted on the area ΔA.

The total pressure is obtained through the integration over all velocity components, namely, $-\infty < c_1 < +\infty$, $-\infty < c_2 < +\infty$ and $0 \leqslant c_3 < +\infty$, yielding

$$p = 2\int_0^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} mc_3^2 f(c_1, c_2, c_3) dc_1 dc_2 dc_3. \tag{1.34}$$

By using the symmetry properties of the Maxwellian distribution function, namely, $f(c_1, c_2, c_3) = f(c_1, c_2, -c_3)$ and the relationship

$$\begin{aligned}&\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} mc_3^2 f(c_1, c_2, c_3) dc_1 dc_2 dc_3 \\ &= \frac{1}{3}\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} m(c_1^2 + c_2^2 + c_3^2) f(c_1, c_2, c_3) dc_1 dc_2 dc_3, \end{aligned} \tag{1.35}$$

it follows the thermal equation of state of the gas

$$p = \frac{1}{3}\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} mc^2 f(c_1, c_2, c_3) dc_1 dc_2 dc_3 = nkT. \tag{1.36}$$

Note that according to (1.11) and (1.36), the pressure and the internal energy density are related through $p = 2\varrho\varepsilon/3$.

Exercises

1.5 Obtain the equation of state $p = nkT$ from the integration of equation (1.34) by using the Maxwellian distribution function (1.15).

1.6 Estimate the molecular flux (1.32) of a helium gas at a temperature of 273 K, with a particle number density $n = 2.68 \times 10^{25}$ molecules/m^3.

1.2.5 Elementary Theory of Transport Processes

In a simple shear flow, a fluid is confined between two parallel plates and—in the continuum regime—it is supposed that there exists a complete adherence of the fluid to the plates. The plate at the bottom ($x_3 = 0$) is at rest while the one at $x_3 = L$ is moving with a constant velocity (see Figure 1.4). The velocity field of the fluid is given by $\mathbf{v} = (0, v_2(x_3), 0)$, and the velocity profile is linear.

The momentum transfer of the molecules at a surface located at a distance x_3 from the bottom is equal to the difference of the momenta of the molecules below and above this surface. Let θ be the angle of the velocity vector of a molecule with respect to the x_3-axis. The distance travelled by a molecule before it collides with another molecule is equal to the mean free path, and the difference between the momenta of molecules located at $x_3 - l\cos\theta$ and $x_3 + l\cos\theta$ is given by

$$\Delta I = mv_2(x_3 - l\cos\theta) - mv_2(x_3 + l\cos\theta) \approx -2m\frac{dv_2}{dx_3} l\cos\theta. \qquad (1.37)$$

Above, the velocity was developed in Taylor series and it was neglected terms of order $\mathcal{O}(l^2)$ and higher order terms.

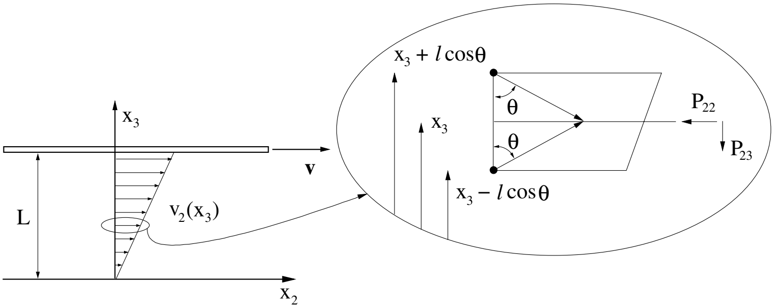

Fig. 1.4 Profile of the velocity in a simple shear flow.

The transfer of momenta of all molecules is obtained by multiplying the difference between the momenta ΔI with the molecular flux $\Delta\phi$ given by equation (1.31) yielding

$$\varDelta p_{23} = -2m\frac{dv_2}{dx_3} l\cos\theta c_3 f(c_1, c_2, c_3)dc_1dc_2dc_3. \tag{1.38}$$

The term $\varDelta p_{23}$ represents a momentum per unit area and time, hence a pressure. This pressure acts on a surface normal to the x_2-axis and parallel to the x_3-axis, being identified as the component $\varDelta p_{23}$ of the pressure tensor. The component p_{23} of the total pressure tensor is obtained through integration, i.e.,

$$\begin{aligned} p_{23} &= -2ml\frac{dv_2}{dx_3}\int_0^\infty\int_0^{\frac{\pi}{2}}\int_0^{2\pi} n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mc^2/(2kT)}c^3\cos^2\theta\sin\theta d\varphi d\theta dc \\ &= -\frac{mln\bar{c}}{3}\frac{dv_2}{dx_3}. \end{aligned} \tag{1.39}$$

The equation (1.39) relates the pressure tensor with a velocity gradient. A fluid which obeys this relationship is called Newtonian fluid. In kinetic theory of gases, such a relationship is also known as Navier–Stokes law.[3] The constant of proportionality is designated as the coefficient of shear viscosity μ. Hence,

$$p_{23} = -\mu\frac{dv_2}{dx_3} \qquad \text{with} \qquad \mu = \frac{mln\bar{c}}{3}. \tag{1.40}$$

According to (1.17), $(1.29)_2$ and $(1.40)_2$, the shear viscosity coefficient can be written as

$$\mu = \frac{2\sqrt{mkT}}{3\pi^{\frac{3}{2}}\mathsf{d}^2}. \tag{1.41}$$

One may infer from (1.41) that the shear viscosity coefficient does not depend on the density of the gas being proportional to the square root of the temperature. This conclusion is due to Maxwell[4] who wrote *"A remarkable result here presented to us in equation (24),* (here equation (1.41)) *is that if this explanation of gaseous friction be true, the coefficient of friction is independent of the density. Such a consequence of a mathematical theory is very startling, and the only experiment I have met with on the subject does not seem to confirm it. We must next compare our theory with what is known of the diffusion of gases, and the conduction of heat through a gas."* Note that the shear viscosity coefficient is related to the transport of linear momentum and has the dimension of Pa s=N s/m^2.

Consider now that the two parallel plates in Figure 1.4 are fixed, the one at $x_3 = 0$ with a temperature T_1 and the other at $x_3 = L$ at a temperature $T_2 > T_1$. The temperature of the confined gas is a function of x_3, i.e., $T = T(x_3)$.

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[3] Claude Louis Marie Henri Navier (1785–1836) French engineer and physicist; George Gabriel Stokes (1819–1903) English mathematician and physicist.

[4] J. C. Maxwell, "Illustrations of the dynamical theory of gases", *Phil. Mag.*, **19** 19-32; **20** 21-37 (1860).

The transfer of translational kinetic energy of the gas molecules to a surface at x_3 is due to the difference of the translational kinetic energy of the molecules that are below and above this surface, hence

$$\varDelta E = \frac{3}{2}kT(x_3 - l\cos\theta) - \frac{3}{2}kT(x_3 + l\cos\theta) \approx -3k\frac{dT}{dx_3}l\cos\theta, \tag{1.42}$$

where $3kT/2$ is the mean translational kinetic energy of a molecule. In equation (1.42), a similar development in Taylor series for the temperature was considered.

From the multiplication of $\varDelta E$ by the molecular flux $\varDelta\phi$—given by the equation (1.31)—it follows the transfer of translational kinetic energy of all molecules that are below and above the surface at x_3:

$$\varDelta q_3 = -3k\frac{dT}{dx_3}l\cos\theta c_3 f(c_1, c_2, c_3)dc_1dc_2dc_3. \tag{1.43}$$

The term $\varDelta q_3$ represents an energy per unit of area and time, i.e., a component of the heat flux vector. The component q_3 of the total heat flux vector is obtained through integration, yielding

$$\begin{aligned} q_3 &= -3kl\frac{dT}{dx_3}\int_0^\infty\int_0^{\frac{\pi}{2}}\int_0^{2\pi} n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mc^2/(2kT)}c^3\cos^2\theta\sin\theta\, d\varphi\, d\theta\, dc \\ &= -\frac{nkl\bar{c}}{2}\frac{dT}{dx_3}. \end{aligned} \tag{1.44}$$

One can conclude from (1.44) that the heat flux vector is proportional to the gradient of temperature, and this relationship is known as Fourier's law.[5] The proportionality factor is called thermal conductivity coefficient whose dimension is J/(m s K)=W/(m K). The equation (1.44) can also be rewritten as

$$q_3 = -\lambda\frac{dT}{dx_3} \qquad \text{with} \qquad \lambda = \frac{nkl\bar{c}}{2}. \tag{1.45}$$

By using (1.17), $(1.29)_2$ and $(1.45)_2$, the thermal conductivity coefficient becomes

$$\lambda = \frac{k}{m}\frac{\sqrt{mkT}}{\pi^{\frac{3}{2}}\mathsf{d}^2}, \tag{1.46}$$

and—like the shear viscosity coefficient—it does not depend on the density and is proportional to $\sqrt{T}$.

From (1.46) and (1.41), one can build the ratio

$$\frac{\lambda}{\mu} = \frac{3}{2}\frac{k}{m}. \tag{1.47}$$

The above result does not agree with the experimental data, since the experiments indicate that this ratio for monatomic gases is

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[5] Jean Baptiste Joseph Fourier (1768–1830) French mathematician and physicist.

$$\frac{\lambda}{\mu} \approx \frac{15}{4}\frac{k}{m}. \tag{1.48}$$

In Chapter 3, it will be shown that the result (1.48) follows from a more elaborated kinetic theory based on the Boltzmann equation.

The diffusion is a process which follows from the thermal motion of the molecules of a gas mixture, when mass transfer from one region to another occurs due to the existence of density gradients of its constituents. The self-diffusion happens in mixtures where the molecules of the constituents have practically the same characteristics, like the isotopes of some element.

Consider a situation where a gas is confined between two fixed parallel plates which are at same temperature, and suppose that the plate at $x_3 = 0$ has a particle number density smaller than the one at $x_3 = L$. In this case, the particle number density is a function of x_3, i.e., $n = n(x_3)$. The molecular flux which crosses a surface at x_3 is equal to the difference between the fluxes of molecules which are below and above this surface. Hence, from (1.31) and (1.15), it follows

$$\begin{aligned}
\Delta j_3 &= \Delta\phi(x_3 - l\cos\theta) - \Delta\phi(x_3 + l\cos\theta)\\
&= c_3\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mc^2/(2kT)}\left[n(x_3 - l\cos\theta) - n(x_3 + l\cos\theta)\right] dc_1 dc_2 dc_3\\
&\approx -2c_3\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mc^2/(2kT)}\frac{dn}{dx_3} l\cos\theta dc_1 dc_2 dc_3.
\end{aligned} \tag{1.49}$$

Above, it was considered a development in Taylor series of the particle number density n. The component j_3 of the total flux is obtained through integration of (1.49), yielding

$$\begin{aligned}
j_3 &= -2\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\frac{dn}{dx_3} l\int_0^\infty\int_0^{\frac{\pi}{2}}\int_0^{2\pi} c^3 e^{-mc^2/(2kT)}\cos^2\theta\sin\theta d\varphi\, d\theta\, dc\\
&= -\frac{\bar{c}l}{3}\frac{dn}{dx_3}.
\end{aligned} \tag{1.50}$$

The equation (1.50) represents Fick's law[6], which relates the molecular flux with the particle number density gradient. The proportionality factor is known as the self-diffusion coefficient which has a dimension of m^2/s. Hence

$$j_3 = -D\frac{dn}{dx_3} \qquad \text{where} \qquad D = \frac{\bar{c}l}{3}. \tag{1.51}$$

The coefficient of self-diffusion D can be rewritten as

$$D = \frac{2}{3\pi^{\frac{3}{2}}}\frac{\sqrt{mkT}}{mn\mathsf{d}^2}, \tag{1.52}$$

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[6] Adolf Eugen Fick (1828–1901) German physiologist.

thanks to (1.17) and $(1.29)_2$. Note that the self-diffusion coefficient is inversely proportional to the particle number density but has the same dependence on the temperature as the shear viscosity and thermal conductivity coefficients.

In "Continuum Thermodynamics"—a branch of mechanics and thermodynamics devoted to the analysis of the properties of materials modeled as a continuum media—the laws of Navier–Stokes, Fourier and Fick are denominated generically as constitutive equations and relate fluxes (effect) to forces (cause) of a given material. Here, the forces are the velocity gradient, the temperature gradient and the particle number density gradient, while the corresponding fluxes are the pressure tensor, the heat flux vector and the molecular flux.

Exercise

1.7 Estimate the coefficients of shear viscosity (1.41), thermal consductivity (1.46) and self-diffusion (1.52) for a gas at the temperature of 273 K, particle number density $n = 2.68 \times 10^{25}$ molecules/m^3 and whose molecules have mass $m = 2 \times 10^{-27}$ kg and diameter $\mathsf{d} = 2 \times 10^{-10}$ m.

1.2.6 Characteristic Dimensions

In Table 1.1, the characteristic dimensions for monatomic gases with particle number density of $n = 2.68 \times 10^{25}$ molecules/m^3, temperature of 273 K and pressure of 1 atm were determined from equations (1.2), (1.4), (1.17) and (1.29) by using the relationship in (1.28). The molecular diameters were calculated from (1.41) by taking into account the data[7] for the shear viscosity coefficient.

Table 1.1 Characteristic dimensions for monatomic gases

Gas	M	μ 10^{-6}Pa s	$\bar{c}$ 10^2 m/s	d 10^{-10}m	l 10^{-8}m	τ 10^{-10}s	τ_c 10^{-13}s
He	4.00	18.81	12.01	1.79	26.37	2.20	1.05
Ne	20.18	30.13	5.35	2.11	18.81	3.52	2.79
Ar	39.95	21.08	3.80	3.00	9.35	2.46	5.57
Kr	83.80	23.43	2.63	3.42	7.18	2.73	9.21
Xe	131.30	21.04	2.10	4.04	5.15	2.46	13.61

From the analysis of Table 1.1, one can infer that, for argon gas (say), the mean free path l of its molecules is of order of 312 times the diameter of its

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[7] J. Kestin; K. Knierim; E. A. Mason; B. Najafi; S. T. Ro & M. Waldman, "Equilibrium and transport properties of the noble gases and their mixtures at low density", *J. Phys. Chem. Ref. Data*, **13**, 229-303 (1984).

molecules d, while the mean free time τ is of order of 442 times the mean collision time τ_c. The collision frequency is of order of 4.1×10^9 collisions per second!

In this book, the motion of the molecules will be described by the Newtonian laws of classical mechanics. Quantum and relativistic effects are neglected so that the following conditions are valid for the gases in study:

(i) the de Broglie wavelength λ_{dB} of a molecule must be smaller than the mean distance between the molecules D

$$\lambda_{dB} = \frac{h}{\sqrt{3mkT}} \ll D, \tag{1.53}$$

where $h = 6.626 \times 10^{-34}$ J s is Planck's constant and[8]

(ii) the mean thermal velocity of a molecule $\bar{c}$ must be smaller than the light speed in vacuum ($\bar{c} \ll 2.998 \times 10^8$ m/s).

Exercise

1.8 Estimate the de Broglie wavelength for an ideal helium gas at a temperature 273 K and compare the result with the molecular mean distance which is of order $D \approx 3.34 \times 10^{-9}$ m.

1.2.7 Potentials of Molecular Interactions

In general, the forces which act on atoms and molecules can be divided into two categories, namely, forces of short range, also called valence or chemical forces, and forces of long range, known as van der Waals forces.[9] The valence forces are repulsive and are due to a superposition of the electronic clouds of the molecules when they get closer to each other. The van der Waals forces are attractive and can be subdivided into: (i) electrostatic contributions (interactions between different multipole moments); (ii) induction contributions (interaction between a charge distribution of one molecule and the induced moments of another molecule) and (iii) dispersion contributions (interaction between two induced charge distributions).

Figure 1.5 shows the interaction potentials which are of most common use in the literature of kinetic theory of gases:

(a) *Potential of Hard Spheres.* This potential represents only the repulsion forces between hard spheres of diameter d

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[8] Louis-Victor-Pierre-Raymond, 7th duc de Broglie (1892–1987) French physicist; Max Planck (1858–1947) German physicist.

[9] Johannes Diderik van der Waals (1837–1923) Dutch physicist.

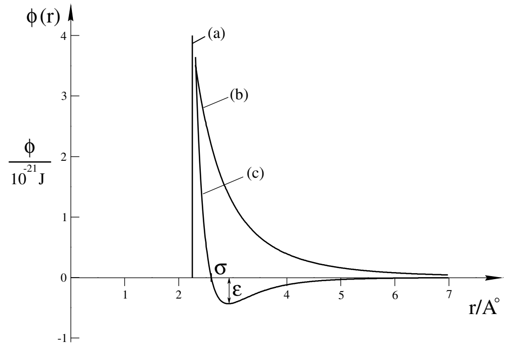

Fig. 1.5 Potentials of molecular interactions: (a) hard spheres; (b) centers of repulsion; (c) Lennard-Jones.

$$\begin{cases} \Phi(r) = \infty & \text{when} \quad r < \mathsf{d}, \\ \Phi(r) = 0 & \text{when} \quad r > \mathsf{d}. \end{cases} \tag{1.54}$$

(b) *Potential of Centers of Repulsion.* The potential function in this model reads

$$\Phi(r) = \frac{\kappa}{\nu - 1}\frac{1}{r^{\nu-1}}, \quad \kappa > 0, \quad \nu > 1, \tag{1.55}$$

and also represents only the repulsion forces. The case where $\nu = 5$ is called Maxwellian potential and the molecules of such a gas are known as Maxwellian molecules.

(c) *Potential (6–12) of Lennard-Jones.*[10] The potential function of this model furnishes a simple and real representation for spherical non-polar molecules:

$$\Phi(r) = 4\,\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{1.56}$$

The term $(\sigma/r)^{12}$ represents the repulsion forces, while the term $-(\sigma/r)^6$ represents the attractive ones. For $r = \sigma$, the potential vanishes, i.e., $\Phi(r) = 0$ and for $r = 2^{1/6}\sigma$, it becomes $\Phi(r) = -\varepsilon$, where ε is the depth of the potential well.

Exercise

1.9 Determine the interaction forces which correspond to the potentials of centers of repulsion and Lennard-Jones.

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[10] John Edward Lennard-Jones (1894–1954) English mathematician.

1.3 Brownian Motion

Robert Brown (1773–1858), a Scotch botanist, observed in 1828 that pollen grains in suspension in water drops had an irregular motion of zigzag nature, and after some experiments, concluded that this kind of movement was not of organic origin. The first theory which has explained satisfactorily this phenomena was due to Einstein[11] in 1905. Perrin[12] by using Einstein's theory and its own experiments on Brownian particles, determined Avogadro's number and gave another strong support to the atomic theory of matter, which was accepted by most of the scientists who were against it at that time.

The explanation of this phenomena is the following: there exist collisions between the molecules of the fluid and the particles which are in suspension on it. Due to the fact that some molecules of the fluid have velocities larger than its mean thermal velocity, there is a net impulse acting on the particles in suspension. Hence, the particles in suspension move across the fluid and are braked by the viscous forces.

Here, the analysis of the Brownian motion will be based on the equation proposed by Langevin[13]. Since the particles in suspension are moving due to an impulse and braked by viscous force, the one dimensional equation of motion of a particle reads

$$m\frac{dv}{dt} = -\frac{m}{\tau}v + F(t). \tag{1.57}$$

where m denotes the mass of a particle in suspension, $v = dx/dt$ its velocity, τ is a constant characteristic time and $F(t)$ is a stationary random force with a vanishing time average, i.e.,

$$\overline{F(t)} = \frac{1}{\theta}\int_0^\theta F(t+t')dt' = 0. \tag{1.58}$$

Langevin's equation (1.57) is valid if the following conditions are fulfilled: (a) the fluid is in a medium where the external actions are constant in time (e.g., the temperature must be constant in time); (b) the mass of the particles in suspension is larger than the mass of the fluid molecules and (c) the particle number density of the suspension particles is small, so that the collisions between themselves are neglected.

The velocities of the suspension particles are associated to random processes, since the second term on the right-hand side of Langevin's equation (1.57) is a stationary random force.

The multiplication of (1.57) by x/m leads to

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[11] Albert Einstein (1879–1955) German physicist.

[12] Jean Baptiste Perrin (1870–1942) French physicist.

[13] Paul Langevin (1872–1946) French physicist.

$$\frac{d}{dt}(xv) + \frac{1}{\tau}(xv) = v^2 + \frac{1}{m}xF(t). \tag{1.59}$$

Now, by taking the average over a discrete set of values of the functions in (1.59), yields

$$\Big\langle \frac{d}{dt}(xv) \Big\rangle + \frac{1}{\tau}\big\langle (xv) \big\rangle = \big\langle v^2 \big\rangle + \frac{1}{m}\Big\langle xF(t) \Big\rangle. \tag{1.60}$$

The symbol $\langle \quad \rangle$ denotes an average over a discrete set of N values, i.e.,

$$\big\langle x \big\rangle = \frac{1}{N}\sum_{k=1}^{N} x^{(k)}. \tag{1.61}$$

Due to the fact that x and $F(t)$ are statistically independent, the following relationships hold

$$\big\langle xF(t) \big\rangle = \big\langle x \big\rangle \big\langle F(t) \big\rangle = \big\langle x \big\rangle \overline{F(t)} = 0. \tag{1.62}$$

In the above equation, the ergodic hypothesis has been used in order to equate the average over a discrete set of values with its time average. This hypothesis can be stated as: a mechanical system will go beyond all possible microstates before returning to a given microstate, i.e., over a long period of time all accessible microstates are equally probable. Under this condition, the average value of a property of a system taken in a long period of time will be equal to its average value taken over all microstates.

According to the energy equipartition principle, a mean energy per molecule equal to $kT/2$ is associated to each degree of freedom, so that in the one-dimensional case it follows that

$$\frac{1}{2}m\big\langle v^2 \big\rangle = \frac{1}{2}kT, \qquad \text{i.e.,} \qquad \big\langle v^2 \big\rangle = \frac{kT}{m}. \tag{1.63}$$

Therefore, (1.60) can be written as

$$\frac{d\big\langle xv \big\rangle}{dt} + \frac{1}{\tau}\big\langle xv \big\rangle = \frac{kT}{m}. \tag{1.64}$$

due to (1.62), (1.63) and the relationship $\big\langle dx/dt \big\rangle = d\big\langle x \big\rangle/dt$.

The solution of (1.64) is given by

$$\big\langle xv \big\rangle = \mathcal{C}e^{-t/\tau} + \frac{\tau kT}{m}, \tag{1.65}$$

where $\mathcal{C}$ is an integration constant.

For the initial condition $x(0) = 0$, the variable $x(t)$ represents the displacement of the particle in suspension, and the constant becomes $\mathcal{C} = -\tau kT/m$. Hence, (1.65) reduces to

$$\langle xv \rangle = \frac{1}{2}\frac{d\langle x^2 \rangle}{dt} = \frac{\tau kT}{m}(1 - e^{-t/\tau}). \tag{1.66}$$

The solution of (1.66), with the above initial condition, is given by

$$\langle x^2 \rangle = \frac{2\tau kT}{m}\Big[t - \tau(1 - e^{-t/\tau})\Big]. \tag{1.67}$$

Two limiting cases of (1.67) are interesting to be analyzed:
(i) for $t \gg \tau$, one has $t - \tau \approx t$ and $e^{-t/\tau} \to 0$, so that it reduces to

$$\langle x^2 \rangle = \frac{2\tau kT}{m}t, \tag{1.68}$$

i.e., the mean square displacement is proportional to time and
(ii) for $t \ll \tau$, it follows from (1.67) that

$$\langle x^2 \rangle = \frac{2\tau kT}{m}\Big[t - \tau\Big(1 - 1 + \frac{t}{\tau} - \frac{1}{2}\frac{t^2}{\tau^2} + \ldots\Big)\Big] \approx \frac{kT}{m}t^2 = \langle v^2 \rangle t^2. \tag{1.69}$$

Hence, for $t \ll \tau$, the suspension particles move as free particles with a velocity equal to its mean square velocity.

The estimation of the characteristic time τ proceeds by supposing that the particles in suspension are spheres of radius r. According to Stokes' law, a sphere with radius r which moves with a velocity v in a fluid with shear viscosity μ suffers a friction force $-\alpha v$ where the coefficient α is given by $\alpha = 6\pi\mu r$. Here, one has

$$\frac{m}{\tau} = 6\pi\mu r, \qquad \text{or} \qquad \tau = \frac{m}{6\pi\mu r}. \tag{1.70}$$

Perrin in some experiments used micro-spheres—made of a resin of an Asian shrub of the family Guttiferae—with mass $m = 4.8 \times 10^{-17}$ kg and radius $r = 2.12 \times 10^{-7}$ m, which were in suspension in water drops with a shear viscosity coefficient $\mu = 10^{-3}$ Pa·s. In this case, from (1.70), one obtains that $\tau = 1.2 \times 10^{-8}$ s. Hence, for experimental observations in a microscope, $t \gg \tau$ and the combined equations (1.68) and (1.70) leads to

$$\langle x^2 \rangle = \frac{kT}{3\pi\mu r}t, \qquad \text{for} \qquad t \gg \tau. \tag{1.71}$$

Perrin determined Avogadro's number $N_A = R/k$ [14] from equation (1.71) and in its experimental data for $\langle x^2 \rangle$ for a given time interval of $t = 30$ s. The results of Perrin for Avogadro's number remained within the range of 6 and 8 $\times 10^{23}$ molecules/mol, which are of the same order of its present known value $N_A \approx 6.022 \times 10^{23}$ molecules/mol.

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[14] $R = 8.3145$ J/(mol·K) is the molar gas constant, also called universal or ideal gas constant.

Exercise

1.10 Obtain the solutions (1.66) and (1.67) from the differential equation (1.64).

1.4 Dynamics of a Binary Collision

1.4.1 Conservation Laws

For rarefied gases, the probability of collisions where three or more molecules participate is negligible in comparison with the binary encounters. Hence, for rarefied gases, it is possible to restrict the analysis of the collision processes to the binary interactions of its molecules.

Consider a collision between two electrically neutral molecules of a single rarefied gas whose masses are denoted by m. By neglecting the influence of external forces during the interval of a mean collision time, the equations of motion for two molecules in a binary encounter read

$$m\ddot{r}_i^1 = -\frac{\partial \Phi(r)}{\partial r_i^1}, \qquad m\ddot{r}_i^2 = -\frac{\partial \Phi(r)}{\partial r_i^2} = \frac{\partial \Phi(r)}{\partial r_i^1}. \tag{1.72}$$

In (1.72), r_i^1 and r_i^2 are the position vectors of the two molecules, while $\mathbf{r} = \mathbf{r}^2 - \mathbf{r}^1$ denotes the relative position vector and $r = |\mathbf{r}^2 - \mathbf{r}^1|$ is its modulus. The interaction potential $\Phi(r)$ is supposed spherically symmetric and of limited range so that $\lim_{r\to\infty} \Phi(r) = 0$.

Furthermore, suppose two molecules of a rarefied gas with asymptotic pre-collisional velocities denoted by $(\mathbf{c}, \mathbf{c}_1)$, while $(\mathbf{c}', \mathbf{c}_1')$ refer to their asymptotic post-collisional velocities. The subindex 1 was introduced only to differ the two molecules which participate in the binary encounter. The relative pre- and post-collisional velocities are defined, respectively, by

$$\mathbf{g} = \mathbf{c}_1 - \mathbf{c} \qquad \text{and} \qquad \mathbf{g}' = \mathbf{c}_1' - \mathbf{c}'. \tag{1.73}$$

The addition of the two equations (1.72) yields

$$m\ddot{r}_i^1 + m\ddot{r}_i^2 = 0. \tag{1.74}$$

Now, the integration of the above equation leads to the momentum conservation law which in terms of the pre- and post-collisional asymptotic velocities reads

$$m\mathbf{c} + m\mathbf{c}_1 = m\mathbf{c}' + m\mathbf{c}_1'. \tag{1.75}$$

From the multiplication of (1.72) by $1/m$ and the subtraction of the resulting equations, one obtains

$$\mu \ddot{\mathbf{r}} = -\frac{\partial \Phi}{\partial r}\frac{\mathbf{r}}{r}, \tag{1.76}$$

where $\mu = m/2$ represents the reduced mass.

The scalar multiplication of (1.76) by $\dot{\mathbf{r}}$ leads to

$$\frac{d}{dt}\left[\frac{\mu}{2}\dot{\mathbf{r}}^2 + \Phi(r)\right] = 0, \tag{1.77}$$

which expresses the energy conservation law during the collision. The integration of (1.77) yields

$$\frac{\mu}{2}\dot{\mathbf{r}}^2 + \Phi(r) = \frac{\mu}{2}g^2 = \frac{\mu}{2}g'^2, \tag{1.78}$$

due to the condition $\lim_{r\to\infty}\Phi(r) = 0$. Hence, the modulus of the asymptotic pre- and post-collisional relative velocities are equal to each other, i.e,

$$g = g'. \tag{1.79}$$

The equation (1.79) can be rewritten, thanks to (1.75), as

$$\frac{1}{2}mc^2 + \frac{1}{2}mc_1^2 = \frac{1}{2}mc'^2 + \frac{1}{2}mc_1'^2, \tag{1.80}$$

which is the common expression for the energy conservation law for two colliding molecules.

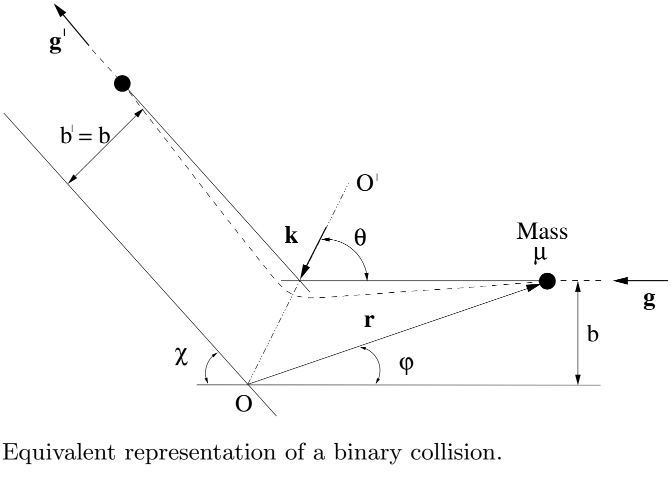

Fig. 1.6 Equivalent representation of a binary collision.

The cross product of (1.76) by $\mathbf{r}$ leads to the angular momentum conservation law, namely,

$$\frac{d}{dt}\left[\mu\dot{\mathbf{r}} \times \mathbf{r}\right] = 0. \tag{1.81}$$

From the integration of the above equation, it follows that

$$\dot{\mathbf{r}} \times \mathbf{r} = \text{constant}, \tag{1.82}$$

so that the relative motion between the molecules is confined to a plane, which is represented in Figure 1.6. If the vector before the collision $\mathbf{r}$ is projected into a plane perpendicular to $\mathbf{g}$ and the vector after the collision $\mathbf{r}'$ into a plane perpendicular to $\mathbf{g}'$, the equation (1.82) implies that $gb\mathbf{n} = g'b'\mathbf{n}$, where b and b' denote the two projections and $\mathbf{n}$ is a unit vector perpendicular to the plane of the relative motion. Since from (1.79) $g = g'$, it follows that $b' = b$. The quantity b is called impact parameter.

In Figure 1.6 is represented, a unit vector $\mathbf{k}$ in the direction of $(\mathbf{g} - \mathbf{g}')$, which is known as collision or apsidal vector. Moreover, in this figure, χ denotes the scattering angle which is related to the angle θ by $\theta = (\pi - \chi)/2$.

The asymptotic post-collisional velocities $\mathbf{c}'$ and $\mathbf{c}_1'$ could not be determined in terms of the asymptotic pre-collisional velocities $\mathbf{c}$ and $\mathbf{c}_1$ by using only the conservation equations (1.75) and (1.80), since they furnish only four scalar equations for the six unknown scalar quantities. In the following subsection it will be shown that a complete determination is possible by using the apsidal vector.

Exercises

1.11 Show that the scalar product of (1.76) by $\dot{\mathbf{r}}$ leads to (1.77) and that its cross product by $\mathbf{r}$ implies (1.81).

1.12 Obtain (1.80) from (1.75) and (1.79).

1.4.2 Asymptotic Post-Collisional Velocities

The apsidal vector $\mathbf{k}$, defined by

$$\mathbf{k} = \frac{\mathbf{g} - \mathbf{g}'}{|\mathbf{g} - \mathbf{g}'|} \tag{1.83}$$

bisects the angle between the asymptotic relative velocities

$$\mathbf{g} \cdot \mathbf{k} = -\mathbf{g}' \cdot \mathbf{k}, \tag{1.84}$$

since according to (1.79), $g = g'$. Hence, one can write the relationship

$$\mathbf{c}_1' - \mathbf{c}' - (\mathbf{c}_1 - \mathbf{c}) = \mathbf{g}' - \mathbf{g} = \mathbf{k}[\mathbf{k} \cdot (\mathbf{g}' - \mathbf{g})] = -2\mathbf{k}(\mathbf{k} \cdot \mathbf{g}). \tag{1.85}$$

The elimination of $\mathbf{c}'$ and $\mathbf{c}$ from (1.85) by using the momentum conservation law (1.75) yields

$$\mathbf{c}_1' = \mathbf{c}_1 - \mathbf{k}(\mathbf{k} \cdot \mathbf{g}). \tag{1.86}$$

Following the same methodology, the elimination of $\mathbf{c}_1$ and $\mathbf{c}_1'$ from (1.85) leads to

$$\mathbf{c}' = \mathbf{c} + \mathbf{k}(\mathbf{k}\cdot\mathbf{g}). \tag{1.87}$$

The equations (1.86) and (1.87) give the asymptotic post-collisional velocities in terms of the asymptotic pre-collisional velocities and of the apsidal vector $\mathbf{k}$.

From (1.86) and (1.87), it follows the inverse transformations

$$\mathbf{c}_1 = \mathbf{c}_1' - \mathbf{k}(\mathbf{k}\cdot\mathbf{g}'), \qquad \mathbf{c} = \mathbf{c}' + \mathbf{k}(\mathbf{k}\cdot\mathbf{g}'), \tag{1.88}$$

which relate the asymptotic pre-collisional velocities in terms of the asymptotic post-collisional velocities and of the apsidal vector $\mathbf{k}$.

The modulus of the Jacobian of the transformation from $(\mathbf{c}, \mathbf{c}_1)$ to $(\mathbf{c}', \mathbf{c}_1')$ and of its inverse transformation are equal to one, i.e.,

$$|J| = \left|\frac{\partial(\mathbf{c}, \mathbf{c}_1)}{\partial(\mathbf{c}', \mathbf{c}_1')}\right| = \left|\frac{\partial(\mathbf{c}', \mathbf{c}_1')}{\partial(\mathbf{c}, \mathbf{c}_1)}\right| = 1. \tag{1.89}$$

Exercises

1.13 Obtain the relationships (1.86) and (1.87).

1.14 Calculate the Jacobian of the transformation from $(\mathbf{c}, \mathbf{c}_1)$ to $(\mathbf{c}', \mathbf{c}_1')$ and show that its modulus is equal to one.

1.4.3 Asymptotic Velocities for Gas Mixtures

In mixtures of gases, a binary collision of the molecules of two constituents of masses m_α and m_β is characterized by the asymptotic pre-collisional velocities $(\mathbf{c}_\alpha, \mathbf{c}_\beta)$, asymptotic post-collisional velocities $(\mathbf{c}_\alpha', \mathbf{c}_\beta')$ and asymptotic relative velocities:

$$\mathbf{g}_{\beta\alpha} = \mathbf{c}_\beta - \mathbf{c}_\alpha \qquad \text{and} \qquad \mathbf{g}_{\beta\alpha}' = \mathbf{c}_\beta' - \mathbf{c}_\alpha'. \tag{1.90}$$

The conservation laws of linear momentum and energy read

$$m_\alpha \mathbf{c}_\alpha + m_\beta \mathbf{c}_\beta = m_\alpha \mathbf{c}_\alpha' + m_\beta \mathbf{c}_\beta', \tag{1.91}$$

$$\frac{1}{2}m_\alpha c_\alpha^2 + \frac{1}{2}m_\beta c_\beta^2 = \frac{1}{2}m_\alpha c_\alpha'^2 + \frac{1}{2}m_\beta c_\beta'^2, \tag{1.92}$$

respectively. The energy conservation law can be expressed also in terms of the asymptotic relative velocities as $g_{\beta\alpha} = g_{\beta\alpha}'$.

The apsidal vector $\mathbf{k}^{\beta\alpha}$ is defined by

$$\mathbf{k}^{\beta\alpha} = \frac{\mathbf{g}_{\beta\alpha} - \mathbf{g}'_{\beta\alpha}}{|\mathbf{g}_{\beta\alpha} - \mathbf{g}'_{\beta\alpha}|}, \tag{1.93}$$

and the asymptotic post-collisional velocities are related to the asymptotic pre-collisional velocities and of the apsidal vector $\mathbf{k}^{\beta\alpha}$ through

$$\mathbf{c}'_\beta = \mathbf{c}_\beta - 2\frac{m_{\alpha\beta}}{m_\beta}\mathbf{k}^{\beta\alpha}(\mathbf{k}^{\beta\alpha}\cdot\mathbf{g}_{\beta\alpha}), \qquad \mathbf{c}'_\alpha = \mathbf{c}_\alpha + 2\frac{m_{\alpha\beta}}{m_\alpha}\mathbf{k}^{\beta\alpha}(\mathbf{k}^{\beta\alpha}\cdot\mathbf{g}_{\beta\alpha}), \tag{1.94}$$

where $m_{\alpha\beta}$ denotes the reduced mass $m_{\alpha\beta} = m_\alpha m_\beta/(m_\alpha + m_\beta)$.

Exercise

1.15 Obtain the relationships in (1.94) and show that the Jacobian of the transformation from $(\mathbf{c}_\alpha, \mathbf{c}_\beta)$ to $(\mathbf{c}'_\alpha, \mathbf{c}'_\beta)$ has modulus equal to one.

1.4.4 Scattering Angle χ

The equations (1.78) and (1.82) can also be expressed in terms of the polar coordinates (r, φ) specified in Figure 1.6 as

$$\frac{\mu}{2}(\dot{r}^2 + r^2\dot{\varphi}^2) + \Phi(r) = \frac{\mu}{2}\,g^2, \tag{1.95}$$

$$r^2\dot{\varphi} = b\,g, \tag{1.96}$$

since $(\dot{r}, r\dot{\varphi})$ are the components of the velocity in polar coordinates.

From the division of (1.95) by the square of (1.96), it follows

$$\left(\frac{ds}{d\varphi}\right)^2 = 1 - s^2 - \frac{2\Phi}{\mu g^2}, \tag{1.97}$$

where $s = b/r$ is a dimensionless variable.[15]

In the intersection of the orbit with the apsidal line—represented by the line OO' in Figure 1.6—r assumes its minimum value $r^{\min}$, while s takes its maximum value $s_{\max} = b/r^{\min}$. In this case, $\varphi = \theta$ and $ds/d\varphi = 0$. Hence, the scattering angle $\chi = (\pi - 2\theta)$ can be determined from the integration of equation (1.97), yielding

$$\chi = \pi - \int_0^{s_{\max}} \left(2\Bigg/\sqrt{1 - s^2 - \frac{2\Phi(b/s)}{\mu g^2}}\right) ds \tag{1.98}$$

---

[15] Note that $\dot{r}/\dot{\varphi} = dr/d\varphi = -b(ds/d\varphi)/s^2$.

where $s_{\max}$ is the positive root of the equation

$$1 - s_{\max}^2 - \frac{2\varPhi(b/s_{\max})}{\mu g^2} = 0. \tag{1.99}$$

From (1.98), one infers that the scattering angle—for a given potential function $\varPhi(r)$—is determined by the impact parameter b and by the relative velocity g.

For the centers of repulsion potential (1.55), the scattering angle χ is given by

$$\chi = \pi - \int_0^{s_{\max}} \left(2\Big/\sqrt{1 - s^2 - \frac{2}{\nu - 1}\Big(\frac{s}{s_0}\Big)^{\nu-1}}\right) ds, \tag{1.100}$$

where s_0 is defined by

$$s_0 = b\Big(\frac{\mu g^2}{\kappa}\Big)^{\frac{1}{\nu-1}}. \tag{1.101}$$

In this case, $s_{\max}$ is the positive root of the equation

$$1 - s_{\max}^2 - \frac{2}{\nu - 1}\Big(\frac{s_{\max}}{s_0}\Big)^{\nu-1} = 0. \tag{1.102}$$

The scattering angle for the hard-sphere potential (1.54) can be obtained as a limiting case of the centers of repulsion potential. Indeed, if in (1.55) one introduces $\kappa = \kappa' \mathsf{d}^{\nu-1}$, where κ' is a constant and d is the molecular diameter, it follows

$$\varPhi(r) = \frac{\kappa'}{\nu - 1}\left(\frac{\mathsf{d}}{r}\right)^{\nu-1}. \tag{1.103}$$

The above potential function has the following limits when $\nu \to \infty$: (a) $\varPhi(r) = 0$ for $r > \mathsf{d}$ and (b) $\varPhi(r) = \infty$ for $r < \mathsf{d}$. Hence, (1.101) can be written as

$$s_0 = \frac{b}{\mathsf{d}}\Big(\frac{\mu g^2}{\kappa'}\Big)^{\frac{1}{\nu-1}}, \qquad \text{so that} \qquad \lim_{\nu\to\infty} s_0 = \frac{b}{\mathsf{d}}. \tag{1.104}$$

For $r \geqslant \mathsf{d}$, it is easy to verify that

$$\lim_{\nu\to\infty} \frac{1}{\nu - 1}\Big(\frac{s}{s_0}\Big)^{\nu-1} = \lim_{\nu\to\infty} \frac{1}{\nu - 1}\Big(\frac{\mathsf{d}}{r}\Big)^{\nu-1}\left(\frac{\kappa'}{\mu g}\right) = 0. \tag{1.105}$$

Now, the scattering angle χ can be written—thanks to (1.100) and (1.105)—as

$$\chi = \pi - \int_0^{s_{\max}} \left(2\Big/\sqrt{1 - s^2}\right) ds = 2\arccos s_{\max}, \tag{1.106}$$

where $s_{\max} = b/r^{\min}$ assumes different values according to the conditions:

(i) Nonexistence of a collision: $s_0 \geqslant 1$. From (1.102), it follows that $s_{\max} = 1$, and (1.106) implies that the scattering angle vanishes, i.e., $\chi = 0$ and

(ii) Existence of a collision: $s_0 < 1$. Since the molecules are hard spheres of diameter d, one infers that $r^{\min} = \mathsf{d}$ and $s_{\max} = b/\mathsf{d}$, and the scattering angle χ is given by

$$\chi = 2 \arccos\left(\frac{b}{\mathsf{d}}\right). \tag{1.107}$$

Exercises

1.16 Obtain (1.97) from (1.95) and (1.96).

1.17 Show that the scattering angles for a generic potential and for centers of repulsion potential are given by the expressions (1.98) and (1.100), respectively.

1.4.5 Differential Cross Section

Consider the relative motion shown in Figure 1.7. The molecules which impinge on a ring element with thickness $d\varepsilon$—located in the circles within the range of b and $b+db$ in the perpendicular plane to $\mathbf{g}$—are scattered according to an angle within the range of χ and $\chi + d\chi$, i.e., are scattered according to the element of solid angle

$$d\Omega = \sin\chi \, d\chi \, d\varepsilon. \tag{1.108}$$

The differential cross section—which is a function of the scattering angle and of the kinetic energy of the relative motion $\sigma(\chi, g)$—is defined as the ratio of the number of scattered particles ΔN per unit of time and per element of solid angle, and the flux of the impinged molecules, i.e.,

$$\sigma(\chi, g) = \frac{\Delta N/(\Delta t \, d\Omega)}{\Delta N/(\Delta t \, b \, db \, d\varepsilon)} = \frac{b \, db \, d\varepsilon}{d\Omega}. \tag{1.109}$$

From (1.108) and (1.109), it follows that the differential cross section can be written as

$$\sigma(\chi, g) = \frac{b}{\sin\chi}\left|\frac{db}{d\chi}\right|. \tag{1.110}$$

In the above equation, the modulus was introduced in order to preserve the positiveness of the differential cross section.

For the calculation of the transport coefficients, it is necessary to know the effective cross section of order l, defined by

$$Q^{(l)}(g) = \int_0^\pi (1 - \cos^l \chi)\sigma(\chi, g) \sin\chi d\chi = \int_0^\infty (1 - \cos^l \chi) b \, db. \tag{1.111}$$

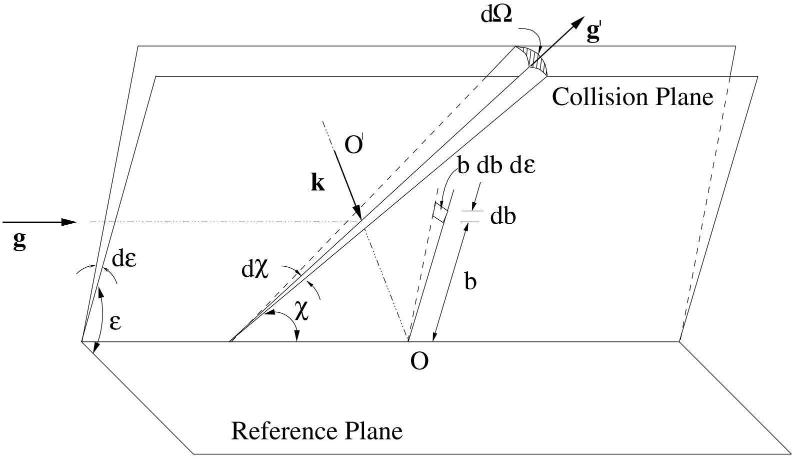

Fig. 1.7 Specification of the element of solid angle $d\Omega$.

The quantity $Q^{(1)}(g)$ is called transport cross section, while $Q^{(2)}(g)$ is known as viscosity cross section.

From (1.110) and (1.111), it is possible to determine the differential and effective cross sections for different interaction potential models. Indeed, for the hard-sphere potential, the scattering angle is given by (1.107) so that

$$\sigma = \frac{1}{4}\mathrm{d}^2, \tag{1.112}$$

$$Q^{(l)} = \frac{1}{4}\mathrm{d}^2\left[2 - \frac{1+(-1)^l}{l+1}\right]. \tag{1.113}$$

For the centers of repulsion potential, it follows from (1.101), (1.110) and (1.111):

$$\sigma = \left(\frac{\kappa}{\mu}\right)^{\frac{2}{\nu-1}} g^{\frac{-4}{(\nu-1)}} \frac{s_0}{\sin\chi}\left|\frac{ds_0}{d\chi}\right|, \tag{1.114}$$

$$Q^{(l)} = \left(\frac{\kappa}{\mu}\right)^{\frac{2}{\nu-1}} g^{\frac{-4}{(\nu-1)}} A_l(\nu), \tag{1.115}$$

where $A_l(\nu)$ represents the integral

$$A_l(\nu) = \int_0^\infty (1-\cos^l\,\chi)s_0\,ds_0. \tag{1.116}$$

Table 1.2 Values for the determination of $A_1(5)$ and $A_2(5)$

ϕ	θ	$I_1 = 2\sqrt{2}(\cos\theta/\sin 2\phi)^2$	$I_2 = \sqrt{2}\,(\sin 2\theta/\sin 2\phi)^2$
$0^o\,00'$	$90^o\,00'$	0	0
$5^o\,00'$	$89^o\,29'$	0.00759	0.01518
$10^o\,00'$	$87^o\,55'$	0.03214	0.06419
$15^o\,00'$	$85^o\,13'$	0.07888	0.15666
$20^o\,00'$	$81^o\,14'$	0.15881	0.31026
$25^o\,00'$	$75^o\,45'$	0.29208	0.54877
$30^o\,00'$	$68^o\,18'$	0.51563	0.89025
$35^o\,00'$	$58^o\,00'$	0.89903	1.29339
$40^o\,00'$	$42^o\,40'$	1.57709	1.44849
$41^o\,00'$	$38^o\,27'$	1.76865	1.36823
$42^o\,00'$	$33^o\,34'$	1.98532	1.21403
$43^o\,00'$	$27^o\,38'$	2.23112	0.95946
$44^o\,00'$	$19^o\,41'$	2.51038	0.56999
$44^o\,30'$	$13^o\,59'$	2.66418	0.31094
$45^o\,00'$	$0^o\,00'$	2.82843	0

In the following, it is shown how Maxwell[16] obtained the numerical values of the integrals $A_1(\nu)$ and $A_2(\nu)$ for a Maxwellian potential, i.e., for centers of repulsion potential where $\nu = 5$. First, one performs the variable transformation $(s_0, s, \chi) \longmapsto (\phi, \psi, \theta)$ by using the relationships

$$s_0 = \sqrt[4]{2\,\cot^2\,2\phi}, \qquad s = \cos\psi\sqrt{1-\tan^2\phi}, \qquad \chi = \pi - 2\theta. \tag{1.117}$$

Next, from (1.100) through (1.102) and (1.116), it follows that

$$\theta = K(\sin\phi)\sqrt{\cos\,2\phi}, \tag{1.118}$$

$$A_1(5) = 2\sqrt{2}\int_0^{\frac{\pi}{4}}\left(\frac{\cos\theta}{\sin 2\phi}\right)^2 d\phi, \tag{1.119}$$

$$A_2(5) = \sqrt{2}\int_0^{\frac{\pi}{4}}\left(\frac{\sin 2\theta}{\sin 2\phi}\right)^2 d\phi. \tag{1.120}$$

In (1.118), $K(\sin\phi)$ is the complete elliptic integral of first kind, namely,

$$K(\sin\phi) = \int_0^{\frac{\pi}{2}} \frac{d\psi}{\sqrt{1-\sin^2\phi\,\sin^2\psi}}. \tag{1.121}$$

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[16] J. C. Maxwell, "On the Dynamical Theory of Gases", *Phil. Trans. R. Soc. London*, **157**, 49-88 (1867).

From the above equations, one can construct[17] Table 1.2 and obtain from the Simpson rule for numerical integration the results:

$$A_1(5) \approx 0.422\,, \qquad\qquad A_2(5) \approx 0.436. \tag{1.122}$$

Exercises

1.18 Show that the differential and viscosity cross sections are given by: (a) equations (1.112) and (1.113) for the hard-sphere potential; (b) equations (1.114) and (1.115) for the centers of repulsion potential.

1.19 Determine the numerical values for the integrals $A_1(5)$ and $A_2(5)$ given in equation (1.122).

1.5 Appendix

For the determination of the integrals in kinetic theory of gases, one makes use of the integral representation of the gamma function, which reads

$$\int_0^\infty x^n e^{-\alpha x^2} dx = \frac{1}{2}\Gamma\Big(\frac{n+1}{2}\Big)\Big(\frac{1}{\alpha}\Big)^{\frac{n+1}{2}}. \tag{1.123}$$

where α is a constant, and the gamma function has the following properties

$$\begin{cases} \Gamma(n+1) = n\Gamma(n), \\ \Gamma(1) = 1, \\ \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}. \end{cases} \tag{1.124}$$

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[17] This table is the same as the one which appears in Maxwell's paper.

Chapter 2
The Boltzmann Equation

2.1 The Boltzmann Equation

Consider a monatomic gas with N molecules enclosed in a recipient of volume V. One molecule of this gas can be specified at a given time by its position $\mathbf{x} = (x_1, x_2, x_3)$ and velocity $\mathbf{c} = (c_1, c_2, c_3)$. Hence, a molecule can be specified as a point in a six-dimensional space spanned by its coordinates and velocity components, the so-called μ-phase space. In the μ-phase space, a system of N molecules is described by N points with coordinates $(\mathbf{x}_\alpha, \mathbf{c}_\alpha)$ for each $\alpha = 1, 2, ..., N$.

The state of a gas in the μ-phase space is characterized by a distribution function $f(\mathbf{x}, \mathbf{c}, t)$ such that

$$f(\mathbf{x}, \mathbf{c}, t) d\mathbf{x}\, d\mathbf{c} \equiv f(\mathbf{x}, \mathbf{c}, t) dx_1 dx_2 dx_3 dc_1 dc_2 dc_3 \tag{2.1}$$

gives, at time t, the number of molecules in the volume element with position vectors within the range $\mathbf{x}$ and $\mathbf{x} + d\mathbf{x}$ and with velocity vectors within the range $\mathbf{c}$ and $\mathbf{c} + d\mathbf{c}$.

By denoting the volume element in the μ-phase space at time t as

$$d\mu(t) = d\mathbf{x}\, d\mathbf{c}, \tag{2.2}$$

the number of molecules in this volume element is given by

$$N(t) = f(\mathbf{x}, \mathbf{c}, t)\, d\mu(t). \tag{2.3}$$

Furthermore, let $d\mu(t + \Delta t)$ denote the volume element in the μ-phase space at time $t + \Delta t$ where

$$N(t + \Delta t) = f(\mathbf{x} + \Delta\mathbf{x}, \mathbf{c} + \Delta\mathbf{c}, t + \Delta t)\, d\mu(t + \Delta t) \tag{2.4}$$

represents the number of molecules in this volume element.

If during the time interval Δt the molecules do not collide, the quantities $N(t)$ and $N(t+\Delta t)$ should be equal to each other. However, by considering time intervals that are larger than the mean free time—i.e., for $\Delta t \gg \tau$—collisions between the gas molecules occur and the difference between the two numbers of molecules does not vanish. Let this difference be denoted by

$$\begin{aligned}\Delta N &= N(t+\Delta t) - N(t)\\ &= f(\mathbf{x}+\Delta\mathbf{x}, \mathbf{c}+\Delta\mathbf{c}, t+\Delta t)\, d\mu(t+\Delta t) - f(\mathbf{x}, \mathbf{c}, t)\, d\mu(t).\end{aligned} \tag{2.5}$$

The changes in the position and velocity vectors of the molecules during the time interval Δt are given by

$$\Delta\mathbf{x} = \mathbf{c}\Delta t, \qquad\qquad \Delta\mathbf{c} = \mathbf{F}\Delta t, \tag{2.6}$$

where $\mathbf{F}(\mathbf{x}, \mathbf{c}, t)$ denotes a specific external force which acts on the molecules. It is a force per unit of mass, i.e., has the dimension of an acceleration.

The relationship between the two volume elements $d\mu(t+\Delta t)$ and $d\mu(t)$ reads

$$d\mu(t+\Delta t) = |J| d\mu(t) \tag{2.7}$$

where J is the Jacobian of the transformation, i.e.,

$$J = \frac{\partial(x_1(t+\Delta t), x_2(t+\Delta t), \dots, c_3(t+\Delta t))}{\partial(x_1(t), x_2(t), \dots, c_3(t))}. \tag{2.8}$$

Up to linear terms in Δt, the Jacobian is approximated by

$$J = 1 + \frac{\partial F_i}{\partial c_i}\Delta t + \mathcal{O}[(\Delta t)^2]. \tag{2.9}$$

Furthermore, the expansion of $f(\mathbf{x}+\Delta\mathbf{x}, \mathbf{c}+\Delta\mathbf{c}, t+\Delta t)$ in Taylor series around $(\mathbf{x}, \mathbf{c}, t)$, and by considering also linear terms up to Δt, becomes

$$f(\mathbf{x}+\Delta\mathbf{x}, \mathbf{c}+\Delta\mathbf{c}, t+\Delta t) \approx f(\mathbf{x}, \mathbf{c}, t) + \frac{\partial f}{\partial t}\Delta t + \frac{\partial f}{\partial x_i}\Delta x_i + \frac{\partial f}{\partial c_i}\Delta c_i + \mathcal{O}[(\Delta t)^2]. \tag{2.10}$$

The combination of (2.5) through (2.10) yields

$$\begin{aligned}\frac{\Delta N}{\Delta t} &= \left[\frac{\partial f}{\partial t} + c_i\frac{\partial f}{\partial x_i} + F_i\frac{\partial f}{\partial c_i} + f\frac{\partial F_i}{\partial c_i}\right] d\mu(t)\\ &= \left[\frac{\partial f}{\partial t} + c_i\frac{\partial f}{\partial x_i} + \frac{\partial f F_i}{\partial c_i}\right] d\mu(t).\end{aligned} \tag{2.11}$$

The determination of $\Delta N/\Delta t$ when the collisions are taken into account are based on the following hypotheses:

1st Hypothesis: For a rarefied gas, the probability of occurrence of collisions in which more than two molecules participate is much smaller than the one which corresponds to binary encounters;

2nd Hypothesis: The effect of external forces on the molecules during the mean collision time τ_c is negligible in comparison with the interacting molecular forces;

3rd Hypothesis: The asymptotic pre-collisional velocities of two molecules are not correlated as well as their post-collisional velocities. This hypothesis is known as the molecular chaos assumption and

4th Hypothesis: The distribution function $f(\mathbf{x}, \mathbf{c}, t)$ does not change very much over a time interval which is larger than the mean collision time but smaller than the mean free time. The same assumption applies to the variation of f over a distance of the order of the range of the intermolecular forces.

Consider now two gas molecules whose asymptotic pre-collisional velocities are denoted by $\mathbf{c}$ and $\mathbf{c}_1$. In Figure 2.1, the molecule which has velocity $\mathbf{c}$ is at the point O, while the other molecule is approaching the plane according to a right angle and with relative velocity $\mathbf{g} = \mathbf{c}_1 - \mathbf{c}$. The relative motion is also characterized by the impact parameter b and by the azimuthal angle ε.

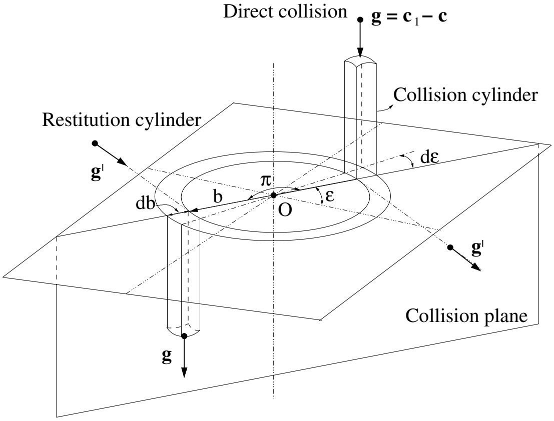


Fig. 2.1 Geometry of a binary collision for determination of $\Delta N/\Delta t$.

From Figure 2.1, one can infer that—during the time interval Δt—all molecules with velocities within the range $\mathbf{c}_1$ and $\mathbf{c}_1 + d\mathbf{c}_1$, and that are inside the cylinder of volume $g\,\Delta t\, b\, db\, d\varepsilon$, will collide with the molecules located in a volume element $d\mathbf{x}$ around the point O and whose velocities are within the range $\mathbf{c}$ and $\mathbf{c} + d\mathbf{c}$. The number of molecules with velocities within the range $\mathbf{c}_1$ and $\mathbf{c}_1 + d\mathbf{c}_1$ inside the collision cylinder is given by $f(\mathbf{x}, \mathbf{c}_1, t)d\mathbf{c}_1\, g\,\Delta t\, b\, db\, d\varepsilon$. These molecules will collide with all molecules with velocities within the range $\mathbf{c}$ and $\mathbf{c}+d\mathbf{c}$ and which are in the volume element $d\mathbf{x}$ around the point O, i.e., $f(\mathbf{x},\mathbf{c},t)\,d\mathbf{x}\,d\mathbf{c}$. Hence, the number of collisions, during the time interval Δt, which occur in the volume element $d\mathbf{x}$, reads

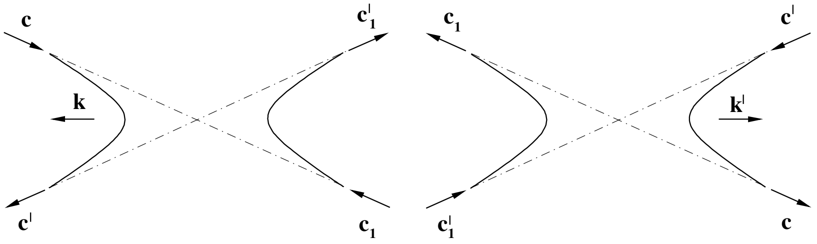
$$f(\mathbf{x},\mathbf{c}_1,t)d\mathbf{c}_1\, g\, \Delta t\, b\, db\, d\varepsilon\, f(\mathbf{x},\mathbf{c},t)\, d\mathbf{x}\, d\mathbf{c}. \tag{2.12}$$

By dividing (2.12) by Δt and integrating the resulting formula over all components of the velocity $-\infty < c_i^1 < +\infty$ $(i = 1, 2, 3)$, over the azimuthal angle $0 \leqslant \varepsilon \leqslant 2\pi$ and over all values of the impact parameter $0 \leqslant b < \infty$, it follows the total number of collisions per time interval Δt in the μ-phase space that annihilates points with velocity $\mathbf{c}$ in the volume element $d\mu(t)$, namely,

$$\left(\frac{\Delta N}{\Delta t}\right)^{-} = d\mu(t)\int f(\mathbf{x},\mathbf{c}_1,t) f(\mathbf{x},\mathbf{c},t)\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1. \tag{2.13}$$

In (2.13), all the five integrals described above were represented by only one symbol of integration.

However, there exist collisions which create points with velocity $\mathbf{c}$ in the volume element $d\mu(t)$. Indeed, they result from collisions of molecules with the following characteristics: (i) asymptotic pre-collisional velocities $\mathbf{c}'$ and $\mathbf{c}_1'$, (ii) asymptotic post-collisional velocities $\mathbf{c}$ and $\mathbf{c}_1$, (iii) apsidal vector $\mathbf{k}' = -\mathbf{k}$, (iv) impact parameter $b' = b$ and (v) azimuthal angle $\varepsilon' = \pi + \varepsilon$. Such collisions are known as restitution collisions, whereas the former are called direct collisions. The geometry of these two collisions are represented in Figures 2.1 and 2.2.



(a) (b)

Fig. 2.2 (a) Direct collision; (b) Restitution collision.

By taking into account the previous analysis, one can infer that the number of collisions, during the time interval Δt, which occur in the volume element $d\mathbf{x}$ for the restitution collisions is given by

$$f(\mathbf{x},\mathbf{c}_1',t)d\mathbf{c}_1'\, g'\, \Delta t\, b\, db\, d\varepsilon\, f(\mathbf{x},\mathbf{c}',t)d\mathbf{x}\, d\mathbf{c}'. \tag{2.14}$$

The above expression can be rewritten in a modified form as follows. First, recall that the modulus of the Jacobian for the equations that relate the post- and pre-collisional asymptotic velocities is equal to one, so that $d\mathbf{c}_1' \, d\mathbf{c}' = d\mathbf{c}_1 \, d\mathbf{c}$. Next, the energy conservation law (1.79) states that the modulus of the pre- and post-collisional relative velocities are equal to each other, i.e., $g' = g$. Hence, (2.14) becomes

$$f(\mathbf{x}, \mathbf{c}_1', t) f(\mathbf{x}, \mathbf{c}', t) d\mathbf{x} \, \varDelta t \, g \, b \, db \, d\varepsilon \, d\mathbf{c} \, d\mathbf{c}_1. \tag{2.15}$$

Now, it follows from the above expression that the total number of collisions per time interval $\varDelta t$, which creates points in the μ-phase space with velocity $\mathbf{c}$ in the volume element $d\mu(t)$, reads

$$\left(\frac{\varDelta N}{\varDelta t}\right)^+ = d\mu(t) \int f(\mathbf{x}, \mathbf{c}_1', t) f(\mathbf{x}, \mathbf{c}', t) \, g \, b \, db \, d\varepsilon \, d\mathbf{c}_1. \tag{2.16}$$

The four hypotheses above and the arguments which lead to (2.13) and (2.16) are designated frequently in the literature by the German word *Stoßzahlansatz*, which means supposition about the number of collisions.

By taking into account the above results, (2.11) with

$$\frac{\varDelta N}{\varDelta t} = \left(\frac{\varDelta N}{\varDelta t}\right)^+ - \left(\frac{\varDelta N}{\varDelta t}\right)^- \tag{2.17}$$

is written in a final form as

$$\frac{\partial f}{\partial t} + \underbrace{c_i \frac{\partial f}{\partial x_i} + \frac{\partial f F_i}{\partial c_i}}_{\text{streaming}} = \underbrace{\int (f_1' f' - f_1 f) g \, b \, db \, d\varepsilon \, d\mathbf{c}_1}_{\text{collision}}, \tag{2.18}$$

which is the *Boltzmann equation*, a non-linear integro-differential equation for the distribution function f. It describes the evolution of the distribution function in the μ-phase space, and one can infer that the temporal change of f has two terms, one of them is a streaming term due to the motion of the molecules, whereas the other is a collision term related to the encounters of the molecules. Above, the following abbreviations were introduced:

$$f' \equiv f(\mathbf{x}, \mathbf{c}', t), \quad f_1' \equiv f(\mathbf{x}, \mathbf{c}_1', t), \quad f \equiv f(\mathbf{x}, \mathbf{c}, t), \quad f_1 \equiv f(\mathbf{x}, \mathbf{c}_1, t). \tag{2.19}$$

If the specific external force does not depend on the velocities of the molecules—as in the case of the gravitational acceleration—or does depend on the velocity through a cross product—like the cases of Coriolis acceleration in non-inertial frames or Lorentz' force in ionized gases—the velocity divergence $\partial F_i / \partial c_i$ vanishes and the Boltzmann equation (2.18) reduces to

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} + F_i \frac{\partial f}{\partial c_i} = \int (f_1' f' - f_1 f) g \, b \, db \, d\varepsilon \, d\mathbf{c}_1. \tag{2.20}$$

In this chapter only the case where $\partial F_i / \partial c_i = 0$ will be analyzed.

Exercises

2.1 Show that the Jacobian (2.8) reduces to the expression (2.9) when terms up to the order Δt are considered.

2.2 Prove that $\partial F_i/\partial c_i$ vanishes when the specific external force is Lorentz' force $\mathbf{F} = e(\mathbf{E} + \mathbf{c} \times \mathbf{B})/m$, where e and m denote the electric charge and mass of a charged particle, respectively, $\mathbf{E}$ is the external electric field and $\mathbf{B}$ the external magnetic induction.

2.2 The BBGKY Hierarchy

2.2.1 The Liouville Theorem

The state of a mechanical system of N molecules can be represented by a point in the Γ-phase space with $6\,N$ dimensions that correspond to $3\,N$ generalized coordinates of position $q_1, q_2, ..., q_{3N}$ and $3\,N$ generalized coordinates of momentum $p_1, p_2, ..., p_{3N}$. The trajectory of this point in the Γ-phase space is determined by Hamilton's equations of motion:

$$\dot{q}_\alpha = \frac{\partial H}{\partial p_\alpha}, \qquad \dot{p}_\alpha = -\frac{\partial H}{\partial q_\alpha}, \qquad \alpha = 1, 2, ..., 3N, \tag{2.21}$$

from its initial condition at $t = 0$. Above, H represents the Hamiltonian function of the system.

Instead of only one system, a large number of replicas of this system will be considered. The replicas are arbitrarily distributed in the Γ-phase space at time $t = 0$ and satisfy Hamilton's equations of motion (2.21). These points are compacted distributed in the Γ-phase space so that it is possible to characterize them by a density function $\varrho(q_1, ..., q_{3N}, p_1, ..., p_{3N}, t)$. At time t, the number of systems in the volume element in the Γ-phase space with coordinates within the range q_1 and $q_1 + dq_1, \dots, q_{3N}$ and $q_{3N} + dq_{3N}$ and momenta within the range p_1 and $p_1 + dp_1, \dots, p_{3N}$ and $p_{3N} + dp_{3N}$ is given by $\varrho(q_1, \dots, q_{3N}, p_1, \dots, p_{3N}, t)\, dq_1 \dots dq_{3N}\, dp_1 \dots dp_{3N}$. One can associate to the replicas a closed surface Σ in the Γ-phase space and describe the motion of these replicas through the motion of the surface Σ. Since the surface Σ always contains the same number of replicas, it follows that

$$\frac{d}{dt}\int_\Omega \varrho d\Omega = 0, \tag{2.22}$$

where Ω is the volume interior to the surface Σ and $d\Omega = dq_1 \dots dp_{3N}$ is its volume element.

The term $d(\int_\Omega \varrho d\Omega)/dt$ has two contributions. The first one is due to a time variation of ϱ in all points of the volume Ω and expressed by

$$\int_\Omega \frac{\partial \varrho}{\partial t} d\Omega. \tag{2.23}$$

The second contribution is due to a change of the volume Ω when the surface Σ moves. The surface motion causes a flux of points in the Γ-phase space across Σ (see Figure 2.3) given by

$$\oint_\Sigma \varrho \mathbf{V} \cdot \mathbf{n}\, d\Sigma, \tag{2.24}$$

where $\mathbf{V} = (\dot{q}_1, \ldots, \dot{q}_{3N}, \dot{p}_1, \ldots, \dot{p}_{3N})$ is the velocity of the surface Σ and $\mathbf{n}$ is its normal unitary vector.

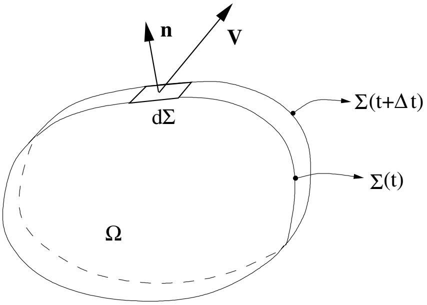


Fig. 2.3 Representation of the volume Ω in the Γ-phase space.

From (2.22) through (2.24), one may write

$$\frac{d}{dt}\int_\Omega \varrho d\Omega = \int_\Omega \frac{\partial \varrho}{\partial t} d\Omega + \oint_\Sigma \varrho \mathbf{V} \cdot \mathbf{n}\, d\Sigma = 0, \tag{2.25}$$

which by the use of the divergence theorem yields

$$\int_\Omega \left[\frac{\partial \varrho}{\partial t} + \nabla \cdot (\varrho \mathbf{V})\right] d\Omega = 0. \tag{2.26}$$

In (2.26), the divergence is defined by

$$\begin{aligned} \nabla \cdot (\varrho \mathbf{V}) &= \sum_{\alpha=1}^{3N} \left[\frac{\partial}{\partial q_\alpha}(\varrho \dot{q}_\alpha) + \frac{\partial}{\partial p_\alpha}(\varrho \dot{p}_\alpha)\right] \\ &= \sum_{\alpha=1}^{3N} \left[\dot{q}_\alpha \frac{\partial \varrho}{\partial q_\alpha} + \dot{p}_\alpha \frac{\partial \varrho}{\partial p_\alpha} + \varrho \left(\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha}\right)\right]. \end{aligned} \tag{2.27}$$

Now, from Hamilton's equations of motion (2.21), it is easy to verify that

$$\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} = \frac{\partial^2 H}{\partial q_\alpha \partial p_\alpha} = \frac{\partial^2 H}{\partial p_\alpha \partial q_\alpha} = -\frac{\partial \dot{p}_\alpha}{\partial p_\alpha}, \tag{2.28}$$

so that (2.27) reduces to

$$\nabla \cdot (\varrho \mathbf{V}) = \sum_{\alpha=1}^{3N} \left[\dot{q}_\alpha \frac{\partial \varrho}{\partial q_\alpha} + \dot{p}_\alpha \frac{\partial \varrho}{\partial p_\alpha} \right]. \tag{2.29}$$

Hence, it follows from (2.26) and (2.29) that

$$\int_\Omega \left[\frac{\partial \varrho}{\partial t} + + \sum_{\alpha=1}^{3N} \left(\dot{q}_\alpha \frac{\partial \varrho}{\partial q_\alpha} + \dot{p}_\alpha \frac{\partial \varrho}{\partial p_\alpha} \right) \right] d\Omega = 0. \tag{2.30}$$

The equation (2.30) must be valid for all volumes Ω in the Γ-phase space, therefore

$$\frac{\partial \varrho}{\partial t} + \sum_{\alpha=1}^{3N} \left(\dot{q}_\alpha \frac{\partial \varrho}{\partial q_\alpha} + \dot{p}_\alpha \frac{\partial \varrho}{\partial p_\alpha} \right) = 0, \tag{2.31}$$

which is the mathematical expression of Liouville's theorem. According to this theorem, the density of the points in the Γ-phase space remains constant for an observer which is moving with a velocity $\mathbf{V}$. Hence, the motion of the points in the Γ-phase space is analogous to the motion of an incompressible fluid in the physical space.

Exercise

2.3 The equation

$$\frac{\partial \varrho}{\partial t} + \nabla \cdot (\varrho \mathbf{v}) = 0$$

is known in the physical space as the continuity equation or the balance of mass density. Show that for an incompressible fluid, the velocity divergence must be zero, i.e., $\nabla \cdot \mathbf{v} = 0$.

2.2.2 Equations of the BBGKY Hierarchy

Consider that the system of Section 2.2.1 represents a gas of N undistinguishable molecules which occupies a recipient of volume V. Let $(\mathbf{x}_\alpha, \dot{\mathbf{x}}_\alpha)$ denote the position and the velocity coordinates of a generic molecule α of the gas with $\alpha = 1, 2, ..., N$. A state of the gas can be described by a distribution function $\mathcal{F}_N$ such that

$$\mathcal{F}_N(\mathbf{x}_1,\ldots,\mathbf{x}_N,\dot{\mathbf{x}}_1,\ldots,\dot{\mathbf{x}}_N,t)\,d\mathbf{x}_1\ldots d\mathbf{x}_N\,d\dot{\mathbf{x}}_1\ldots d\dot{\mathbf{x}}_N \tag{2.32}$$

gives the probability to find, at time t, N molecules with position vectors within the range $\mathbf{x}_\alpha$ and $\mathbf{x}_\alpha + d\mathbf{x}_\alpha$ and with velocity vectors within the range $\dot{\mathbf{x}}_\alpha$ and $\dot{\mathbf{x}}_\alpha + d\dot{\mathbf{x}}_\alpha$, $(\alpha = 1, 2, \ldots, N)$. The distribution is normalized for all time t, i.e.,

$$\int \mathcal{F}_N(\mathbf{x}_1,\ldots,\dot{\mathbf{x}}_N,t)\,d\mathbf{x}_1\ldots d\dot{\mathbf{x}}_N = 1. \tag{2.33}$$

Moreover, due to the fact that the molecules of the gas are undistinguishable, $\mathcal{F}_N$ is considered a symmetric function of all pairs $(\mathbf{x}_\alpha, \dot{\mathbf{x}}_\alpha)$ and for all $\alpha = 1, 2, \cdots, N$.

From the distribution function $\mathcal{F}_N$, one can define another distribution function $\mathcal{F}_n$ such that

$$\begin{aligned}&\mathcal{F}_n(\mathbf{x}_1,\ldots,\dot{\mathbf{x}}_n,t)\,d\mathbf{x}_1\ldots d\dot{\mathbf{x}}_n\\ &= \left[\int \mathcal{F}_N(\mathbf{x}_1,\ldots,\dot{\mathbf{x}}_N,t)\,d\mathbf{x}_{n+1}\ldots d\dot{\mathbf{x}}_N\right] d\mathbf{x}_1\ldots d\dot{\mathbf{x}}_n\end{aligned} \tag{2.34}$$

gives the probability to find, at time t, n molecules with position vectors within the range $\mathbf{x}_\alpha$ and $\mathbf{x}_\alpha + d\mathbf{x}_\alpha$ and with velocity vectors within the range $\dot{\mathbf{x}}_\alpha$ and $\dot{\mathbf{x}}_\alpha + d\dot{\mathbf{x}}_\alpha$, $(\alpha = 1, 2, \ldots, n)$.

The time evolution of $\mathcal{F}_N$ satisfies Liouville's equation (2.31), i.e.,

$$\frac{\partial \mathcal{F}_N}{\partial t} + \sum_{\alpha=1}^{N}\left(\dot{x}_i^\alpha \frac{\partial \mathcal{F}_N}{\partial x_i^\alpha} + \ddot{x}_i^\alpha \frac{\partial \mathcal{F}_N}{\partial \dot{x}_i^\alpha}\right) = 0. \tag{2.35}$$

For the distributions functions $\mathcal{F}_n (n < N)$, the time evolution is obtained through the multiplication of equation (2.35) by $d\mathbf{x}_{n+1}\ldots d\dot{\mathbf{x}}_N$ and subsequent integration of the resulting expression, yielding

$$\int \left[\frac{\partial \mathcal{F}_N}{\partial t} + \sum_{\alpha=1}^{N}\left(\dot{x}_i^\alpha \frac{\partial \mathcal{F}_N}{\partial x_i^\alpha} + \ddot{x}_i^\alpha \frac{\partial \mathcal{F}_N}{\partial \dot{x}_i^\alpha}\right)\right] d\mathbf{x}_{n+1}\ldots d\dot{\mathbf{x}}_N = 0. \tag{2.36}$$

In equation (2.36), it is possible to change the order of the time derivative and the integral since the integration limits do not depend on time, i.e.,

$$\int \frac{\partial \mathcal{F}_N}{\partial t} d\mathbf{x}_{n+1}\ldots d\dot{\mathbf{x}}_N = \frac{\partial \mathcal{F}_n}{\partial t}. \tag{2.37}$$

Furthermore, the spatial gradients of (2.36) can be rewritten according to the following conditions:

(i) if $\alpha \leqslant n$, one obtains

$$\int \sum_{\alpha=1}^{n} \dot{x}_i^\alpha \frac{\partial \mathcal{F}_N}{\partial x_i^\alpha} d\mathbf{x}_{n+1}\ldots d\dot{\mathbf{x}}_N = \sum_{\alpha=1}^{n} \dot{x}_i^\alpha \frac{\partial \mathcal{F}_n}{\partial x_i^\alpha}; \tag{2.38}$$

(ii) if $\alpha \geqslant n+1$, one infers that for all α it holds

$$\int \dot{x}_i^\alpha \frac{\partial \mathcal{F}_N}{\partial x_i^\alpha} d\mathbf{x}_{n+1} \dots d\dot{\mathbf{x}}_N = \int \left[\oint_S \dot{x}_i^\alpha \mathcal{F}_N e_i \, dS \right] \frac{d\mathbf{x}_{n+1} \dots d\dot{\mathbf{x}}_N}{d\mathbf{x}_\alpha}. \tag{2.39}$$

In (2.39), the divergence theorem was used in order to transform the volume integral into a surface integral, where $d\mathbf{x}_\alpha$ denotes a volume element and e_i represents a unit vector normal to the area element dS of the surface S which contains the molecules of the gas. Since the walls of the recipient are impermeable, $\mathcal{F}_N$ vanishes at the surface and the corresponding integral of (2.39) vanishes for all $\alpha \geqslant n+1$.

The analysis of the term in (2.36) which involves the velocity gradients proceeds as follows. Consider that the acceleration of a molecule α is represented by a sum of two terms, namely, $\ddot{x}_i^\alpha = F_i^\alpha + X_i^\alpha$. The first term F_i^α corresponds to an external force per unit of mass which acts on the molecule α being independent of the molecular velocities. The second one X_i^α is given by

$$X_i^\alpha = \sum_{\beta=1}^{N} X_i^{\alpha\beta} \qquad \text{with} \qquad X_i^{\alpha\alpha} = 0, \tag{2.40}$$

where $X_i^{\alpha\beta} = X_i^{\alpha\beta}(|\mathbf{x}^\beta - \mathbf{x}^\alpha|)$ represents the force per unit of mass which acts on the molecule α due to its interaction with the molecule β. Here, the following conditions can be analyzed:

(i) if $\alpha \leqslant n$, one obtain

$$\begin{aligned}
\int \sum_{\alpha=1}^{n} (F_i^\alpha + X_i^\alpha) \frac{\partial \mathcal{F}_N}{\partial \dot{x}_i^\alpha} d\mathbf{x}_{n+1} \dots d\dot{\mathbf{x}}_N &= \sum_{\alpha=1}^{n} \left(F_i^\alpha + \sum_{\beta=1}^{n} X_i^{\alpha\beta} \right) \frac{\partial \mathcal{F}_n}{\partial \dot{x}_i^\alpha} \\
+ \sum_{\alpha=1}^{n} \sum_{\beta=n+1}^{N} \frac{\partial}{\partial \dot{x}_i^\alpha} \int X_i^{\alpha\beta} \mathcal{F}_N d\mathbf{x}_{n+1} \dots d\dot{\mathbf{x}}_N &= \sum_{\alpha=1}^{n} \left(F_i^\alpha + \sum_{\beta=1}^{n} X_i^{\alpha\beta} \right) \frac{\partial \mathcal{F}_n}{\partial \dot{x}_i^\alpha} \\
&+ \sum_{\alpha=1}^{n} (N-n) \frac{\partial}{\partial \dot{x}_i^\alpha} \int X_i^{\alpha,n+1} \mathcal{F}_{n+1} d\mathbf{x}_{n+1} \, d\dot{\mathbf{x}}_{n+1},
\end{aligned} \tag{2.41}$$

where the last term of the second equality follows from the assumption that the molecules are undistinguishable.

(ii) if $\alpha \geqslant n+1$, one concludes that for all α it remains valid

$$\begin{aligned}
&\int (F_i^\alpha + X_i^\alpha) \frac{\partial \mathcal{F}_N}{\partial \dot{x}_i^\alpha} d\mathbf{x}_{n+1} \dots d\dot{\mathbf{x}}_N \\
&= \int \left[\oint_{S'} (F_i^\alpha + X_i^\alpha) \mathcal{F}_N e_i' dS' \right] \frac{d\mathbf{x}_{n+1} \dots d\dot{\mathbf{x}}_N}{d\dot{\mathbf{x}}_\alpha},
\end{aligned} \tag{2.42}$$

where the divergence theorem was employed for the volume element $d\dot{\mathbf{x}}_\alpha$. In equation (2.42), e'_i is a unit vector normal to the area element dS' of a surface which is situated far away in the velocity space. Since $\mathcal{F}_N$ decreases rapidly for large values of $\dot{\mathbf{x}}_\alpha$, the integral (2.42) vanishes for all $\alpha \geqslant n+1$.

Therefore, the time evolution of the distribution function $\mathcal{F}_n$ can be written, thanks to (2.36) through (2.42), as

$$\frac{\partial \mathcal{F}_n}{\partial t} + \sum_{\alpha=1}^{n} \left[\dot{x}_i^\alpha \frac{\partial \mathcal{F}_n}{\partial x_i^\alpha} + \left(F_i^\alpha + \sum_{\beta=1}^{n} X_i^{\alpha\beta} \right) \frac{\partial \mathcal{F}_n}{\partial \dot{x}_i^\alpha} \right] = -\sum_{\alpha=1}^{n} (N-n) \frac{\partial}{\partial \dot{x}_i^\alpha} \int X_i^{\alpha, n+1} \mathcal{F}_{n+1} d\mathbf{x}_{n+1} d\dot{\mathbf{x}}_{n+1}. \tag{2.43}$$

Equation (2.43) indicates that the time evolution of the distribution function $\mathcal{F}_n$ does depend on $\mathcal{F}_{n+1}$. Hence, (2.43) represents a hierarchy of coupled equations, which is known in the literature as BBGKY hierarchy, since it was deduced independently by the researchers Bogoliubov; Born and Green; Kirkwood and Yvon.[1]

The first two equations of the BBGKY hierarchy read

$$\frac{\partial \mathcal{F}_1}{\partial t} + \dot{x}_i^1 \frac{\partial \mathcal{F}_1}{\partial x_i^1} + F_i^1 \frac{\partial \mathcal{F}_1}{\partial \dot{x}_i^1} = -(N-1) \frac{\partial}{\partial \dot{x}_i^1} \int X_i^{12} \mathcal{F}_2 d\mathbf{x}_2 d\dot{\mathbf{x}}_2, \tag{2.44}$$

$$\frac{\partial \mathcal{F}_2}{\partial t} + \dot{x}_i^1 \frac{\partial \mathcal{F}_2}{\partial x_i^1} + \dot{x}_i^2 \frac{\partial \mathcal{F}_2}{\partial x_i^2} + (F_i^1 + X_i^{12}) \frac{\partial \mathcal{F}_2}{\partial \dot{x}_i^1} + (F_i^2 + X_i^{21}) \frac{\partial \mathcal{F}_2}{\partial \dot{x}_i^2} = -(N-2) \frac{\partial}{\partial \dot{x}_i^1} \int X_i^{13} \mathcal{F}_3 d\mathbf{x}_3 d\dot{\mathbf{x}}_3 - (N-2) \frac{\partial}{\partial \dot{x}_i^2} \int X_i^{23} \mathcal{F}_3 d\mathbf{x}_3 d\dot{\mathbf{x}}_3. \tag{2.45}$$

Exercises

2.4 Verify the right-hand side of equation (2.41).

2.5 Obtain the first two equations of the BBGKY hierarchy (2.44) and (2.45).

2.2.3 The Boltzmann Equation

The main objective of this section is to derive the Boltzmann equation from the BBGKY hierarchy. In the literature, one can find several methods

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[1] Nikolay Nikolaevich Bogolyubov (1909–1996) Russian mathematician and physicist; Max Born (1882–1970) German physicist; Herbert Sydney Green (1920–1999) British physicist; John Gamble Kirkwood (1907–1959) American chemist and physicist; Jacques Yvon, French scientist.

to achieve this aim here, the employed methodology follows Kirkwood's paper.[2]

Let τ^* be a time interval sufficiently large in comparison with the mean collision time τ_c but sufficiently small in comparison with the mean free time τ, i.e., $\tau_c \ll \tau^* \ll \tau$. Moreover, let

$$\overline{\mathcal{F}_1}(\mathbf{x}_1, \dot{\mathbf{x}}_1, t) = \frac{1}{\tau^*} \int_0^{\tau^*} \mathcal{F}_1(\mathbf{x}_1, \dot{\mathbf{x}}_1, t+s) ds \tag{2.46}$$

be the time average of the distribution function $\mathcal{F}_1(\mathbf{x}_1, \dot{\mathbf{x}}_1, t)$ taken over the time interval τ^*.

By considering the time average of (2.44), it follows that

$$\frac{\partial \overline{\mathcal{F}_1}}{\partial t} + \dot{x}_i^1 \frac{\partial \overline{\mathcal{F}_1}}{\partial x_i^1} + \overline{F_i^1} \frac{\partial \overline{\mathcal{F}_1}}{\partial \dot{x}_i^1}$$
$$= -\frac{(N-1)}{\tau^*} \int \int_0^{\tau^*} X_i^{12} \frac{\partial \mathcal{F}_2(\mathbf{x}_1, \mathbf{x}_2, \dot{\mathbf{x}}_1, \dot{\mathbf{x}}_2, t+s)}{\partial \dot{x}_i^1} \, ds \, d\mathbf{x}_2 \, d\dot{\mathbf{x}}_2. \tag{2.47}$$

In (2.47), it has been taken into account that $\overline{F_i^1 \mathcal{F}_1} = \overline{F_i^1} \, \overline{\mathcal{F}_1}$, since the specific external force F_i^1 is statistically independent of the distribution function $\mathcal{F}_1$.

The derivation of the Boltzmann equation from (2.47) is based on the hypotheses formulated in Section 2.1, namely,

1st Hypothesis: For a rarefied gas, only the interactions between the pairs of molecules—i.e., binary encounters—are considered. Therefore, (2.45) for $\mathcal{F}_2(\mathbf{x}_1, \mathbf{x}_2, \dot{\mathbf{x}}_1, \dot{\mathbf{x}}_2, t)$ reduces to

$$\frac{\partial \mathcal{F}_2}{\partial t} + \dot{x}_i^1 \frac{\partial \mathcal{F}_2}{\partial x_i^1} + \dot{x}_i^2 \frac{\partial \mathcal{F}_2}{\partial x_i^2} + (F_i^1 + X_i^{12}) \frac{\partial \mathcal{F}_2}{\partial \dot{x}_i^1} + (F_i^2 + X_i^{21}) \frac{\partial \mathcal{F}_2}{\partial \dot{x}_i^2} = 0. \tag{2.48}$$

2nd Hypothesis: By considering that the effect of the external forces on the molecules is small in comparison with the effect of the interaction forces between the molecules, the solution of (2.48) reads

$$\mathcal{F}_2(\mathbf{x}_1, \mathbf{x}_2, \dot{\mathbf{x}}_1, \dot{\mathbf{x}}_2, t + \mathit{\Delta} t)$$
$$= \mathcal{F}_2(\mathbf{x}_1 - \dot{\mathbf{x}}_1 \mathit{\Delta} t, \mathbf{x}_2 - \dot{\mathbf{x}}_2 \mathit{\Delta} t, \dot{\mathbf{x}}_1 - \mathbf{X}^{12} \mathit{\Delta} t, \dot{\mathbf{x}}_2 - \mathbf{X}^{21} \mathit{\Delta} t, t), \tag{2.49}$$

or by identifying $\mathit{\Delta} t \equiv s$, one may write the above equation as

$$\mathcal{F}_2(\mathbf{x}_1, \mathbf{x}_2, \dot{\mathbf{x}}_1, \dot{\mathbf{x}}_2, t+s) = \mathcal{F}_2(\mathbf{x}_1 - \mathit{\Delta}\mathbf{x}_1, \mathbf{x}_2 - \mathit{\Delta}\mathbf{x}_2, \dot{\mathbf{x}}_1 - \mathit{\Delta}\dot{\mathbf{x}}_1, \dot{\mathbf{x}}_2 - \mathit{\Delta}\dot{\mathbf{x}}_2, t). \tag{2.50}$$

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[2] J.G. Kirkwood, "The Statistical Mechanical Theory of Transport Processes II. Transport in Gases", *J. Chem. Phys.*, **15** 72-76 (1947).

3rd Hypothesis: If at time $s = 0$, the molecules are far from each other and with uncorrelated velocities, the molecular chaos assumption is valid, so that

$$\mathcal{F}_2(\mathbf{x}_1, \mathbf{x}_2, \dot{\mathbf{x}}_1, \dot{\mathbf{x}}_2, t+s) = \mathcal{F}_1(\mathbf{x}_1 - \Delta\mathbf{x}_1, \dot{\mathbf{x}}_1 - \Delta\dot{\mathbf{x}}_1, t)\mathcal{F}_1(\mathbf{x}_2 - \Delta\mathbf{x}_2, \dot{\mathbf{x}}_2 - \Delta\dot{\mathbf{x}}_2, t). \tag{2.51}$$

4th Hypothesis: If the variation of the distribution function is small along a distance comparable with the size of the molecules, one can neglect $\Delta\mathbf{x}_1$ and $\Delta\mathbf{x}_2$ and consider $\mathbf{x}_1 = \mathbf{x}_2 = \mathbf{x}$. Since $\Delta\dot{\mathbf{x}}_1 = -\Delta\dot{\mathbf{x}}_2$ and $X_i^{12} = -X_i^{21}$, it follows that

$$\begin{aligned}
&- X_i^{12} \frac{\partial \mathcal{F}_2(\mathbf{x}_1, \mathbf{x}_2, \dot{\mathbf{x}}_1, \dot{\mathbf{x}}_2, t+s)}{\partial \dot{x}_i^1} \\
&= -X_i^{12} \frac{\partial \mathcal{F}_1(\mathbf{x}, \dot{\mathbf{x}}_1 - \Delta\dot{\mathbf{x}}_1, t)}{\partial \dot{x}_i^1} \mathcal{F}_1(\mathbf{x}, \dot{\mathbf{x}}_2 - \Delta\dot{\mathbf{x}}_2, t) \\
&- X_i^{21} \mathcal{F}_1(\mathbf{x}, \dot{\mathbf{x}}_1 - \Delta\dot{\mathbf{x}}_1, t) \frac{\partial \mathcal{F}_1(\mathbf{x}, \dot{\mathbf{x}}_2 - \Delta\dot{\mathbf{x}}_2, t)}{\partial \dot{x}_i^2} \\
&= \frac{\partial}{\partial s} \left[\mathcal{F}_1(\mathbf{x}, \dot{\mathbf{x}}_1 - \Delta\dot{\mathbf{x}}_1, t) \mathcal{F}_1(\mathbf{x}, \dot{\mathbf{x}}_2 - \Delta\dot{\mathbf{x}}_2, t) \right].
\end{aligned} \tag{2.52}$$

The substitution of (2.52) into (2.47) and the integration of the right-hand side of the resulting expression with respect to the variable s leads to

$$\begin{aligned}
&\frac{\partial \overline{\mathcal{F}_1}}{\partial t} + \dot{x}_i^1 \frac{\partial \overline{\mathcal{F}_1}}{\partial x_i^1} + \overline{F_i^1} \frac{\partial \overline{\mathcal{F}_1}}{\partial \dot{x}_i^1} \\
&= \frac{(N-1)}{\tau^*} \int \left[\mathcal{F}_1(\mathbf{x}, \dot{\mathbf{x}}_1 - \Delta\dot{\mathbf{x}}_1(\tau^*), t) \mathcal{F}_1(\mathbf{x}, \dot{\mathbf{x}}_2 - \Delta\dot{\mathbf{x}}_2(\tau^*), t) \right. \\
&\qquad \left. - \mathcal{F}_1(\mathbf{x}, \dot{\mathbf{x}}_1 - \Delta\dot{\mathbf{x}}_1(0), t) \mathcal{F}_1(\mathbf{x}, \dot{\mathbf{x}}_2 - \Delta\dot{\mathbf{x}}_2(0), t) \right] d\mathbf{x}_2 d\dot{\mathbf{x}}_2.
\end{aligned} \tag{2.53}$$

Equation (2.53) is written only in terms of the distribution function $\mathcal{F}_1$ and the Boltzmann equation can be obtained from it by using the arguments stated below.

Since the molecules are undistinguishable, the change of the pairs $(\mathbf{x}_\alpha, \dot{\mathbf{x}}_\alpha)$, with $\alpha = 1, 2, \ldots, N$, does not alter the distribution of the molecules in the μ-phase space. However, this change defines a new point in the Γ-phase space. Therefore, a single distribution of N molecules in the μ-phase space corresponds to $N!$ points in the Γ-phase space. In this case, the state of a gas in the μ-phase space is described by the distribution function $f_N(\mathbf{x}_1, \ldots, \mathbf{x}_N, \dot{\mathbf{x}}_1, \ldots, \dot{\mathbf{x}}_N, t)$ such that

$$f_N(\mathbf{x}_1, \ldots, \dot{\mathbf{x}}_N, t) d\mathbf{x}_1 \ldots d\dot{\mathbf{x}}_N = N! \mathcal{F}_N(\mathbf{x}_1, \ldots, \dot{\mathbf{x}}_N, t) d\mathbf{x}_1 \ldots d\dot{\mathbf{x}}_N \tag{2.54}$$

gives, at time t, the expected value that N molecules have position vectors within the range $\mathbf{x}_\alpha$ and $\mathbf{x}_\alpha + d\mathbf{x}_\alpha$ and with velocity vectors within the range $\dot{\mathbf{x}}_\alpha$ and $\dot{\mathbf{x}}_\alpha + d\dot{\mathbf{x}}_\alpha$ $(\alpha = 1, 2, \ldots, N)$. Likewise,

$$f_n(\mathbf{x}_1,\dots,\dot{\mathbf{x}}_n,t)d\mathbf{x}_1\dots d\dot{\mathbf{x}}_n=\frac{N!}{(N-n)!}\mathcal{F}_n(\mathbf{x}_1,\dots,\dot{\mathbf{x}}_n,t)d\mathbf{x}_1\dots d\dot{\mathbf{x}}_n \tag{2.55}$$

gives, at time t, the expected value that n molecules have position vectors within the range $\mathbf{x}_\alpha$ and $\mathbf{x}_\alpha+d\mathbf{x}_\alpha$ and with velocity vectors within the range $\dot{\mathbf{x}}_\alpha$ and $\dot{\mathbf{x}}_\alpha+d\dot{\mathbf{x}}_\alpha$ $(\alpha=1,2,\dots,n)$.

In particular, it follows from (2.55)

$$\begin{cases} f_1(\mathbf{x}_1,\dot{\mathbf{x}}_1,t)=N\mathcal{F}_1(\mathbf{x}_1,\dot{\mathbf{x}}_1,t), \\ f_2(\mathbf{x}_1,\mathbf{x}_2,\dot{\mathbf{x}}_1,\dot{\mathbf{x}}_2,t)=N(N-1)\mathcal{F}_2(\mathbf{x}_1,\mathbf{x}_2,\dot{\mathbf{x}}_1,\dot{\mathbf{x}}_2,t). \end{cases} \tag{2.56}$$

Therefore, by taking the time average of (2.53), the evolution equation for the distribution function $\overline{f_1}$ becomes

$$\begin{aligned} &\frac{\partial\overline{f_1}}{\partial t}+\dot{x}_i^1\frac{\partial\overline{f_1}}{\partial x_i^1}+\overline{F_i^1}\frac{\partial\overline{f_1}}{\partial\dot{x}_i^1} \\ &=\frac{1}{\tau^*}\int\Big[\overline{f_1(\mathbf{x},\dot{\mathbf{x}}_1-\Delta\dot{\mathbf{x}}_1(\tau^*),t)f_1(\mathbf{x},\dot{\mathbf{x}}_2-\Delta\dot{\mathbf{x}}_2(\tau^*),t)} \\ &\quad-\overline{f_1(\mathbf{x},\dot{\mathbf{x}}_1-\Delta\dot{\mathbf{x}}_1(0),t)f_1(\mathbf{x},\dot{\mathbf{x}}_2-\Delta\dot{\mathbf{x}}_2(0),t)}\Big]\,d\mathbf{x}_2d\dot{\mathbf{x}}_2. \end{aligned} \tag{2.57}$$

In (2.57), it was considered that $(N-1)\approx N$ because N is of order of 10^{23} molecules.

Now the Boltzmann equation (2.20) can be obtained from (2.57) by employing the procedures:

(i) the $\mathbf{x}_2$ integration is substituted by the integration in the relative distance $(\mathbf{x}_2-\mathbf{x}_1)$ and it is adopted for the latter cylindrical coordinates (z,b,ε), centered at molecule with index 1 and with the z-axis in the direction anti-parallel to the relative velocity $\mathbf{g}=\dot{\mathbf{x}}_2-\dot{\mathbf{x}}_1$. In this case, it holds the relationship $d(\mathbf{x}_2-\mathbf{x}_1)=g\,\tau^*\,b\,db\,d\varepsilon$;

(ii) the following approximation holds

$$\overline{f_1^1f_2^1}=\overline{f_1^1}\;\overline{f_2^1}. \tag{2.58}$$

In (2.58), the indexes 1 and 2 in the distribution functions refer to two molecules with velocities $\dot{\mathbf{x}}_1$ and $\dot{\mathbf{x}}_2$, respectively. In order to verify the validity of the approximation (2.58), one develops its left- and right-hand sides in Taylor series around t, yielding

$$\begin{aligned} \overline{f_1^1f_1^2}&=\frac{1}{\tau^*}\int_0^{\tau^*}f_1^1(t+s)\,f_1^2(t+s)\,ds \\ &=f_1^1(t)\,f_1^2(t)+\frac{\tau^*}{2}\left(f_1^1\frac{\partial f_1^2}{\partial t}+f_1^2\frac{\partial f_1^1}{\partial t}\right)+\mathcal{O}(\tau^{*\,2}), \end{aligned} \tag{2.59}$$

$$\begin{aligned}\overline{f_1^1}\,\overline{f_1^2} &= \left(\frac{1}{\tau^*}\int_0^{\tau^*} f_1^1(t+s)\,ds\right)\left(\frac{1}{\tau^*}\int_0^{\tau^*} f_1^2(t+s)\,ds\right)\\ &= f_1^1(t)f_1^2(t) + \frac{\tau^*}{2}\left(f_1^1\frac{\partial f_1^2}{\partial t} + f_1^2\frac{\partial f_1^1}{\partial t}\right) + \mathcal{O}(\tau^{*\,2}),\end{aligned} \tag{2.60}$$

Due to the fact that the variation of the distribution function is small for a time interval sufficiently large in comparison with the mean collision time—recall the 4th hypothesis—one infers from (2.59) and (2.60) that (2.58) holds.

Therefore, by collecting the above arguments, (2.57) becomes

$$\begin{aligned}\frac{\partial\overline{f_1}}{\partial t} &+ \dot{x}_i^1\frac{\partial\overline{f_1}}{\partial x_i^1} + \overline{F_i^1}\frac{\partial\overline{f_1}}{\partial\dot{x}_i^1}\\ = \int\Big[&\overline{f_1(\mathbf{x},\dot{\mathbf{x}}_1 - \varDelta\dot{\mathbf{x}}_1(\tau^*),t)}\ \overline{f_1(\mathbf{x},\dot{\mathbf{x}}_2 - \varDelta\dot{\mathbf{x}}_2(\tau^*),t)}\\ -\overline{f_1(\mathbf{x},\dot{\mathbf{x}}_1 - \varDelta\dot{\mathbf{x}}_1(0),t)}&\ \overline{f_1(\mathbf{x},\dot{\mathbf{x}}_2 - \varDelta\dot{\mathbf{x}}_2(0),t)}\Big]\,g\,b\,db\,d\varepsilon d\dot{\mathbf{x}}_2,\end{aligned} \tag{2.61}$$

which represents the Boltzmann equation.

Exercises

2.6 Verify the right-hand side of (2.52).

2.7 Show that the time average of (2.53) leads to (2.57).

2.3 The Transfer Equation

The multiplication of the Boltzmann equation (2.20) by an arbitrary function $\psi \equiv \psi(\mathbf{x},\mathbf{c},t)$ and the integration of the resulting equation over all values of the velocity components $\mathbf{c}$ leads to

$$\int\frac{\partial f}{\partial t}\psi\,d\mathbf{c} + \int c_i\frac{\partial f}{\partial x_i}\psi\,d\mathbf{c} + \int F_i\frac{\partial f}{\partial c_i}\psi\,d\mathbf{c} = \int\psi(f_1'f' - f_1f)g\,b\,db\,d\varepsilon\,d\mathbf{c}_1d\mathbf{c}, \tag{2.62}$$

or equivalently

$$\begin{aligned}\frac{\partial}{\partial t}\int\psi f\,d\mathbf{c} + \frac{\partial}{\partial x_i}\int\psi c_i f\,d\mathbf{c} - \int\left[\frac{\partial\psi}{\partial t} + c_i\frac{\partial\psi}{\partial x_i} + F_i\frac{\partial\psi}{\partial c_i}\right]f\,d\mathbf{c}\\ = \int\psi(f_1'f' - f_1f)g\,b\,db\,d\varepsilon\,d\mathbf{c}_1\,d\mathbf{c}.\end{aligned} \tag{2.63}$$

In (2.63), it was considered that

$$\int \frac{\partial \psi F_i f}{\partial c_i}\, d\mathbf{c} = \oint_s \psi F_i\, f\, e_i\, dS = 0. \tag{2.64}$$

In the first equality above, the divergence theorem was used, where e_i denotes a unitary vector and dS an element of a surface situated far away in the velocity space. The integral (2.64) vanishes because the distribution function f decreases rapidly for large values of $\mathbf{c}$.

The right hand side of (2.63) can be rewritten as

$$\begin{aligned}\int \psi(f_1'f' - f_1 f) g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\mathbf{c} &= \int \psi(f_1'f' - f_1 f) g'\, b'\, db'\, d\varepsilon'\, d\mathbf{c}_1'\, d\mathbf{c}' \\ &= -\int \psi'(f_1'f' - f_1 f) g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\mathbf{c}.\end{aligned} \tag{2.65}$$

The first equality above follows from the equations which are valid for a restitution collision, i.e.,

$$g' = g, \quad d\varepsilon' = d\varepsilon, \quad b' = b, \qquad d\mathbf{c}_1'\, d\mathbf{c}' = d\mathbf{c}_1\, d\mathbf{c}. \tag{2.66}$$

The second one results from the change of the velocities $(\mathbf{c}, \mathbf{c}_1) \longmapsto (\mathbf{c}', \mathbf{c}_1')$. Therefore, from (2.65), one has

$$\begin{aligned}\int \psi(f_1'f' - f_1 f) g\, b\, db\, d\varepsilon\, d\mathbf{c}_1 d\mathbf{c} &= \int (\psi' - \psi) f_1 f\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1 d\mathbf{c} \\ &= \frac{1}{2}\int (\psi - \psi')(f_1'f' - f_1 f) g\, b\, db\, d\varepsilon\, d\mathbf{c}_1 d\mathbf{c}.\end{aligned} \tag{2.67}$$

Furthermore, by changing the role of the colliding molecules, i.e., by replacing $(\mathbf{c}, \mathbf{c}') \longmapsto (\mathbf{c}_1, \mathbf{c}_1')$, it follows

$$\begin{aligned}&\frac{1}{2}\int (\psi - \psi')(f_1'f' - f_1 f) g\, b\, db\, d\varepsilon\, d\mathbf{c}_1 d\mathbf{c} \\ &= \frac{1}{2}\int (\psi_1 - \psi_1')(f_1'f' - f_1 f) g\, b\, db\, d\varepsilon\, d\mathbf{c}_1 d\mathbf{c}.\end{aligned} \tag{2.68}$$

Hence, (2.63) can be expressed as

$$\begin{aligned}&\frac{\partial}{\partial t}\int \psi f\, d\mathbf{c} + \frac{\partial}{\partial x_i}\int \psi c_i f\, d\mathbf{c} - \int \left[\frac{\partial \psi}{\partial t} + c_i \frac{\partial \psi}{\partial x_i} + F_i \frac{\partial \psi}{\partial c_i}\right] f\, d\mathbf{c} \\ &= \int \psi(f_1'f' - f_1 f) g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\mathbf{c} = \int (\psi' - \psi) f_1 f\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\mathbf{c} \\ &= \frac{1}{4}\int (\psi_1 + \psi - \psi_1' - \psi')(f_1'f' - f_1 f) g\, b\, db\, d\varepsilon\, d\mathbf{c}_1 d\mathbf{c},\end{aligned} \tag{2.69}$$

thanks to the relationships (2.67) and (2.68).

Equation (2.69), known as the transfer equation, can be written in the following abbreviated form

$$\frac{\partial \Psi}{\partial t}+\frac{\partial}{\partial x_i}(\Psi v_i+\Phi_i)=S+P. \tag{2.70}$$

where Ψ denotes the density of an arbitrary additive quantity, Φ_i its flux density, S its supply density which is related with external forces and P its production term. The expressions for Ψ, Φ_i, S and P are given by

$$\Psi=\int \psi f\, d\mathbf{c}, \qquad \Phi_i=\int \psi C_i f\, d\mathbf{c}, \qquad S=\int F_i\frac{\partial \psi}{\partial c_i} f\, d\mathbf{c}, \tag{2.71}$$

$$P=P_1+P_2, \qquad P_1=\int\left[\frac{\partial \psi}{\partial t}+c_i\frac{\partial \psi}{\partial x_i}\right] f\, d\mathbf{c}, \tag{2.72}$$

$$P_2=\frac{1}{4}\int(\psi_1+\psi-\psi_1'-\psi')(f_1'f'-f_1f)g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\mathbf{c}. \tag{2.73}$$

Note that: (i) the flux density Φ_i given by $(2.71)_2$ is expressed in terms of the molecular peculiar velocity $C_i=c_i-v_i$, which is the molecular velocity measured by an observer in a frame which is moving with the hydrodynamic velocity v_i (see (2.87)) and (ii) the production term is a sum of two contributions P_1 and P_2, the former is related with the space–time variation of the arbitrary function $\psi(\mathbf{x},\mathbf{c},t)$, while the latter is connected with the collisions between the molecules.

Exercise

2.8 Verify the expressions given by (2.65) and (2.67).

2.4 Summational Invariants

An important result which follows from the analysis of the production term due to the collisions (2.73) is that it vanishes for any kind of distribution function f when

$$\psi_1+\psi=\psi_1'+\psi'. \tag{2.74}$$

A function ψ which fulfills (2.74) is called summational invariant and it satisfies the following theorems.

Theorem 1. *A continuous function $\psi(\mathbf{c})$ is a summational invariant if and only if*

$$\psi(\mathbf{c})=A+\mathbf{B}\cdot\mathbf{c}+Dc^2, \tag{2.75}$$

where A and D are two scalar functions and $\mathbf{B}$ a vectorial function, all of them being independent of $\mathbf{c}$.

Proof. It is easy to verify that (2.74) is satisfied by (2.75), once A cancels and according to the conservation laws of momentum and energy the relationships $\mathbf{c}+\mathbf{c}_1 = \mathbf{c}'+\mathbf{c}_1'$ and $c^2+c_1^2 = {c'}^2+{c_1'}^2$ hold, respectively. This proves the sufficiency of the theorem. A non-rigorous proof of the necessity condition is based on the fact that no combination which is linearly independent of $\psi = (m, mc_x, mc_y, mc_z, mc^2)$ could exist, because there are just five scalar quantities which express the conservation laws.

In the following, a rigorous mathematical proof of the necessity condition is presented which is based on the work by Grad[3] and which makes use of the concepts of antipodal points and antipodal functions.

The antipodal points can be introduced here through a graphic representation—shown in Figure 2.4—of the equations

$$\mathbf{c}' = \mathbf{c} + \mathbf{k}\,(\mathbf{k}\cdot\mathbf{g}), \qquad \mathbf{c}_1' = \mathbf{c}_1 - \mathbf{k}\,(\mathbf{k}\cdot\mathbf{g}), \tag{2.76}$$

which relate the asymptotic post-collisional velocities with the pre-collisional ones and the apsidal vector. The vector ends $(\mathbf{c},\mathbf{c}_1)$ and $(\mathbf{c}',\mathbf{c}_1')$ are pairs of antipodal points on the sphere.

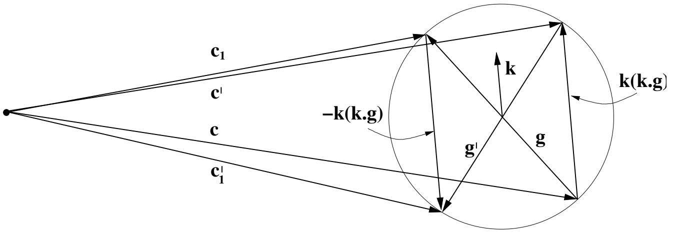

Fig. 2.4 Graphic representation of the asymptotic velocities

An antipodal function $F(\mathbf{c})$ is defined as a function where for all antipodal points at the surface of an arbitrary sphere the following relationship holds:

$$F(\mathbf{c}) + F(\mathbf{c}_1) = F(\mathbf{c}') + F(\mathbf{c}_1'). \tag{2.77}$$

Therefore, each summational invariant represents an antipodal function.

The proof of the necessity condition of the above theorem is based on the following lemma.

Lemma 1. *A continuous antipodal function F that vanishes at the points* $(0,0,0)$, $(1,0,0)$, $(0,1,0)$, $(-1,0,0)$ *and* $(0,0,1)$ *is identically null.*

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[3] H. Grad, "On the Kinetic Theory of Rarefied Gases", *Commun. Pure Appl. Math.*, **2** 331-407 (1949). Harold Grad (1923–1986) American mathematician.

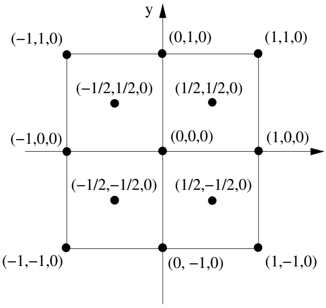

Fig. 2.5 Geometrical construction for proof of the lemma.

Proof. Consider the xy plane and the points marked in Figure 2.5. It is easy to verify that an antipodal function F which vanishes at the points $(0,0,0)$, $(1,0,0)$, $(0,1,0)$ and $(-1,0,0)$ vanishes also at the points $(1,1,0)$, $(-1,1,0)$, $(0,-1,0)$, $(-1,-1,0)$ and $(1,-1,0)$. For the interior points $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2},-\frac{1}{2},0)$, $(-\frac{1}{2},\frac{1}{2},0)$ and $(-\frac{1}{2},-\frac{1}{2},0)$, the following relationships hold:

$$F\left(\frac{1}{2},\frac{1}{2},0\right)+F\left(-\frac{1}{2},\frac{1}{2},0\right)=F(0,0,0)+F(0,1,0)=0, \tag{2.78}$$

$$F\left(\frac{1}{2},\frac{1}{2},0\right)+F\left(\frac{1}{2},-\frac{1}{2},0\right)=F(0,0,0)+F(1,0,0)=0, \tag{2.79}$$

$$F\left(-\frac{1}{2},-\frac{1}{2},0\right)+F\left(\frac{1}{2},-\frac{1}{2},0\right)=F(0,0,0)+F(0,-1,0)=0, \tag{2.80}$$

$$F\left(-\frac{1}{2},\frac{1}{2},0\right)+F\left(-\frac{1}{2},-\frac{1}{2},0\right)=F(0,0,0)+F(-1,0,0)=0, \tag{2.81}$$

$$F\left(\frac{1}{2},\frac{1}{2},0\right)+F\left(-\frac{1}{2},-\frac{1}{2},0\right)=F\left(-\frac{1}{2},\frac{1}{2},0\right)+F\left(\frac{1}{2},-\frac{1}{2},0\right). \tag{2.82}$$

From the system of equations (2.78) through (2.82), it is easy to conclude that

$$F\left(\frac{1}{2},\frac{1}{2},0\right)=F\left(-\frac{1}{2},-\frac{1}{2},0\right)=F\left(-\frac{1}{2},\frac{1}{2},0\right)=F\left(\frac{1}{2},-\frac{1}{2},0\right)=0. \tag{2.83}$$

By following the same methodology, it is possible to prove that the antipodal function F vanishes in an arbitrary dense lattice of points in the xy plane. The extension for the points in the xz and yz planes is trivial; therefore, the lemma is proved.

Theorem 2. *If $F(\mathbf{c})$ is an antipodal function, its representation is given by*

$$F(\mathbf{c})=A+\mathbf{B}\cdot\mathbf{c}+Dc^2. \tag{2.84}$$

Proof. It is easy to verify that one can construct another antipodal function

$$F^*(\mathbf{c}) = F(\mathbf{c}) - A - \mathbf{B}\cdot\mathbf{c} - Dc^2, \tag{2.85}$$

from the antipodal function $F(\mathbf{c})$. By choosing A, B_x, B_y, B_z and D such that $F^*(\mathbf{c})$ vanishes in the five points (0,0,0), (1,0,0), (0,1,0), (-1,0,0) and (0,0,1), then according to the lemma $F^*(\mathbf{c})$ it is identically null. Therefore, the expression for the antipodal function $F(\mathbf{c})$ is given by (2.84) proving the theorem.

The proof of the necessity condition of Theorem 1 is an immediate consequence of Theorem 2.

Exercise

2.9 Obtain the relationships (2.78) through (2.82) and conclude that the expressions (2.83) are valid.

2.5 Macroscopic Description

2.5.1 Moments of the Distribution Function

In kinetic theory, the quantities that characterize a macroscopic state of a gas are defined in terms of the distribution function $f(\mathbf{x},\mathbf{c},t)$. Indeed, based on the microscopic quantities of the gas molecules like mass m, linear momentum mc_i and energy $mc^2/2$, one defines the mass density ϱ, momentum density ϱv_i and total energy density ϱu of the gas through the relationships

$$\varrho(\mathbf{x},t) = \int mf(\mathbf{x},\mathbf{c},t)\,d\mathbf{c} \qquad - \quad \text{mass density,} \tag{2.86}$$

$$\varrho v_i(\mathbf{x},t) = \int mc_i f(\mathbf{x},\mathbf{c},t)\,d\mathbf{c} \qquad - \quad \text{momentum density,} \tag{2.87}$$

$$\varrho u(\mathbf{x},t) = \frac{1}{2}\int mc^2 f(\mathbf{x},\mathbf{c},t)\,d\mathbf{c} \qquad - \quad \text{energy density.} \tag{2.88}$$

The substitution of the molecular velocity in (2.88) by the peculiar velocity $C_i = c_i - v_i$ leads to

$$\varrho u = \frac{1}{2}\varrho v^2 + \varrho\varepsilon, \qquad \text{where} \qquad \varrho\varepsilon(\mathbf{x},t) = \frac{1}{2}\int mC^2 f(\mathbf{x},\mathbf{c},t)\,d\mathbf{c}. \tag{2.89}$$

Therefore, the total energy density of the gas is given by a sum of its kinetic energy density $\varrho v^2/2$ and its internal energy density $\varrho\varepsilon$. Note that: (i) in

(1.11), the definition of the internal energy density refers to a gas at rest where $\mathbf{v} = \mathbf{0}$; (ii) the transformation $\mathbf{c} \longmapsto \mathbf{C}$ is only a translation so that $d\mathbf{c} = d\mathbf{C}$ and (iii) for the derivation of $(2.89)_1$, the following relationship was used

$$\int mC_i f \, d\mathbf{c} = \int mc_i f \, d\mathbf{c} - \int mv_i f \, d\mathbf{c} = 0. \tag{2.90}$$

The moment of the distribution function of order N is defined by

$$p_{i_1 i_2 \dots i_N}(\mathbf{x}, t) = \int mC_{i_1} C_{i_2} \dots C_{i_N} f(\mathbf{x}, \mathbf{c}, t) \, d\mathbf{c}, \tag{2.91}$$

and it represents a symmetric tensor of order N with $(N+1)(N+2)/2$ distinct components.

The zeroth moment represents the mass density (2.86), while the first moment vanishes as a consequence of (2.90).

The second moment

$$p_{ij}(\mathbf{x}, t) = \int mC_i C_j f(\mathbf{x}, \mathbf{c}, t) d\mathbf{c} \tag{2.92}$$

is called pressure tensor, and its expression with a minus sign is known as the stress tensor, i.e., $t_{ij} = -p_{ij}$. The pressure deviator $p_{\langle ij \rangle}$ represents the traceless part of the pressure tensor, namely,

$$p_{\langle ij \rangle} = p_{ij} - \frac{1}{3} p_{rr} \delta_{ij}. \tag{2.93}$$

Moreover, the hydrostatic pressure of the gas p is identified with the trace of pressure tensor, i.e.,

$$p(\mathbf{x}, t) = \frac{1}{3} p_{rr} = \frac{1}{3} \int mC^2 f(\mathbf{x}, \mathbf{c}, t) \, d\mathbf{c}. \tag{2.94}$$

From the definition of the internal energy density $\varrho\varepsilon$, given by $(2.89)_2$, one infers that the pressure and the internal energy density are related to each other by $p = 2\varrho\varepsilon/3$. By recalling that the equation of state of an ideal gas reads $p = nkT$, one can obtain the following expression for the absolute temperature of a monatomic gas written in terms of the distribution function:

$$T(\mathbf{x}, t) = \frac{p}{nk} = \frac{2}{3} \frac{m}{k} \varepsilon = \frac{1}{3nk} \int mC^2 f(\mathbf{x}, \mathbf{c}, t) \, d\mathbf{c}, \tag{2.95}$$

The contracted third order moment

$$q_i(\mathbf{x}, t) = \frac{1}{2} p_{jji} = \frac{1}{2} \int mC^2 C_i f(\mathbf{x}, \mathbf{c}, t) \, d\mathbf{c} \tag{2.96}$$

is known as the heat flux vector, while the moments of higher order do not have specific proper names.

Exercises

2.10 Show that the velocity gradient can be written as

$$\frac{\partial v_i}{\partial x_j}=\frac{\partial v_{(i}}{\partial x_{j)}}+\frac{\partial v_{[i}}{\partial x_{j]}}=\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}+\frac{1}{3}\frac{\partial v_k}{\partial x_k}\delta_{ij}+\frac{\partial v_{[i}}{\partial x_{j]}},$$

where the following notations were introduced

$$\begin{cases}\frac{\partial v_{(i}}{\partial x_{j)}}=\frac{1}{2}\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_j}{\partial x_i}\right), & \text{symmetric part,}\\ \frac{\partial v_{[i}}{\partial x_{j]}}=\frac{1}{2}\left(\frac{\partial v_i}{\partial x_j}-\frac{\partial v_j}{\partial x_i}\right), & \text{antisymmetric part,}\\ \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}=\frac{\partial v_{(i}}{\partial x_{j)}}-\frac{1}{3}\frac{\partial v_k}{\partial x_k}\delta_{ij}, & \text{traceless symmetric part.}\end{cases}$$

2.11 By using the exercise 2.10 show that

$$p_{\langle ij\rangle}\frac{\partial v_i}{\partial x_j}=p_{ij}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}=p_{\langle ij\rangle}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}.$$

2.5.2 Balance Equations for the Moments

The balance equations for the moments of the distribution function are obtained from the transfer equation (2.69) by choosing $\psi(\mathbf{x},\mathbf{c},t)$ equal to:

(a) *Balance of mass density* ($\psi=m$):

$$\frac{\partial \varrho}{\partial t}+\frac{\partial \varrho v_i}{\partial x_i}=0, \tag{2.97}$$

(b) *Balance of momentum density* ($\psi=mc_i$):

$$\frac{\partial \varrho v_i}{\partial t}+\frac{\partial}{\partial x_j}(\varrho v_i v_j+p_{ij})=\varrho F_i, \tag{2.98}$$

(c) *Balance of total energy density* ($\psi=mc^2/2$):

$$\frac{\partial}{\partial t}\left[\varrho\left(\varepsilon+\frac{1}{2}v^2\right)\right]+\frac{\partial}{\partial x_i}\left[\varrho\left(\varepsilon+\frac{1}{2}v^2\right)v_i+q_i+p_{ij}v_j\right]=\varrho F_i v_i, \tag{2.99}$$

(d) *Balance of Nth order moment* ($\psi=mC_{i_1}C_{i_2}\dots C_{i_N}$):

$$\frac{\partial p_{i_1i_2\dots i_N}}{\partial t}+\frac{\partial}{\partial x_k}(p_{i_1i_2\dots i_Nk}+p_{i_1i_2\dots i_N}v_k)-\frac{N}{\varrho}p_{(i_1i_2\dots i_{N-1}}\frac{\partial p_{i_N)k}}{\partial x_k}$$
$$+Np_{k(i_1i_2\dots i_{N-1}}\frac{\partial v_{i_N)}}{\partial x_k}=P_{i_1i_2\dots i_N}. \tag{2.100}$$

Equation (2.100) was obtained by eliminating the time derivative of the velocity v_i by the use of (2.98). In the above equation, the parenthesis around the indexes indicate a sum over all $N!$ permutations of these indexes divided by $N!$. The production term due to the molecular collisions $P_{i_1 i_2 \dots i_N}$ is defined by

$$P_{i_1 i_2 \dots i_N} = \int m(C'_{i_1} C'_{i_2} \dots C'_{i_N} - C_{i_1} C_{i_2} \dots C_{i_N}) f\, f_1\, g\, b\, db\, d\varepsilon\, d\mathbf{c}\, d\mathbf{c}_1. \tag{2.101}$$

The production terms due to the molecular collisions of (2.97), (2.98) and (2.99) vanish became mass, momentum and total energy are conservative quantities or, in other words, m, mc_i and $mc^2/2$ are summational invariants.

By subtracting from the balance equation of the total energy density (2.99) the momentum balance equation (2.98) multiplied by the bulk velocity v_i, one obtains the balance equation for the internal energy density, namely,

$$\frac{\partial \varrho\varepsilon}{\partial t} + \frac{\partial}{\partial x_i}(\varrho\varepsilon v_i + q_i) + p_{ij}\frac{\partial v_i}{\partial x_j} = 0. \tag{2.102}$$

Exercises

2.12 Obtain (2.100) for the balance of the Nth order moment from the transfer equation (2.69).

2.13 Determine the balance equation for the internal energy density (2.102) from the balance equations of total energy density (2.99) and momentum density (2.98).

2.6 The Definition of Equilibrium

2.6.1 The Maxwellian Distribution Function

The right-hand side of the Boltzmann equation (2.20) is related to the difference between the number of molecules which enter and leave a volume element in the μ-phase space per time interval, due to molecular encounters. This difference should vanish when a gas is at an equilibrium state, therefore

$$\mathcal{Q}|_E \equiv \int (f'_1|_E f'|_E - f_1|_E f|_E)\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1 = 0, \tag{2.103}$$

where $|_E$ represents the equilibrium value of a function.

The above equation is fulfilled when $f|_E f_1|_E = f'|_E f'_1|_E$, and by taking the logarithm of this last expression one obtains

$$\ln f|_E + \ln f_1|_E = \ln f'|_E + \ln f_1'|_E. \tag{2.104}$$

By comparing (2.104) with (2.74), one may infer that $\ln f|_E$ is a summational invariant, which—according to (2.75)—has the representation

$$\ln f|_E = A + \mathbf{B}\cdot\mathbf{c} + Dc^2. \tag{2.105}$$

By introducing $A = \ln a^\star - b^\star u^2$, $\mathbf{B} = 2b^\star\mathbf{u}$ and $D = -b^\star$, where $a^\star$ and $b^\star$ are two scalar functions and $\mathbf{u}$ is a vectorial function, one may rewrite (2.105) as

$$f|_E = a^\star e^{-b^\star(\mathbf{c}-\mathbf{u})^2}. \tag{2.106}$$

The conditions $a^\star > 0$ and $b^\star > 0$ guarantee the positiveness of the distribution function and its integrability over all velocity space.

The quantities $a^\star$, $b^\star$ and $\mathbf{u}$ are determined from the substitution of the equilibrium distribution function (2.106) into (2.86), (2.87) and (2.95)—which are related with the definitions of the fields of mass density ϱ, bulk velocity $\mathbf{v}$ and temperature T, respectively—and subsequent integration of the resulting equations. Hence, it follows that the equilibrium distribution function is a Maxwellian distribution function $f^{(0)}$, i.e.,

$$f|_E \equiv f^{(0)} = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2kT}(\mathbf{c}-\mathbf{v})^2} = n\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} e^{-\beta(\mathbf{c}-\mathbf{v})^2}, \tag{2.107}$$

where $\beta \equiv m/(2kT)$.

Therefore, the right-hand side of the Boltzmann equation —represented by (2.103)—vanishes when the distribution function is Maxwellian. This means that the Maxwellian distribution function represents an equilibrium distribution function, since it implies that the number of collisions which creates points in the μ-phase space with a given velocity is equal to that which annihilates points with the same velocity.

Note that the Maxwellian distribution function (2.107) differs from the one given by (1.15). Indeed, whereas the former does depend on the gas velocity through the peculiar velocity, the latter does not since the gas was supposed to be at rest. In the following subsection, the equilibrium conditions for a gas which is moving with a bulk velocity $\mathbf{v}$ will be analyzed.

Exercise

2.14 Determine $a^\star$, $b^\star$ and $\mathbf{u}$ from (2.86), (2.87), (2.95) and (2.106) and obtain the Maxwellian distribution function (2.107).

2.6.2 Equilibrium States

It is important to determine the equilibrium values of the pressure tensor $p_{ij}|_E$ and of the heat flux vector $q_i|_E$ before the analysis of the restrictions imposed by the Boltzmann equation on the equilibrium states of a gas is carried out. For this end, the substitution of the Maxwellian distribution function (2.107) into the definitions of p_{ij} and q_i—given by (2.92) and (2.96), respectively—and subsequent integration of the resulting equations lead to[4]

$$p_{ij}|_E = \int m C_i C_j f^{(0)} d\mathbf{c} = p\,\delta_{ij}, \tag{2.108}$$

$$q_i|_E = \frac{1}{2}\int m C^2 C_i f^{(0)} d\mathbf{c} = 0. \tag{2.109}$$

A fluid which has constitutive equations given by (2.108) and (2.109) is known in the literature as an Eulerian fluid.

It was shown in the previous subsection that the Maxwellian distribution function (2.107) is an equilibrium distribution function which turns the right-hand side of the Boltzmann equation identically to zero, i.e., the relationship (2.103) holds. This result is valid for all values of the fields of mass density $\varrho(\mathbf{x}, t)$, bulk velocity $\mathbf{v}(\mathbf{x}, t)$ and temperature $T(\mathbf{x}, t)$, and it is evident that in equilibrium these fields cannot assume arbitrary values. Indeed, the left-hand side of the Boltzmann equation (2.20) imposes some restrictions on the space–time variations of these fields, which will be analyzed below.

The substitution of f by the Maxwellian distribution function $f^{(0)}$ into the Boltzmann equation (2.20), yields

$$\frac{\partial f^{(0)}}{\partial t} + c_i \frac{\partial f^{(0)}}{\partial x_i} + F_i \frac{\partial f^{(0)}}{\partial c_i} = 0, \tag{2.110}$$

which by the use of (2.107) becomes

$$\begin{aligned} &\frac{\mathcal{D}\varrho}{\varrho} + \left(\frac{mC^2}{2kT} - \frac{3}{2}\right)\frac{\mathcal{D}T}{T} + \frac{m}{kT} C_i \left(\mathcal{D}v_i - F_i\right) \\ &+ C_i \left\{\frac{1}{\varrho}\frac{\partial \varrho}{\partial x_i} + \frac{1}{T}\frac{\partial T}{\partial x_i}\left(\frac{mC^2}{2kT} - \frac{3}{2}\right) + \frac{m}{kT} C_j \frac{\partial v_j}{\partial x_i}\right\} = 0. \end{aligned} \tag{2.111}$$

In the above equation, the material time derivative was introduced, defined by $\mathcal{D} \equiv \partial/\partial t + v_i \partial/\partial x_i$.

---

[4] In the determination of $p_{ij}|_E$, the following relationship

$$\int C_i C_j e^{\frac{mC^2}{2kT}} d\mathbf{C} = \frac{1}{3}\delta_{ij} \int C^2 e^{\frac{mC^2}{2kT}} d\mathbf{C},$$

was used. This expression is valid for all vectors $\mathbf{C}$ in a three-dimensional vector space, and a list containing other integrals is given in the appendix of this chapter. The heat flux vector in equilibrium vanishes because $C^2 C_i$ is an odd function of the peculiar velocity $\mathbf{C}$, whereas $f^{(0)}$ is an even function of it.

Equation (2.111) is a polynomial equation of the peculiar velocity **C**, which may be written as

$$\alpha^0 + \alpha_i^1 C_i + \alpha_{ij}^2 C_i C_j + \alpha_i^3 C^2 C_i = 0, \tag{2.112}$$

where the coefficients $\alpha^0, \alpha_i^1, \alpha_{ij}^2$ and α_i^3 do not depend on the peculiar velocity **C**.

Since (2.112) is valid for all values of the peculiar velocity **C**, the coefficients $\alpha^0, \alpha_i^1, \alpha_{ij}^2$ and α_i^3 must vanish identically, i.e.,

$$\frac{\mathcal{D}\varrho}{\varrho} - \frac{3}{2}\frac{\mathcal{D}T}{T} = 0, \tag{2.113}$$

$$\varrho\mathcal{D}v_i + \frac{kT}{m}\left(\frac{\partial \varrho}{\partial x_i} - \frac{3}{2}\frac{\varrho}{T}\frac{\partial T}{\partial x_i}\right) - \varrho F_i = 0, \tag{2.114}$$

$$\frac{\mathcal{D}T}{T}\delta_{ij} + \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) = 0, \tag{2.115}$$

$$\frac{\partial T}{\partial x_i} = 0. \tag{2.116}$$

Equations (2.113) through (2.116) can be manipulated as follows. First, the trace and the traceless part of (2.115) lead to

$$\frac{\mathcal{D}T}{T} + \frac{2}{3}\frac{\partial v_k}{\partial x_k} = 0, \tag{2.117}$$

$$\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} \equiv \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) - \frac{1}{3}\frac{\partial v_r}{\partial x_r}\delta_{ij} = 0, \tag{2.118}$$

respectively. The term $\partial v_{\langle i}/\partial x_{j\rangle}$ is called velocity gradient deviator.

Next, the following steps are considered: **(i)** the substitution of the term $\mathcal{D}T$ in equation (2.113) by the use of (2.117); **(ii)** the substitution of the term $\partial\varrho/\partial x_i$ by $m(\partial p/\partial x_i)/kT$ in (2.114), thanks to $p = \varrho kT/m$ and $\partial T/\partial x_i = 0$, and **(iii)** the substitution of the term $\mathcal{D}T$ by $2m\mathcal{D}\varepsilon/3k$ in (2.117), due to $\varepsilon = 3kT/2m$. Therefore, (2.113), (2.114) and (2.117) can be rewritten as

$$\mathcal{D}\varrho + \varrho\frac{\partial v_i}{\partial x_i} = 0, \tag{2.119}$$

$$\varrho\mathcal{D}v_i + \frac{\partial p}{\partial x_i} = \varrho F_i, \tag{2.120}$$

$$\varrho\mathcal{D}\varepsilon + p\frac{\partial v_r}{\partial x_r} = 0. \tag{2.121}$$

By taking into account the constitutive equations of an Eulerian fluid, namely, $p_{ij} = p\,\delta_{ij}$ and $q_i = 0$ into the balance equations (2.98) and (2.102) they reduce to (2.120) and (2.121), respectively. Hence, an Eulerian fluid represents a fluid in equilibrium where conditions (2.116) and (2.118) hold, which state that in equilibrium the temperature gradient and the velocity gradient deviator must vanish.

For the determination of the solutions which follow from the system of differential equations given by (2.113) through (2.116), a derivative of (2.115) with respect to x_k is performed, yielding

$$\frac{\partial^2 v_i}{\partial x_k \partial x_j} + \frac{\partial^2 v_j}{\partial x_k \partial x_i} = 0, \tag{2.122}$$

due to $\partial T/\partial x_k = 0$. Furthermore, it follows from the permutations of the indexes in (2.122):

$$\frac{\partial^2 v_k}{\partial x_i \partial x_j} + \frac{\partial^2 v_j}{\partial x_i \partial x_k} = 0, \qquad \frac{\partial^2 v_i}{\partial x_j \partial x_k} + \frac{\partial^2 v_k}{\partial x_j \partial x_i} = 0. \tag{2.123}$$

Now, the addition of the two equations in (2.123) and the subtraction of (2.122) lead to

$$2\frac{\partial^2 v_k}{\partial x_i \partial x_j} = 0. \tag{2.124}$$

The solution of the partial differential equation (2.124) is given by

$$v_k(\mathbf{x}, t) = u_k(t) + A_{kl}(t) x_l. \tag{2.125}$$

In (2.125), u_k is an arbitrary vector and A_{kl} is a second order tensor, both depending only on time. From the substitution of (2.125) into (2.115), one can verify that the second-order tensor $A_{kl}(t)$ can be written as

$$A_{kl}(t) = -\frac{\partial \ln \sqrt{T}}{\partial t}\delta_{kl} + W_{kl}(t), \tag{2.126}$$

where $W_{kl}(t) = -W_{lk}(t)$ is an antisymmetric tensor. Therefore, on the basis of (2.125) and (2.126), the velocity becomes

$$\mathbf{v}(\mathbf{x}, t) = \mathbf{u}(t) - \frac{\partial \ln \sqrt{T}}{\partial t}\mathbf{x} + \mathbf{w}(t) \times \mathbf{x}. \tag{2.127}$$

In the above equation, $\mathbf{w}(t)$ is an axial vector related to the antisymmetric tensor $\mathbf{W}(t)$ through the relationship $\mathbf{Wa} = \mathbf{w} \times \mathbf{a}$ (or in Cartesian components $W_{ij} a_j = \varepsilon_{ijk} w_j a_k$), which is valid for an arbitrary vector field $\mathbf{a}$. One infers from (2.127) that the possible motions for a gas in equilibrium are superpositions of: **(i)** a translational motion $\mathbf{u}(t)$; **(ii)** a radial expansion when $\partial T/\partial t < 0$ or a radial contraction when $\partial T/\partial t > 0$ and **(iii)** a rigid body rotation with angular velocity $\mathbf{w}(t)$.

The substitution of the expression (2.127) into (2.114) leads to

$$\frac{\partial u_i}{\partial t} - \frac{\partial^2 \ln\sqrt{T}}{\partial t^2} x_i + \varepsilon_{ijk}\frac{\partial w_j}{\partial t} x_k + \frac{kT}{m}\frac{\partial \ln\varrho}{\partial x_i} - F_i$$
$$+ \left(u_j - \frac{\partial \ln\sqrt{T}}{\partial t} x_j + \varepsilon_{jrs} w_r x_s\right)\left(-\frac{\partial \ln\sqrt{T}}{\partial t}\delta_{ij} + \varepsilon_{ilj} w_l\right) = 0. \quad (2.128)$$

Moreover, the rotational of (2.128) becomes

$$\nabla \times \mathbf{F} = 2T\frac{\partial \mathbf{w}/T}{\partial t}. \quad (2.129)$$

Therefore, the solution of (2.129) reads

$$\mathbf{F} = -\frac{1}{m}\nabla\varphi + T\frac{\partial \mathbf{w}/T}{\partial t} \times \mathbf{x}, \quad (2.130)$$

where $\varphi(\mathbf{x}, t)$ is a potential function that depends on the space–time coordinates. Hence, the spatial variation of the mass density follows from (2.128) and (2.130), yielding

$$\frac{\partial \ln\varrho}{\partial x_i} = \frac{m}{kT}\Bigg\{ -\frac{1}{m}\frac{\partial\varphi}{\partial x_i} + T\varepsilon_{ijk}\frac{\partial w_j/T}{\partial t} x_k - \frac{\partial u_i}{\partial t} + \frac{\partial^2 \ln\sqrt{T}}{\partial t^2} x_i - \varepsilon_{ijk}\frac{\partial w_j}{\partial t} x_k$$
$$- \left(u_j - \frac{\partial \ln\sqrt{T}}{\partial t} x_j + \varepsilon_{jrs} w_r x_s\right)\left(-\frac{\partial \ln\sqrt{T}}{\partial t}\delta_{ij} + \varepsilon_{ilj} w_l\right)\Bigg\}. \quad (2.131)$$

The time evolution of the mass density is obtained from (2.113), which represents the balance of mass density, i.e.,

$$\frac{\partial \ln\varrho}{\partial t} = -v_i\frac{\partial \ln\varrho}{\partial x_i} + \frac{3}{2}\frac{\partial \ln T}{\partial t}. \quad (2.132)$$

Equations (2.131) and (2.132) compose a system of differential equations for the determination of the mass density of a gas at equilibrium.

In the following, a stationary solution for the fields of mass density, bulk velocity and temperature will be determined, i.e., a solution where the fields do not depend on time. In this case, (2.116), (2.127) and (2.130) read

$$T = \text{constant}, \quad (2.133)$$
$$\mathbf{v} = \mathbf{u} + \mathbf{w} \times \mathbf{x}, \quad (2.134)$$
$$\mathbf{F} = -\frac{1}{m}\nabla\varphi, \quad (2.135)$$

while (2.131) and (2.132) become

$$\frac{\partial \ln\varrho}{\partial x_i} = \frac{m}{kT}\left\{-\frac{1}{m}\frac{\partial\varphi}{\partial x_i} - \left[w_i(\mathbf{x}\cdot\mathbf{w}) - w^2 x_i\right] - \varepsilon_{ilj} w_l u_j\right\}, \quad (2.136)$$

$$\mathbf{v} \cdot \nabla \varphi = 0. \tag{2.137}$$

Therefore, a gas in a stationary state at equilibrium has a constant temperature field and a constant bulk velocity which is a superposition of a translational motion and a rigid body rotation. Moreover, the mass density must satisfy (2.136) and, according to (2.137), the gas flow is alongside of equipotential lines.

By choosing a rotational axis where $\mathbf{w}$ is parallel to $\mathbf{u}$ so that $\varepsilon_{ilj} w_l u_j = 0$, the integration of (2.136) yields

$$\varrho = \varrho_0 \exp\left[-\frac{\varphi}{kT} + \frac{m}{2kT}(w^2 x^2 - w_i w_j x_i x_j)\right], \tag{2.138}$$

where ϱ_0 is an integration constant. From (2.138), it is important to analyze the following cases:

(i) For an air gas in the presence of Earth's gravitational field, integration of (2.135) leads to $\varphi(r) = mgr$, where $\mathrm{g} = 9.81\ \mathrm{m/s^2}$ is the gravitational acceleration and r is the height above sea level. Furthermore, if the angular velocity $\mathbf{w}$ vanishes, the mass density ϱ is expressed by the barometric formula

$$\varrho = \varrho_0 \exp\left[-\frac{\varphi}{kT}\right] = \varrho_0 \exp\left[-\frac{M\mathrm{g}r}{RT}\right], \tag{2.139}$$

where $M = 0.029$ kg/mol denotes the molar mass of Earth's air and $R = 8.3145$ J/(mol K) is the molar gas constant. One infers from the above equation that the mass density decreases with the increasing of the height above the sea level.

(ii) For a vanishing angular velocity, the Maxwellian distribution function (2.107) can be written—due to (2.139)—as

$$f^{(0)} = \frac{\varrho_0}{m}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left[-\left(\frac{\varphi}{kT} + \frac{m(\mathbf{c}-\mathbf{v})^2}{2kT}\right)\right]. \tag{2.140}$$

Equation (2.140) represents the Maxwell–Boltzmann distribution function, whose more familiar expression is $f^{(0)} \propto \exp(-E/kT)$, where $E = E_P + E_K$, denotes the total energy of the gas which is a sum of its potential E_P and kinetic E_K energies.

(iii) By considering a gas in the absence of external forces and adopting a cylindrical coordinate system where $\mathbf{w} = (0, 0, w)$ and $\mathbf{x} = (r\cos\phi, r\mathrm{sen}\phi, z)$, it follows that

$$\varrho = \varrho_0 \exp\left(\frac{m}{2kT} w^2 r^2\right). \tag{2.141}$$

The expression of the mass density given by (2.141) represents a centrifugation of the gas at a constant angular velocity.

Exercises

2.15 If $S_{ij}=S_{ji}$ is a symmetric tensor and $A_{ij}=-A_{ji}$ an antisymmetric tensor, then show that $S_{ij}A_{ji}=0$.

2.16 Obtain the relationships (2.113) through (2.116) from the polynomial equation (2.111).

2.17 Show that $A_{kl}(t)$ is given by expression (2.126).

2.18 Obtain (2.133) through (2.135) for the stationary case.

2.19 The mass density of air at sea level is $\varrho_0 = 1.23$ kg/m^3. Calculate the mass density at a height above sea level: (a) $r = 20$ m and $T = 216.65$ K; (b) $r = 50$ m and $T = 270.65$ K.

2.7 Entropy and Entropy Flux

Another choice for the arbitrary function ψ in the transfer equation (2.69) which leads to an important result is $\psi = -k\ln \mathtt{b}f$, where k denotes Boltzmann's constant and $\mathtt{b}$ is a constant which makes the argument of the logarithm function dimensionless. Hence, it follows

$$\frac{\partial}{\partial t}\int(-kf\ln\mathtt{b}f)d\mathbf{c}+\frac{\partial}{\partial x_i}\int(-kf\ln\mathtt{b}f)\,c_i d\mathbf{c}+\underline{k\int\left[\frac{\partial f}{\partial t}+c_i\frac{\partial f}{\partial x_i}+F_i\frac{\partial f}{\partial c_i}\right]d\mathbf{c}}$$
$$=-\frac{k}{4}\int\ln\frac{ff_1}{f'f_1'}\left(1-\frac{ff_1}{f'f_1'}\right)f'f_1'\,g\,b\,db\,d\varepsilon\,d\mathbf{c}_1\,d\mathbf{c}. \quad (2.142)$$

The underlined term can be replaced, due to the Boltzmann equation (2.20), by

$$\int\left[\frac{\partial f}{\partial t}+c_i\frac{\partial f}{\partial x_i}+F_i\frac{\partial f}{\partial c_i}\right]d\mathbf{c}=\int(f'f_1'-ff_1)\,g\,b\,db\,d\varepsilon\,d\mathbf{c}_1\,d\mathbf{c}=0. \quad (2.143)$$

The above expression is zero, since it corresponds to a function $\psi=1$ in the right-hand side of (2.69).

It is easy to verify that the right-hand side of (2.142) is positive semi-definite due to the inequality $(1-x)\ln x\leqslant 0$, which is valid for all $x>0$ with the equality sign just if and only if $x=1$. From the identification of $x=ff_1/f'f_1'$ and owing to the positiveness of the distribution functions, it follows that the production term due to the molecular collisions of (2.142) is always positive semi-definite. Therefore, one can introduce the quantities

$$\varrho s=\int(-kf\ln\mathtt{b}f)d\mathbf{c}, \quad (2.144)$$

$$\varphi_i = \int (-kf \ln \mathtt{b} f) C_i d\mathbf{c}, \tag{2.145}$$

so that (2.142) can be written as

$$\frac{\partial \varrho s}{\partial t} + \frac{\partial}{\partial x_i}(\varrho s v_i + \varphi_i) \geqslant 0. \tag{2.146}$$

For the interpretation of the quantities given by (2.144) and (2.145) their equilibrium values will be determined. First, the insertion of the Maxwellian distribution function (2.107) into (2.144) and integration of the resulting equation becomes

$$\varrho s|_E = \frac{k\varrho}{m}\left\{\frac{3}{2}\ln T - \ln \varrho + A\right\}. \tag{2.147}$$

In (2.147), $A = \left\{3/2 - \ln\left[m^{\frac{1}{2}}\mathtt{b}/(2\pi k)^{\frac{3}{2}}\right]\right\}$ is a constant.

Now, one can build the differential of $s|_E$, yielding

$$ds|_E = \frac{k}{m}\left\{\frac{3}{2}\frac{dT}{T} - \frac{d\varrho}{\varrho}\right\} = \frac{1}{T}\left\{d\varepsilon - \frac{p}{\varrho^2}d\varrho\right\}, \tag{2.148}$$

where in the second equality above, the constitutive equations for the pressure $p = \varrho kT/m$ and for the specific internal energy $\varepsilon = 3kT/(2m)$ were introduced. From the comparison of (2.148) with the Gibbs equation of thermodynamics

$$ds|_E = \frac{1}{T}\left\{d\varepsilon - \frac{p}{\varrho^2}d\varrho\right\}, \tag{2.149}$$

one may infer that $s|_E$ is the specific entropy in equilibrium.

Furthermore, the equilibrium value of φ_i follows from the insertion of the Maxwellian distribution function (2.107) into its definition (2.145) and subsequent integration of the resulting equation, implying that

$$\varphi_i|_E = \int \left(-kf^{(0)} \ln \mathtt{b} f^{(0)}\right) C_i \, d\mathbf{c} = 0. \tag{2.150}$$

Hence, φ_i is identified with the entropy flux, a quantity that vanishes in equilibrium. Moreover, due to the fact that the entropy production density is also zero in equilibrium, one recognizes (2.146) as the balance equation for the entropy density, which is also known as the entropy density inequality.

The entropy of the gas $\mathcal{S}$ is defined by

$$\mathcal{S} = \int_V \varrho s d\mathbf{x}, \tag{2.151}$$

with V denoting the volume of the recipient where the gas is confined.

By integrating (2.146) over the volume V occupied by the gas, it follows that[5]

$$\frac{d\mathcal{S}}{dt} \geqslant -\int_V \frac{\partial \varphi_i}{\partial x_i} dV = -\int_{\partial V} \varphi_i \hat{n}_i dA. \tag{2.152}$$

In the above equation, $\hat{n}_i$ is a unit normal vector outwards the impermeable boundary surface ∂V which is at rest and delimits the gas.

One can rewrite (2.152) from the knowledge that the entropy flux in a linearized thermodynamic theory is equal to the heat flux vector divided by the temperature, i.e., $\varphi_i = q_i/T$ (see Sections 3.1 and 4.1.4). If the surface is also diathermic, the temperature is a continuous function across this surface and the gas temperature is equal to the temperature T_0 of the wall which separates the gas from the solid. Furthermore, across this surface the entropy flux and the heat flux vector are continuous functions provided that the gas and the surface are at rest. Hence, $\varphi_i = q_i^S/T_0$, where q_i^S is the heat flux vector corresponding to the solid surface. By taking into account these conditions, it follows that

$$\frac{d\mathcal{S}}{dt} \geqslant \int_{\partial V} -\frac{q_i^S \hat{n}_i}{kT_0} dA. \tag{2.153}$$

Now, by recalling that the heat transferred from the solid to the gas is given by $dQ = -(q_i^S \hat{n}_i) dA dt$, (2.153) becomes

$$d\mathcal{S} \geqslant \int \frac{dQ}{T_0}. \tag{2.154}$$

Note that by convention the heat supplied to a body is considered as a positive quantity and, in this case, $\hat{n}_i$ points outwards, whereas q_i^S points inwards the surface.

The inequality (2.153) is the mathematical expression of the second law of thermodynamics, which can be interpreted as: the entropy change of a body in a thermodynamic process cannot be smaller than the exchanged heat divided by the temperature.

Exercises

2.20 Obtain the expression (2.147) for the specific entropy in equilibrium.

2.21 Show that the entropy flux vanishes in equilibrium.

---

[5] In order to obtain (2.152), the transport theorem

$$\frac{d}{dt}\int_V \psi d\mathbf{x} = \int_V \left(\frac{\partial \psi}{\partial t} + \frac{\partial \psi v_i}{\partial x_i}\right) d\mathbf{x}$$

was used, which is valid for a continuous differentiable scalar field ψ that represents some property defined in the volume V.

2.8 The $\mathcal{H}$-Theorem

2.8.1 Interactions of Gas Molecules with Solid Surfaces

Consider a wall represented by a closed surface which delimitates the region occupied by the gas. The following premises will be taken into account: (a) the wall is at rest; (b) there exist no chemical reactions between the molecules of the gas and the wall and (c) the residence time of a gas particle in the wall, the so-called adsorption time, is much smaller than a characteristic time of the problem in study.

Let $\mathbf{x}$ denote an arbitrary point at the wall and $\mathbf{n}$ a unit normal vector pointing in the direction of its interior (see Figure 2.6). Consider that at time t a molecule impinges the wall at point $\mathbf{x}$ with a velocity $\mathbf{c}^I$ and that it is remitted at the same point and at the same time with a velocity $\mathbf{c}^R$.

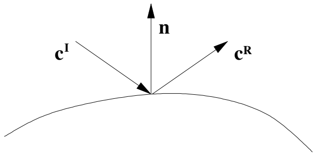

Fig. 2.6 Incidence and remission of a molecule from a wall.

The distribution function at the wall is a sum of two contributions, namely,

$$f(\mathbf{x},\mathbf{c},t)=f^I(\mathbf{x},\mathbf{c},t)+f^R(\mathbf{x},\mathbf{c},t), \tag{2.155}$$

where the incident $f^I(\mathbf{x},\mathbf{c},t)$ and remitted $f^R(\mathbf{x},\mathbf{c},t)$ distribution functions are given by[6]

$$f^I(\mathbf{c})=\begin{cases} f(\mathbf{c}) & \text{if } \mathbf{c}\cdot\mathbf{n}<0,\\ 0 & \text{if } \mathbf{c}\cdot\mathbf{n}>0,\end{cases}\qquad f^R(\mathbf{c})=\begin{cases} 0 & \text{if } \mathbf{c}\cdot\mathbf{n}<0,\\ f(\mathbf{c}) & \text{if } \mathbf{c}\cdot\mathbf{n}>0.\end{cases} \tag{2.156}$$

From (2.155) and (2.156), it is possible to express the moments of the distribution function at the wall points as a sum of two contributions, one related with the incident molecules and another with the remitted ones. Indeed, the mass density, momentum density, pressure tensor and heat flux vector can be written as

$$\varrho=\int_{\mathbf{c}\cdot\mathbf{n}<0} mf^I(\mathbf{c})d\mathbf{c}+\int_{\mathbf{c}\cdot\mathbf{n}>0} mf^R(\mathbf{c})d\mathbf{c}=\varrho_I+\varrho_R, \tag{2.157}$$

---

[6] From now on the dependence of the distributions functions on the variables $\mathbf{x}$ and t will be omitted.

$$\varrho v_i = \int_{\mathbf{c}\cdot\mathbf{n}<0} mc_i f^I(\mathbf{c})d\mathbf{c} + \int_{\mathbf{c}\cdot\mathbf{n}>0} mc_i f^R(\mathbf{c})d\mathbf{c} = \varrho_I v_i^I + \varrho_R v_i^R, \tag{2.158}$$

$$p_{ij} = \int_{\mathbf{c}\cdot\mathbf{n}<0} mC_iC_j f^I(\mathbf{c})d\mathbf{c} + \int_{\mathbf{c}\cdot\mathbf{n}>0} mC_iC_j f^R(\mathbf{c})d\mathbf{c} = p_{ij}^I + p_{ij}^R, \tag{2.159}$$

$$q_i = \frac{1}{2}\int_{\mathbf{c}\cdot\mathbf{n}<0} mC^2C_i f^I(\mathbf{c})d\mathbf{c} + \frac{1}{2}\int_{\mathbf{c}\cdot\mathbf{n}>0} mC^2C_i f^R(\mathbf{c})d\mathbf{c} = q_i^I + q_i^R. \tag{2.160}$$

The wall is supposed to be non-porous and non-absorbing, so that all incident molecules will be remitted. In this case, the following relationship holds

$$\varrho_I v_i^I n_i = -\varrho_R v_i^R n_i, \qquad \text{i.e.,} \qquad \varrho v_i n_i = 0. \tag{2.161}$$

Furthermore, if $\mathbf{t}$ denotes a unit vector perpendicular to the unit normal vector $\mathbf{n}$, so that $n_i t_i = 0$, the velocity can be written as $\mathbf{v} = (\mathbf{v}\cdot\mathbf{t})\mathbf{t}$.

Now, it is supposed that the molecules are in thermal equilibrium with the wall with a temperature T_0 and are remitted according to a Maxwellian distribution function, denoted by f_w. In this case, f_w reads

$$f^R = f_w = \zeta \exp\left[-\frac{mc^2}{2kT_0}\right], \tag{2.162}$$

where ζ is a factor obtained from the condition of a non-porous and non absorbing wall. For calculation simplicity, let the unit normal be directed along the x_1-axis, so that one can write from (2.158), (2.161) and (2.162):

$$\begin{aligned} 0 &= \int_{\mathbf{c}\cdot\mathbf{n}<0} mc_i n_i f^I(\mathbf{c})d\mathbf{c} + \int_{\mathbf{c}\cdot\mathbf{n}>0} mc_i n_i \zeta \exp\left[-\frac{mc^2}{2kT_0}\right] d\mathbf{c} \\ &= \varrho_I v_i^I n_i + \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{0}^{+\infty} mc_1 \zeta \exp\left[-\frac{mc^2}{2kT_0}\right] dc_1 dc_2 dc_3. \end{aligned} \tag{2.163}$$

From the above equation, one obtains ζ, so that (2.162) becomes

$$f_w = \frac{1}{2\pi}\frac{m}{(kT_0)^2}\varrho_R(\mathbf{v}^R\cdot\mathbf{n})\exp\left[-\frac{mc^2}{2kT_0}\right]. \tag{2.164}$$

The oldest model used to describe the interactions of gas molecules and solid surfaces is due to Maxwell.[7] In this model, a fraction $(1-\alpha)$ of the gas molecules is specularly reflected with a velocity $\mathbf{c} - 2\mathbf{n}(\mathbf{c}\cdot\mathbf{n})$, whereas a fraction α of the gas molecules is diffusively remitted according to a Maxwellian distribution function with the temperature of the wall T_0, i.e.,

$$f^R(\mathbf{c}) = (1-\alpha)f^I(\mathbf{c} - 2\mathbf{n}(\mathbf{c}\cdot\mathbf{n})) + \alpha\frac{1}{2\pi}\frac{m}{(kT_0)^2}\varrho_R(\mathbf{v}^R\cdot\mathbf{n})\exp\left[-\frac{mc^2}{2kT_0}\right]. \tag{2.165}$$

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[7] J. C. Maxwell, "On stresses in rarefied gases arising from inequalities of temperature", *Phil. Trans. R. Soc. London*, **170** 231-256 (1879).

For the remitted molecules, the pressure tensor and the heat flux vector reads

$$p_{ij}^R t_j n_i = -(1-\alpha) p_{ij}^I t_j n_i - \alpha \left[\varrho_R (\mathbf{v}^R \cdot \mathbf{n})(\mathbf{v} \cdot \mathbf{t}) \right], \tag{2.166}$$

$$\mathbf{q}^R \cdot \mathbf{n} = -(1-\alpha)(\mathbf{q}^I \cdot \mathbf{n}) + \alpha \left\{ 2\frac{kT_0}{m} \varrho_R (\mathbf{v}^R \cdot \mathbf{n}) \left[1 + \frac{m}{4kT_0} v^2 \right] \right\}, \tag{2.167}$$

due to their definitions given by (2.159) and (2.160), respectively, and to the distribution function (2.165).

One can infer from (2.166) and (2.167) that: **(i)** for a genuine diffusive remission ($\alpha = 1$), the pressure tensor of the remitted molecules tangential to the wall is associated with a velocity slip, whereas the corresponding heat flux vector normal to the wall is connected with the remitted energy flux of the molecules, and **(ii)** for a pure specular reflection ($\alpha = 0$), the total pressure tensor tangential to the wall is zero, i.e., $p_{ij} t_j n_i = 0$, indicating that there exists no slip while the total heat flux vector normal to the wall vanishes, i.e., $\mathbf{q} \cdot \mathbf{n} = 0$.

Exercises

2.22 Show that the Maxwellian distribution function f_w is given by (2.164).

2.23 Obtain (2.166) and (2.167).

2.8.2 Scattering Kernels

Let $P(\mathbf{c}^I \to \mathbf{c}^R; \mathbf{x}, t) d\mathbf{c}^I d\mathbf{c}^R$ be the probability that a molecule is remitted at time t from a point $\mathbf{x}$ at the wall with velocities in the range $\mathbf{c}^R$ and $\mathbf{c}^R + d\mathbf{c}^R$, when it impinges at the same wall point and time with velocities in the range $\mathbf{c}^I$ and $\mathbf{c}^I + d\mathbf{c}^I$. One may say that the number of molecules with velocities in the range $\mathbf{c}^I$ and $\mathbf{c}^I + d\mathbf{c}^I$ which impinges on a unit area of the wall per unit time is given by[8]

$$dN^I = \mid \mathbf{c}^I \cdot \mathbf{n} \mid f(\mathbf{c}^I) d\mathbf{c}^I. \tag{2.168}$$

The impinged molecules with velocities in the range $\mathbf{c}^I$ and $\mathbf{c}^I + d\mathbf{c}^I$ will be remitted from the wall with velocities in the range $\mathbf{c}^R$ and $\mathbf{c}^R + d\mathbf{c}^R$, so that the number of remitted molecules per unit wall area and time is given in terms of probability of remission $P(\mathbf{c}^I \to \mathbf{c}^R)$, i.e,

$$dN^{IR} = \mid \mathbf{c}^I \cdot \mathbf{n} \mid f(\mathbf{c}^I) P(\mathbf{c}^I \to \mathbf{c}^R) d\mathbf{c}^I d\mathbf{c}^R. \tag{2.169}$$

---

[8] The dependence of the functions f and P on $\mathbf{x}$ and t will also be omitted from now on.

Hence, in order to determine the total number of remitted molecules per unit wall area and time and with velocities in the range $\mathbf{c}^R$ and $\mathbf{c}^R + d\mathbf{c}^R$, one has to perform an integration over all impinged molecular velocities $\mathbf{c}^I$, yielding

$$dN^R = \mid \mathbf{c}^R \cdot \mathbf{n} \mid f(\mathbf{c}^R) d\mathbf{c}^R = d\mathbf{c}^R \int_{\mathbf{c}^I \cdot \mathbf{n} < 0} \mid \mathbf{c}^I \cdot \mathbf{n} \mid f(\mathbf{c}^I) P(\mathbf{c}^I \to \mathbf{c}^R) d\mathbf{c}^I. \tag{2.170}$$

The probability density $P(\mathbf{c}^I \to \mathbf{c}^R)$, known as scattering kernel, has the following properties:

(a) The scattering kernel is positive semi-definite:

$$P(\mathbf{c}^I \to \mathbf{c}^R) \geqslant 0. \tag{2.171}$$

This property is evident because $P(\mathbf{c}^I \to \mathbf{c}^R)$ represents a probability density.

(b) The scattering kernel is normalized, i.e.,

$$\int_{\mathbf{c}^R \cdot \mathbf{n} > 0} P(\mathbf{c}^I \to \mathbf{c}^R) d\mathbf{c}^R = 1. \tag{2.172}$$

This property is a consequence of the condition that the wall restitutes all incident molecules.

(c) The scattering kernel satisfies the reciprocity law or detailed balance law:

$$\mid \mathbf{c}^I \cdot \mathbf{n} \mid f_w(\mathbf{c}^I) P(\mathbf{c}^I \to \mathbf{c}^R) = \mid \mathbf{c}^R \cdot \mathbf{n} \mid f_w(\mathbf{c}^R) P(-\mathbf{c}^R \to -\mathbf{c}^I). \tag{2.173}$$

In the above equation, f_w is the Maxwellian distribution function (2.164) for a wall at rest and with temperature T_0. The physical interpretation of the reciprocity law is the following: a gas which is at equilibrium with a wall at temperature T_0 has a distribution function equal to f_w, so that the number of molecules—per unit of area and time—that are scattered from the range of velocities $\mathbf{c}^I$ and $(\mathbf{c}^I + d\mathbf{c}^I)$ to the one $\mathbf{c}^R$ and $(\mathbf{c}^R + d\mathbf{c}^R)$ is equal to the number of molecules that are scattered from the range of velocities $-\mathbf{c}^R$ and $-(\mathbf{c}^R + d\mathbf{c}^R)$ to the one $-\mathbf{c}^I$ and $-(\mathbf{c}^I + d\mathbf{c}^I)$.

An immediate consequence of (2.172) and (2.173) is that a distribution function of the incident molecules equal to f_w does not suffer any disturbance when the molecules interact with the wall, so that the distribution function of the remitted molecules remains unchanged and equal to f_w. Indeed, by integrating (2.173) with respect to $d\mathbf{c}^I$ and using (2.172) yields

$$\int_{\mathbf{c}^I \cdot \mathbf{n} < 0} \mid \mathbf{c}^I \cdot \mathbf{n} \mid f_w(\mathbf{c}^I) P(\mathbf{c}^I \to \mathbf{c}^R) d\mathbf{c}^I = \mid \mathbf{c}^R \cdot \mathbf{n} \mid f_w(\mathbf{c}^R). \tag{2.174}$$

The specification of a scattering kernel is not a simple problem because the physical phenomena associated with the interacting processes of the gas molecules and the solid surface is too complicated. One simple example of scattering kernel is the one which corresponds to the model proposed by

Maxwell and whose expression for $f^R(\mathbf{c})$ is given by (2.165). In this case, $P(\mathbf{c}^I \to \mathbf{c}^R)$ is written as

$$P(\mathbf{c}^I \to \mathbf{c}^R) = \frac{\mid \mathbf{c}^R \cdot \mathbf{n} \mid}{\mid \mathbf{c}^I \cdot \mathbf{n} \mid}\Bigg\{(1-\alpha)\delta(\mathbf{c}^I - \mathbf{c}^R + 2(\mathbf{c}^R \cdot \mathbf{n})\mathbf{n}) \\ - \alpha\frac{1}{2\pi}\left(\frac{m}{kT_0}\right)^2 (\mathbf{c}^I \cdot \mathbf{n}) \exp\left[-\frac{mc_R^2}{2kT_0}\right]\Bigg\}. \qquad (2.175)$$

It is easy to verify that the scattering kernel given by (2.175) satisfies the conditions given by (2.171) through (2.174).

The proof of the $\mathcal{H}$-theorem is based on a theorem for the scattering kernels due to Darrozes and Giraud[9] and Cercignani[10], which will be analyzed afterwards.

For the proof of the theorem on scattering kernels, one makes use of the concept and properties of convex functions. A real function $\mathcal{F}$ is convex in the interval (a, b) if for all $0 \leqslant t \leqslant 1$ and for all values of $x, y \in (a, b)$ the following inequality holds:

$$\mathcal{F}((1-t)x + ty) \leqslant (1-t)\mathcal{F}(x) + t\mathcal{F}(y). \qquad (2.176)$$

A convex function is geometrically interpreted as a function which lies below the straight line segment connecting any two points in the interval (a, b).

An important property of convex functions refers to the so-called Jensen inequality[11] which can be stated as: If μ is a positive measure in the set $\mathcal{R}$ such that

$$\int_{\mathcal{R}} d\mu = 1, \qquad (2.177)$$

with $\mathcal{F}$ being a convex function in the interval (a, b), hence

$$\mathcal{F}\Big(\int_{\mathcal{R}} g d\mu\Big) \leqslant \int_{\mathcal{R}} \mathcal{F}(g) d\mu \qquad (2.178)$$

for all measurable function g which are positive, finite and integrable in $\mathcal{R}$. The cases $a = -\infty$ and $b = +\infty$ are not excluded from this proposition.

On the basis of the above results, the following theorem can now be proved.

Theorem: *If $\mathcal{F}(g)$ is a convex function of its argument g, then for all scattering kernel $P(\mathbf{c}^I \to \mathbf{c}^R)$ which satisfies (2.171), (2.172) and (2.174), it holds the inequality*

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[9] J. Darrozes and J. P. Giraud, "Généralisation formelle du théorème H en présence de parois. Applications", *Compt. Rend. Acad. Sci. Paris* **A262**, 1368-1371 (1966).

[10] C. Cercignani, "Scattering kernels for gas-surface interactions", *Transp. Theory Stat. Phys.* **2**, 27-53 (1972).

[11] See, e.g., W. Rudin, *Real and complex analysis* (McGraw-Hill, New York, 1987).

$$\int (\mathbf{c}\cdot\mathbf{n}) f_w \mathcal{F}(g) d\mathbf{c} \leqslant 0, \tag{2.179}$$

where $g = f/f_w$*. Furthermore, for* $\mathcal{F}(g) = g \ln g$*, one has*

$$\int (\mathbf{c}\cdot\mathbf{n}) f \ln f d\mathbf{c} \leqslant -\frac{(q_i^G + p_{ij}^G v_j^G) n_i}{kT_0}, \tag{2.180}$$

where q_i^G*,* p_{ij}^G *and* v_j^G *denote the heat flux vector, the pressure tensor and the velocity of the gas at the wall, respectively.*

Proof: For the proof of the first part of the theorem, let $\mathcal{P}(\mathbf{c}^I)$ denote the transition probability for a fixed value of $\mathbf{c}^R$

$$\mathcal{P}(\mathbf{c}^I) = \frac{P(\mathbf{c}^I \to \mathbf{c}^R) \mid \mathbf{c}^I\cdot\mathbf{n} \mid f_w(\mathbf{c}^I)}{\mid \mathbf{c}^R\cdot\mathbf{n} \mid f_w(\mathbf{c}^R)}. \tag{2.181}$$

According to (2.174), its integration over all values of $\mathbf{c}^R$ becomes

$$\int_{\mathbf{c}^I\cdot\mathbf{n}<0} \mathcal{P}(\mathbf{c}^I) d\mathbf{c}^I = 1. \tag{2.182}$$

By identifying the condition (2.182) with the one given by (2.177), one may write the Jensen inequality (2.178) as

$$\mathcal{F}\Big(\int_{\mathbf{c}^I\cdot\mathbf{n}<0} \mathcal{P}(\mathbf{c}^I) g(\mathbf{c}^I) d\mathbf{c}^I\Big) \leqslant \int_{\mathbf{c}^I\cdot\mathbf{n}<0} \mathcal{P}(\mathbf{c}^I) \mathcal{F}(g(\mathbf{c}^I)) d\mathbf{c}^I. \tag{2.183}$$

The substitution of (2.181) into (2.183) leads to

$$\begin{aligned} \mathcal{F}(g(\mathbf{c}^R)) \equiv \mathcal{F}\left(\int_{\mathbf{c}^I\cdot\mathbf{n}<0} \frac{P(\mathbf{c}^I \to \mathbf{c}^R)|\mathbf{c}^I\cdot\mathbf{n}| f_w(\mathbf{c}^I)}{|\mathbf{c}^R\cdot\mathbf{n}| f_w(\mathbf{c}^R)} g(\mathbf{c}^I) d\mathbf{c}^I\right) \\ \leqslant \int_{\mathbf{c}^I\cdot\mathbf{n}<0} \frac{P(\mathbf{c}^I \to \mathbf{c}^R)|\mathbf{c}^I\cdot\mathbf{n}| f_w(\mathbf{c}^I)}{|\mathbf{c}^R\cdot\mathbf{n}| f_w(\mathbf{c}^R)} \mathcal{F}(g(\mathbf{c}^I)) d\mathbf{c}^I, \end{aligned} \tag{2.184}$$

thanks to (2.173). Furthermore, the multiplication of the above equation by $|\mathbf{c}^R\cdot\mathbf{n}| f_w(\mathbf{c}^R)$ and the integration of the resulting equation over all values of $d\mathbf{c}^R$ leads to

$$\int_{\mathbf{c}^R\cdot\mathbf{n}>0} |\mathbf{c}^R\cdot\mathbf{n}| f_w(\mathbf{c}^R) \mathcal{F}(g(\mathbf{c}^R)) d\mathbf{c}^R \leqslant \int_{\mathbf{c}^I\cdot\mathbf{n}<0} |\mathbf{c}^I\cdot\mathbf{n}| f_w(\mathbf{c}^I) \mathcal{F}(g(\mathbf{c}^I)) d\mathbf{c}^I, \tag{2.185}$$

by using the condition (2.172). Hence, the first part of the theorem is proved.

For the proof of the second part of the theorem, one inserts

$$\mathcal{F}(g) = g \ln g = \frac{f}{f_w}(\ln f - \ln f_w), \tag{2.186}$$

into (2.179). By considering that f_w is given by (2.162) and that $(\mathbf{c}\cdot\mathbf{n}) = (\mathbf{C}\cdot\mathbf{n})$—since $\mathbf{v}$ satisfies the condition (2.161)—it follows that

$$\int (\mathbf{c}\cdot\mathbf{n}) f \ln f d\mathbf{c} \leqslant \int (\mathbf{c}\cdot\mathbf{n}) f \left(\ln\zeta - \frac{mc^2}{2kT_0}\right) d\mathbf{c}$$

$$= \int (\mathbf{C}\cdot\mathbf{n}) f \left[\ln\zeta - \frac{m}{2kT_0}\left(C^2 + 2C_r v_r + v^2\right)\right] d\mathbf{c} = \frac{-(q_i^G + p_{ij}^G v_j^G) n_i}{kT_0}, \tag{2.187}$$

which is the inequality (2.180), thus proving the above theorem.

The energy conservation law at the wall rest frame with unit normal vector n_i is given by

$$\varrho_G\left(\varepsilon_G + \frac{1}{2}v_G^2\right) v_i^G n_i + p_{ij}^G n_i v_j^G + q_i^G n_i$$

$$= \varrho_S\left(\varepsilon_S + \frac{1}{2}v_S^2\right) v_i^S n_i + p_{ij}^S n_i v_j^S + q_i^S n_i, \tag{2.188}$$

where the indexes G and S refer to the gas and solid, respectively. Since, by hypothesis the solid is at rest $v_i^S = 0$ and the wall does not absorb molecules of the gas $v_i^G n_i = 0$, (2.188) reduces to

$$p_{ij}^G n_i v_j^G + q_i^G n_i = q_i^S n_i. \tag{2.189}$$

The above equation shows that the normal component of the heat flux vector across the wall is not a continuous function and that its discontinuity is related with shear stresses and the velocity slip of the gas.

Now, the inequality (2.187) can be written as

$$\int (\mathbf{c}\cdot\mathbf{n}) f \ln f d\mathbf{c} \leqslant -\frac{1}{kT_0} q_i^S n_i, \tag{2.190}$$

due to (2.189).

As a final comment one can verify that the above theorem is valid also for the particular cases of specular reflection and diffuse remission because both cases satisfy the premisses of the theorem.

Exercises

2.24 Show that the scattering kernel (2.175) satisfies the conditions given by equations (2.171) through (2.174).

2.25 Obtain the inequality (2.187).

2.26 Show that (2.188) follows from the energy conservation law (2.99) for a steady state and in the absence of the specific external force, namely,

$$\frac{\partial}{\partial x_i}\left[\varrho\left(\varepsilon + \frac{1}{2}v^2\right) v_i + q_i + p_{ij} v_j\right] = 0.$$

2.8.3 The $\mathcal{H}$-Theorem

The results of previous sections are important to analyze the function $\mathcal{H}$, which is defined in terms of the entropy by the relationship $\mathcal{S} = -k\mathcal{H}$. In this case, the inequality (2.152) becomes

$$-k\frac{d\mathcal{H}}{dt} \geqslant -\int_{\partial V} \varphi_i \hat{n}_i dA. \tag{2.191}$$

One may rewrite the above inequality by using the definition of the entropy flux (2.145), namely, $\varphi_i = \int(-kf\ln \mathsf{b}f)C_i d\mathbf{c}$, as

$$\frac{d\mathcal{H}}{dt} \leqslant \int_{\partial V}\Big[\int(\mathbf{c}\cdot\mathbf{n})f\ln f d\mathbf{c}\Big]dA. \tag{2.192}$$

In (2.192), $n_i = -\hat{n}_i$ is the normal unit vector pointing inwards to the surface ∂V, which encloses the gas. Furthermore, it was supposed that the surface ∂V is at rest and is impermeable, i.e., $v_i n_i = 0$.

For the analysis of the inequality (2.192), one has to introduce the concept of linear impermeable wall. A linear impermeable wall is defined as a wall where the total number of remitted molecules per unit of area and time obeys (2.170) and whose scattering kernel satisfies (2.171)–(2.174). Particular cases of linear impermeable walls are those where the incident molecules are reflected specularly or diffusively from the wall. For linear impermeable walls, the theorem of previous section holds, and the inequality (2.192) can be written as

$$\frac{d\mathcal{H}}{dt} \leqslant -\int_{\partial V} \frac{dQ}{kT_0}, \tag{2.193}$$

by taking into account (2.190) and by introducing the heat transferred by the solid to the gas $dQ = (q_i^S n_i)dAdt$. From the inequality (2.193), one can state the following theorem.

$\mathcal{H}$-Theorem: *The time variation of $\mathcal{H}$ always decreases for a gas limited by a linear impermeable wall if in all points of ∂V, $dQ > 0$, i.e., if the heat is flowing from the solid to the gas. The function $\mathcal{H}$ remains constant if and only if the distribution function is a Maxwellian.*

Exercises

2.27 Obtain the inequality (2.192).

2.28 Show that $d\mathcal{H}/dt \leqslant 0$ when the distribution function does not depend on the position coordinates $\mathbf{x}$ and give a physical interpretation of this result.

2.8.4 The Paradoxes of Loschmidt and Zermelo

The attainment of the second law of thermodynamics from a microscopic model based on the kinetic gas theory by Boltzmann was not in consensus among the scientists who have criticized this procedure, since it was based on the laws of classical mechanics. The most important objections were enounced in terms of two paradoxes, which will be analyzed in the following.

The reversibility paradox of Loschmidt (*Umkehreinwand*) is based on the assertion: the molecules of the gas obey the laws of classical mechanics which are symmetric with respect to the time reversal $t \to -t$; hence, the time inversion leads to $d\mathcal{H}/d(-t) < 0$, i.e., $d\mathcal{H}/dt > 0$, which contradicts the $\mathcal{H}$-theorem.

The Loschmidt paradox is elucidated on the basis of the following arguments: the Liouville's equation (2.31) is an exact equation and invariant under time transformation $t \to -t$, whereas the Boltzmann equation (2.20) could be considered as an approximation of the BBGKY hierarchy (see Section 2.2.3), which is not invariant under this transformation. Indeed, the left-hand side of the Boltzmann equation changes its sign under the transformation $t \to -t$ and $\mathbf{c} \to -\mathbf{c}$, whereas its right-hand side remains invariant.

The recurrence paradox (*Wiederkehreinwand*) of Zermelo is based on the recurrence paradox of Poincaré, which can be enunciated as: any conservative system, isolated and finite, should return to a neighborhood arbitrarily small of its initial state after a sufficient long time interval. Hence, the $\mathcal{H}(t)$ function cannot always decrease, since it should approximate its initial value $\mathcal{H}(0)$ after a finite time interval, known as Poincaré's recurrence time.

This paradox is solved by noting that Poincaré's recurrence time is so long that it is practically impossible to observe time intervals where the $\mathcal{H}$ function could increase. Boltzmann's arguments were:[12] *... a recurrence of an initial state is not mathematically impossible, and indeed is to be expected if the time of motion is sufficiently long, since the probability of finding a state very close to the initial state is very small but not zero. The consequence of Poincaré's theorem ... is therefore in complete agreement with my theory.*

To end this section, one recalls a remark by Chandrasekhar[13] on reversible and irreversible processes: *... a process appears irreversible (or reversible) according as whether the initial state is characterized by a long (or short) average time of recurrence compared to the times during which the system is under observation.*

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[12] L. Boltzmann, “Entgegnung auf die wärmetheoretischen Betrachtungen des Hrn. E. Zermelo”, *Ann. Phys. Leipzig*, **57** 773-784 (1896).

[13] S. Chandrasekhar, Stochastic problems in physics and astronomy, *Rev. Mod. Phys.*, **15** 1-89 (1943). Subrahmanyan Chandrasekhar (1910–1995) Indian American astrophysicist.

2.9 The Many Faces of Entropy

In this section, further expressions for the equilibrium entropy will be deduced which are commonly used in equilibrium statistical mechanics.

Let one start with the expression for the entropy, given by

$$\mathcal{S} = -k \int_V \int (f \ln \mathtt{b} f) d\mathbf{c}\, d\mathbf{x}, \tag{2.194}$$

due to (2.144) and (2.151).

At equilibrium, the distribution function is a Maxwellian and one can write it from (2.107) as

$$f^{(0)} = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mC^2}{2kT}} = \frac{N}{V} \frac{e^{-\frac{mC^2}{2kT}}}{\int e^{-\frac{mC^2}{2kT}} d\mathbf{c}} = \frac{N}{V} p_\mathbf{c}, \tag{2.195}$$

where $p_\mathbf{c}$ gives the probability to find molecules with velocities within the range $\mathbf{c}$ and $\mathbf{c} + d\mathbf{c}$.

The insertion of (2.195) into the definition of the entropy (2.194), yields

$$\mathcal{S}|_E = -kN \int (p_\mathbf{c} \ln p_\mathbf{c}) d\mathbf{c} = -kN \sum_{\mathbf{c}=-\infty}^{+\infty} (p_\mathbf{c} \ln p_\mathbf{c}), \tag{2.196}$$

by choosing $\mathtt{b} = 1/N$ and by converting the velocities into discrete variables. This expression for the entropy is similar to the one used in statistical mechanics for a canonical ensemble, i.e., a system of fixed number of particles N and volume V and in contact to a thermal reservoir at temperature T.

Note that one may also express the probability as

$$p_\mathbf{c} = \frac{e^{-E_\mathbf{c}/kT}}{Z}, \qquad \text{where} \qquad Z = \sum_{\mathbf{c}=-\infty}^{+\infty} e^{-E_\mathbf{c}/kT} \tag{2.197}$$

is the so-called partition function and $E_\mathbf{c} = mC^2/kT$ is the (kinetic) energy. The above expression for the probability is known as the Maxwell–Boltzmann distribution.

By introducing the number of molecules $N_\mathbf{c} = Np_\mathbf{c}$ whose velocities are within the range $\mathbf{c}$ and $\mathbf{c} + d\mathbf{c}$, the entropy (2.196) becomes

$$\mathcal{S}|_E = -k\left(\sum_{\mathbf{c}=-\infty}^{+\infty} N_\mathbf{c} \ln N_\mathbf{c} - N \ln N\right), \qquad \text{since} \qquad N = \sum_{\mathbf{c}=-\infty}^{+\infty} N_\mathbf{c}. \tag{2.198}$$

The above equation can be rewritten as

$$S = k \ln W, \qquad \text{where} \qquad W = \left[N! \Bigg/ \prod_{\mathbf{c}=-\infty}^{+\infty} N_{\mathbf{c}}! \right], \tag{2.199}$$

due to Stirling's formula

$$\ln N! \approx N \ln N - N, \qquad \text{which is valid for all} \qquad N \gg 1. \tag{2.200}$$

The expression (2.199) for the entropy is similar to the one used in statistical mechanics for a microcanonical ensemble, i.e., a system of fixed number of particles N, volume V and energy E. The term W, known as the statistical weight, represents the number of possible microstates comprising a macrostate characterized by (E, V, N).

In statistical mechanics, the expressions for the entropy (2.196) and (2.199) are applied not only for ideal gases but for a wide class of materials.

Exercise

2.30 Obtain (2.199) from (2.196).

2.10 Appendix

The integrals commonly used in kinetic theory of gases are of the type:

$$\int C_{i_1} C_{i_2} \dots C_{i_N} f^{(0)} d\mathbf{c} = n \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \int C_{i_1} C_{i_2} \dots C_{i_N} e^{-\beta C^2} d\mathbf{c}, \tag{2.201}$$

where $\beta = m/2kT$. The above integral always vanishes whenever the number of peculiar velocities $\mathbf{C}$ is odd.

If $N = 2$, the integral (2.201) can be written as

$$\int C_i C_j f^{(0)} d\mathbf{c} = -n \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \frac{1}{2\beta} \left[\int \frac{\partial C_i e^{-\beta C^2}}{\partial C_j} d\mathbf{c} - \int e^{-\beta C^2} \delta_{ij} d\mathbf{c} \right]. \tag{2.202}$$

The first integral on the right-hand side vanishes, since the exponential function tends to zero for large values of $\mathbf{C}$. Hence, (2.202) reduces to

$$\int C_i C_j f^{(0)} d\mathbf{c} = n \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \frac{1}{2\beta} \delta_{ij} \int e^{-\beta C^2} d\mathbf{c} = n \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \frac{\delta_{ij}}{3} \int C^2 e^{-\beta C^2} d\mathbf{c}, \tag{2.203}$$

due to (1.123). The final expression for the integral reads

$$\int C_i C_j f^{(0)} d\mathbf{c} = \frac{1}{3}\delta_{ij} \int C^2 f^{(0)} d\mathbf{c}. \tag{2.204}$$

For $N = 4$, the integral (2.201) becomes

$$\begin{aligned}
\int C_i C_j C_k C_l f^{(0)} d\mathbf{c} &= -n\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \frac{1}{2\beta} \int C_i C_j C_k \frac{\partial e^{-\beta C^2}}{\partial C_l} d\mathbf{c} \\
&= n\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \frac{1}{2\beta} \int \left(\delta_{il} C_j C_k + C_i \delta_{jl} C_k + C_i C_j \delta_{kl}\right) e^{-\beta C^2} d\mathbf{c} \\
&= n\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \frac{1}{2\beta}\frac{1}{3} \left(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl} + \delta_{ij}\delta_{kl}\right) \int C^2 e^{-\beta C^2} d\mathbf{c},
\end{aligned} \tag{2.205}$$

by using (2.204). Now, according to (1.123), one has $\int C^2 e^{-\beta C^2} d\mathbf{c} = (2\beta/5) \int C^4 e^{-\beta C^2} d\mathbf{c}$, so that the final expression for the integral becomes

$$\int C_i C_j C_k C_l f^{(0)} d\mathbf{c} = \frac{1}{15}\big(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl} + \delta_{ij}\delta_{kl}\big) \int C^4 f^{(0)} d\mathbf{c}. \tag{2.206}$$

The following result for $N = 6$ can be obtained by using the same methodology described above

$$\begin{aligned}
\int C_i C_j C_k C_l C_m C_n f^{(0)} d\mathbf{c} = \frac{1}{105}\big(&\delta_{ij}\delta_{kl}\delta_{mn} + \delta_{ij}\delta_{km}\delta_{ln} + \delta_{ij}\delta_{kn}\delta_{lm} \\
&+\delta_{ik}\delta_{jl}\delta_{mn} + \delta_{ik}\delta_{jm}\delta_{ln} + \delta_{ik}\delta_{jn}\delta_{lm} + \delta_{il}\delta_{jk}\delta_{mn} + \delta_{il}\delta_{jm}\delta_{kn} \\
&+\delta_{il}\delta_{jn}\delta_{km} + \delta_{im}\delta_{jk}\delta_{ln} + \delta_{im}\delta_{jl}\delta_{kn} + \delta_{im}\delta_{jn}\delta_{kl} + \delta_{in}\delta_{jk}\delta_{lm} \\
&+\delta_{in}\delta_{jl}\delta_{km} + \delta_{in}\delta_{jm}\delta_{kl}\big) \int C^6 f^{(0)} d\mathbf{c}.
\end{aligned} \tag{2.207}$$

Chapter 3
The Chapman–Enskog Method

3.1 Thermodynamics of a Single Fluid

In this section, a single fluid is analyzed within the framework of the thermodynamic theory of irreversible processes, the so-called TIP.

In this theory, the fluid is described macroscopically by the five scalar fields of mass density $\varrho(\mathbf{x},t)$, hydrodynamic velocity $v_i(\mathbf{x},t)$ and temperature $T(\mathbf{x},t)$. The balance equations for these fields—given by (2.97), (2.98) and (2.102)—are written here in terms of the material time derivative ($\mathcal{D} \equiv \partial/\partial t + v_i\partial/\partial x_i$) as

$$\frac{\partial \varrho}{\partial t} + \frac{\partial \varrho v_i}{\partial x_i} = 0, \implies \mathcal{D}\varrho + \varrho\frac{\partial v_i}{\partial x_i} = 0, \tag{3.1}$$

$$\frac{\partial \varrho v_i}{\partial t} + \frac{\partial}{\partial x_j}(\varrho v_i v_j + p_{ij}) = \varrho F_i, \implies \varrho\mathcal{D}v_i + \frac{\partial p_{ij}}{\partial x_j} = \varrho F_i, \tag{3.2}$$

$$\frac{\partial \varrho\varepsilon}{\partial t} + \frac{\partial}{\partial x_i}(\varrho\varepsilon v_i + q_i) + p_{ij}\frac{\partial v_i}{\partial x_j} = 0, \implies \varrho\mathcal{D}\varepsilon + \frac{\partial q_i}{\partial x_i} + p_{ij}\frac{\partial v_i}{\partial x_j} = 0. \tag{3.3}$$

The system of partial differential equations (3.1) through (3.3) cannot be considered a system of field equations for the five scalar fields ϱ, v_i and T, since they depend on the unknown quantities: pressure tensor p_{ij}, heat flux vector q_i and internal energy density $\varrho\varepsilon$.

It is common in kinetic theory of gases and in thermodynamics to decompose the pressure tensor as

$$p_{ij} = p_{\langle ij\rangle} + \frac{1}{3}p_{rr}\delta_{ij} = p_{\langle ij\rangle} + (p + \varpi)\delta_{ij}, \tag{3.4}$$

where $p_{\langle ij\rangle}$ is the pressure deviator, p the hydrostatic pressure and ϖ denotes a non-equilibrium pressure, known as dynamic pressure. Although the dynamic pressure vanishes for rarefied monatomic gases, it plays an important role for polyatomic and dense gases (see Chapters 5 and 6).

For fluids, the hydrostatic pressure and the internal energy density are known functions of the mass density and of the temperature through the thermal and energy equations of state, respectively. Hence, the unknowns in the system of equations (3.1) through (3.3) are: the pressure deviator $p_{\langle ij\rangle}$, the dynamic pressure ϖ and the heat flux vector q_i. The relationships of these quantities as functions of the basic fields depend on the material, and in the thermodynamic theory of materials, are known as constitutive equations.

The main objective of this chapter is to determine the constitutive equations within the framework of the Chapman–Enskog method applied to the Boltzmann equation, but first they will be derived from a phenomenological theory based on the thermodynamic theory of irreversible processes.

The starting point of the thermodynamic theory of irreversible processes is the Gibbs equation (2.149), which can be written in terms of the material time derivative as

$$\mathcal{D}s = \frac{1}{T}\left(\mathcal{D}\varepsilon - \frac{p}{\varrho^2}\mathcal{D}\varrho\right). \tag{3.5}$$

The elimination of the material time derivatives $\mathcal{D}\varepsilon$ and $\mathcal{D}\varrho$ from the Gibbs equation (3.5) by the use of the balance equations of mass density (3.1) and specific internal energy (3.3) leads, after some rearrangements, to[1]

$$\frac{\partial \varrho s}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho s v_i + \frac{q_i}{T}\right) = -\frac{1}{T}\varpi\frac{\partial v_i}{\partial x_i} - \frac{1}{T}p_{\langle ij\rangle}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} - \frac{1}{T^2}q_i\frac{\partial T}{\partial x_i} \equiv \varsigma. \tag{3.6}$$

Equation (3.6) can be interpreted as the balance equation for the entropy density. Indeed, from the comparison of (3.6) and (2.146), it is possible to identify q_i/T as the entropy flux φ_i and ς as the entropy production density, which is a positive semi-definite quantity, i.e.,

$$\varphi_i = \frac{q_i}{T}, \qquad \varsigma = -\frac{1}{T}\varpi\frac{\partial v_i}{\partial x_i} - \frac{1}{T}p_{\langle ij\rangle}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} - \frac{1}{T^2}q_i\frac{\partial T}{\partial x_i} \geqslant 0. \tag{3.7}$$

One may infer from the inequality $(3.7)_2$ that the entropy production density is a sum of products of thermodynamic forces with thermodynamic fluxes, which can be interpreted as a cause–effect relationship (see Table 3.1).

Table 3.1 Thermodynamic forces and fluxes

Thermodynamic forces (cause)	*Thermodynamic fluxes (effect)*
$\frac{\partial v_i}{\partial x_i},\ \frac{\partial T}{\partial x_i},\ \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}$	$\varpi,\ q_i,\ p_{\langle ij\rangle}$

Within the framework of the thermodynamic theory of irreversible processes, linear constitutive equations are assumed, i.e., linear relationships between the thermodynamic fluxes and thermodynamic forces, namely,

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[1] Note that $p_{\langle ij\rangle}\frac{\partial v_i}{\partial x_j} = p_{ij}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} = p_{\langle ij\rangle}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}$.

$$\varpi = -\eta \frac{\partial v_i}{\partial x_i}, \qquad p_{\langle ij \rangle} = -2\mu \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \qquad q_i = -\lambda \frac{\partial T}{\partial x_i}. \tag{3.8}$$

The relations (3.8) are the constitutive equations for a viscous and thermal conducting fluid within a linear constitutive theory. By combining equations (3.4) and $(3.8)_{1,2}$, one can write the pressure tensor as

$$p_{ij} = \left(p - \eta \frac{\partial v_r}{\partial x_r}\right) \delta_{ij} - 2\mu \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}. \tag{3.9}$$

Equations $(3.8)_3$ and (3.9) represent, respectively, the laws of Fourier and Navier–Stokes, where λ denotes the thermal conductivity coefficient, η the bulk viscosity coefficient and μ the shear viscosity coefficient.

Now, the insertion of (3.8) into $(3.7)_2$ leads to

$$\frac{\eta}{T} \frac{\partial v_i}{\partial x_i} \frac{\partial v_j}{\partial x_j} + \frac{2\mu}{T} \frac{\partial v_{\langle i}}{\partial x_{j\rangle}} \frac{\partial v_{\langle i}}{\partial x_{j\rangle}} + \frac{\lambda}{T^2} \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i} \geqslant 0. \tag{3.10}$$

The above inequality is of the type $AX^2 + BY^2 + CZ^2 \geqslant 0$, which is valid for all values of X, Y and Z. Hence, one must have $A \geqslant 0$, $B \geqslant 0$ and $C \geqslant 0$, i.e.,

$$\eta \geqslant 0, \qquad \mu \geqslant 0, \qquad \lambda \geqslant 0, \tag{3.11}$$

showing that the coefficients of bulk viscosity η, shear viscosity μ and thermal conductivity λ are positive semi-definite quantities.

Exercise

3.1 Obtain the expression (3.6).

3.2 Simplified Version of the Chapman–Enskog Method

3.2.1 The Integral Equation

The basic idea of the Chapman–Enskog method in a simplified version is to write the distribution function as a sum of two terms. The first term corresponds to the Maxwellian distribution function, which gives the local values of the fields of mass density, hydrodynamical velocity and temperature. This term is the first approximation to the distribution function. The second term—which is associated with the second approximation—refers to a deviation from the Maxwellian distribution function. From the latter, one obtains the transport quantities associated with the pressure tensor deviator $p_{\langle ij\rangle}$ and heat flux vector q_i. Hence, the distribution function is written as

$$f(\mathbf{x},\mathbf{c},t) = f^{(0)}(\mathbf{x},\mathbf{c},t) + f^{(1)}(\mathbf{x},\mathbf{c},t) = f^{(0)}(\mathbf{x},\mathbf{c},t)\left[1+\phi(\mathbf{x},\mathbf{c},t)\right], \quad (3.12)$$

where $f^{(0)}$ is the Maxwellian distribution function

$$f^{(0)}(\mathbf{x},\mathbf{c},t) = n\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} e^{-\beta C^2}. \quad (3.13)$$

By writing $f^{(1)} = f^{(0)}\phi$, the quantity ϕ becomes the deviation of the Maxwellian from the equilibrium state. This does not define a rule for the approximation, and in order to define the method in a better way, one must assume that the mean free path l is small with respect to a typical length L over which mass density, hydrodynamical velocity and temperature vary in a significant way. This assumption is suitable to obtain a continuum description from the Boltzmann equation. Hence, it is assumed that ϕ is of order of l/L.

From the definitions of mass density ϱ, hydrodynamic velocity $\mathbf{v}$ and temperature T, given by (2.86), (2.87) and (2.95), respectively, it is easy to verify that

$$\varrho = \int mf d\mathbf{c} = \int mf^{(0)} d\mathbf{c}, \quad (3.14)$$

$$v_i = \frac{1}{\varrho}\int mc_i f d\mathbf{c} = \frac{1}{\varrho}\int mc_i f^{(0)} d\mathbf{c}, \quad (3.15)$$

$$T = \frac{m}{3k\varrho}\int mC^2 f d\mathbf{c} = \frac{m}{3k\varrho}\int mC^2 f^{(0)} d\mathbf{c}. \quad (3.16)$$

One infers from the above equations that

$$\int \psi f^{(0)}\phi d\mathbf{c} = 0, \quad (3.17)$$

where ψ represents a summational invariant, i.e., m, mc_i (or mC_i), mc^2 (or mC^2).

The deviation of the distribution function from the equilibrium state in the Chapman-Enskog method is determined from the Boltzmann equation (2.20), namely,

$$\frac{\partial f}{\partial t} + c_i\frac{\partial f}{\partial x_i} + F_i\frac{\partial f}{\partial c_i} = \int (f_1' f' - f_1 f)\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1. \quad (3.18)$$

The substitution of the representation of the distribution function (3.12) into the Boltzmann equation (3.18) leads to

$$\left(\frac{\partial}{\partial t}+c_i\frac{\partial}{\partial x_i}+F_i\frac{\partial}{\partial c_i}\right)f^{(0)}=\int f^{(0)}f_1^{(0)}\left(\phi_1'+\phi'-\phi_1-\phi\right)g\,b\,db\,d\varepsilon\,d\mathbf{c}_1, \tag{3.19}$$

by maintaining only the most important term in each side of the equation. This means that on the right-hand side of (3.19) one considers the linear terms in the deviation $f^{(0)}\phi$, whereas in its left-hand side only the derivatives of the Maxwellian distribution function are taken into account, since these derivatives correspond to the thermodynamic forces that induce the appearance of the deviation $f^{(0)}\phi$. Furthermore, in (3.19), the equilibrium relationship $f_1^{(0)}f^{(0)}=f_1'^{(0)}f'^{(0)}$ was used.

One may write (3.19) in a compact form as

$$\mathrm{D}f^{(0)}=\mathcal{I}\left[\phi\right], \tag{3.20}$$

where the differential operator D and the integral operator $\mathcal{I}$ are defined by

$$\mathrm{D}\equiv\frac{\partial}{\partial t}+c_i\frac{\partial}{\partial x_i}+F_i\frac{\partial}{\partial c_i}, \tag{3.21}$$

$$\mathcal{I}\left[\phi\right]\equiv\int f^{(0)}f_1^{(0)}\left(\phi_1'+\phi'-\phi_1-\phi\right)g\,b\,db\,d\varepsilon\,d\mathbf{c}_1. \tag{3.22}$$

Equation (3.20) is no longer an integro-differential equation, but an inhomogeneous integral equation for the deviation ϕ and its determination is one of the fundamental problems of kinetic theory of gases, since it leads to the knowledge of the transport coefficients in terms of molecular interactions.

The deviation ϕ becomes a solution of the integral equation (3.20) once its left-hand side satisfies the condition

$$\int\psi\left(\mathrm{D}f^{(0)}\right)d\mathbf{c}=0, \tag{3.23}$$

where ψ is a summational invariant, i.e., $\psi_1'+\psi'=\psi_1+\psi$. The above condition is a consequence of the following result, which is valid for all functions $\varphi(\mathbf{x},\mathbf{c},t)$:

$$\int\varphi\mathcal{I}\left[\phi\right]d\mathbf{c}=\int\varphi f^{(0)}f_1^{(0)}\left(\phi_1'+\phi'-\phi_1-\phi\right)g\,b\,db\,d\varepsilon\,d\mathbf{c}_1d\mathbf{c}$$
$$=\int\phi f^{(0)}f_1^{(0)}\left(\varphi_1'+\varphi'-\varphi_1-\varphi\right)g\,b\,db\,d\varepsilon\,d\mathbf{c}_1d\mathbf{c}=\int\phi\mathcal{I}[\varphi]d\mathbf{c}. \tag{3.24}$$

The third equality in the above equation is obtained by using similar arguments as those employed in Section 2.3 in order to deduce the right-hand side of (2.69). In particular, when φ is a summational invariant, the integral (3.24) vanishes and it follows the expression (3.23).

The derivatives $\mathrm{D}f^{(0)}$ are calculated by the insertion of (3.13) into (3.21), yielding

$$\mathrm{D}f^{(0)} = f^{(0)}\left\{\frac{\mathcal{D}\varrho}{\varrho} + \left(\beta C^2 - \frac{3}{2}\right)\frac{\mathcal{D}T}{T} + 2\beta C_i\left(\mathcal{D}v_i - F_i\right)\right.$$
$$\left. + C_i\left[\frac{1}{\varrho}\frac{\partial \varrho}{\partial x_i} + \frac{1}{T}\frac{\partial T}{\partial x_i}\left(\beta C^2 - \frac{3}{2}\right) + 2\beta C_j\frac{\partial v_j}{\partial x_i}\right]\right\}. \qquad (3.25)$$

The substitution of (3.25) into (3.23) and the integration of the resulting equations over all values of **c** leads to the balance equations

$$\mathcal{D}\varrho + \varrho\frac{\partial v_i}{\partial x_i} = 0, \qquad \varrho\mathcal{D}v_i + \frac{\partial p}{\partial x_i} = \varrho F_i, \qquad \frac{3}{2}\varrho\frac{k}{m}\mathcal{D}T + p\frac{\partial v_i}{\partial x_i} = 0, \quad (3.26)$$

when the values of ψ are chosen as m, mc_i and mc^2, respectively. Now, from the comparison of (3.26) with (3.1)–(3.3) one verifies that the former are particular cases of the latter. Indeed, equation (3.26) represent the field equations of an Eulerian fluid, i.e., a non-viscous and non-heat conducting fluid where $p_{ij} = p\,\delta_{ij}$ and $q_i = 0$.

Equations (3.26) are used to eliminate the time derivatives of the mass density, hydrodynamic velocity and temperature from (3.25), yielding

$$\mathrm{D}f^{(0)} = f^{(0)}\left\{\frac{1}{T}\left(\beta C^2 - \frac{5}{2}\right)C_i\frac{\partial T}{\partial x_i} + 2\beta C_iC_j\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}\right\}. \qquad (3.27)$$

Finally, the non-homogeneous integral equation for the deviation ϕ reduces to

$$f^{(0)}\left\{\frac{1}{T}\left(\beta C^2 - \frac{5}{2}\right)C_i\frac{\partial T}{\partial x_i} + 2\beta C_iC_j\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}\right\} = \mathcal{I}[\phi]$$
$$= \int f^{(0)}f_1^{(0)}\left(\phi_1' + \phi' - \phi_1 - \phi\right)g\,b\,db\,d\varepsilon\,d\mathbf{c}_1, \qquad (3.28)$$

thanks to (3.20), (3.22) and (3.27).

Exercises

3.3 Show that (3.24) holds.

3.4 Obtain (3.27) from (3.25) and (3.26).

3.2.2 Solution of the Integral Equation

From the analysis of the left-hand side of (3.28), one infers that a good approximation for the deviation of the distribution function ϕ is given by

$$\phi = -\mathcal{A}\left(\beta C^2 - \frac{5}{2}\right)\frac{C_i}{T}\frac{\partial T}{\partial x_i} - 2\beta\mathcal{B}C_iC_j\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \tag{3.29}$$

where $\mathcal{A} = \mathcal{A}(\varrho, T)$ and $\mathcal{B} = \mathcal{B}(\varrho, T)$ are two scalar coefficients to be determined from (3.28). In Section 3.3, a more elaborated theory will be developed, where the coefficients depend also on the peculiar velocity.

Now, the insertion of (3.29) into (3.28) leads to the integral equations

$$f^{(0)}\left(\beta C^2 - \frac{5}{2}\right)C_i = -\mathcal{A}\mathcal{I}\left[\left(\beta C^2 - \frac{5}{2}\right)C_i\right], \tag{3.30}$$

$$f^{(0)}C_{\langle i}C_{j\rangle} = -\mathcal{B}\mathcal{I}[C_{\langle i}C_{j\rangle}], \tag{3.31}$$

by equating the coefficients of $\partial T/\partial x_i$ and $\partial v_{\langle i}/\partial x_{j\rangle}$ to zero.

The determination of the coefficient $\mathcal{A}$ proceeds as follows. First, (3.30) is multiplied by $(\beta C)^2C_i$ and the resulting equation is integrated over all velocities $\mathbf{c}$, yielding

$$\frac{15}{4}n = -\mathcal{A}\beta^2\int C^2C_i\mathcal{I}\left[\left(\beta C^2 - \frac{5}{2}\right)C_i\right]d\mathbf{c}, \tag{3.32}$$

thanks to (2.204).

Let the integral in the right-hand side of (3.32) be denoted by I_1. According to (3.24), this integral may be expressed as

$$I_1 = \int C^2C_i\mathcal{I}\left[\left(\beta C^2 - \frac{5}{2}\right)C_i\right]d\mathbf{c} = \int\left(\beta C^2 - \frac{5}{2}\right)C_i\mathcal{I}\left[C^2C_i\right]d\mathbf{c}. \tag{3.33}$$

For the calculation of the integral I_1, a change of the integration variables is performed by replacing the velocities $\mathbf{C}$ and $\mathbf{C}_1$ by the relative velocity $\mathbf{g}$ and by the center of mass velocity $\mathbf{G}$, defined by

$$\mathbf{g} = \mathbf{C}_1 - \mathbf{C}, \qquad \mathbf{G} = \frac{\mathbf{C}_1 + \mathbf{C}}{2}. \tag{3.34}$$

The linear momentum conservation law implies that $\mathbf{G}' = \mathbf{G}$, so that one has from (3.34):

$$\mathbf{C} = \mathbf{G} - \frac{1}{2}\mathbf{g}, \qquad \mathbf{C}_1 = \mathbf{G} + \frac{1}{2}\mathbf{g}, \qquad \mathbf{C}' = \mathbf{G} - \frac{1}{2}\mathbf{g}', \qquad \mathbf{C}_1' = \mathbf{G} + \frac{1}{2}\mathbf{g}'. \tag{3.35}$$

Furthermore, the Jacobian of the transformation of the volume elements has modulus equal to one implying that $d\mathbf{C}d\mathbf{C}_1 = d\mathbf{g}d\mathbf{G}$.

Now, on the basis of (3.35), one obtains

$$(C^2C_i)^{1\prime} + (C^2C_i)' - (C^2C_i)^1 - (C^2C_i) = G_j\left(g_i'g_j' - g_ig_j\right), \tag{3.36}$$

so that the integral I_1—thanks to (3.13), (3.35) and (3.36)—can be rewritten as

$$I_1 = n^2\left(\frac{\beta}{\pi}\right)^3\int e^{-2\beta G^2}e^{-\frac{\beta}{2}g^2}\left[\beta\left(G^2 - G_s g_s + \frac{1}{4}g^2\right) - \frac{5}{2}\right] \times\left(G_i - \frac{1}{2}g_i\right)G_j\left(g'_j g'_i - g_j g_i\right) g\, b\, db\, d\varepsilon\, d\mathbf{G}\, d\mathbf{g}. \quad (3.37)$$

The integration of (3.37) with respect to $\mathbf{G}$ yields

$$I_1 = \frac{n^2}{8}\left(\frac{\beta}{2\pi}\right)^{\frac{3}{2}}\int e^{-\frac{\beta}{2}g^2} g_i g_j\left(g'_i g'_j - g_i g_j\right) g\, b\, db\, d\varepsilon\, d\mathbf{g}. \quad (3.38)$$

The final expression for I_1 is obtained from the integration of the above equation with respect to the azimuthal angle ε and to the angles of the spherical coordinates of $\mathbf{g}$, which leads to

$$I_1 = -\sqrt{\pi} n^2\left(\frac{2}{\beta}\right)^{\frac{5}{2}}\Omega^{(2,2)}. \quad (3.39)$$

In the above equation, the following collision integral was introduced

$$\Omega^{(l,r)} = \int_0^\infty e^{-\gamma^2}\gamma^{2r+3}Q^{(l)}(\gamma)\, d\gamma = \int_0^\infty\int_0^\infty e^{-\gamma^2}\gamma^{2r+3}\left(1 - \cos^l\chi\right) b\, db\, d\gamma, \quad (3.40)$$

which is written in terms of the effective cross section $Q^{(l)}(\gamma)$ defined by (1.111). Furthermore, $\chi = \arccos(\mathbf{g}'\cdot\mathbf{g}/g^2)$ is the scattering angle, and $\gamma = \sqrt{\beta/2}\, g$ represents a dimensionless relative velocity.

Once the integral I_1 is known, the coefficient $\mathcal{A}$ becomes

$$\mathcal{A} = \frac{15}{32n\Omega^{(2,2)}}\sqrt{\frac{m}{\pi kT}}. \quad (3.41)$$

due to (3.32) and (3.39).

For the determination of the coefficient $\mathcal{B}$, one proceeds as follows: (3.31) is multiplied by $\beta^2 C_{\langle i}C_{j\rangle}$, the resulting equation is integrated over all velocities $\mathbf{c}$. By using (2.206), it follows that

$$\frac{5}{2}n = -\mathcal{B}\beta^2\int C_{\langle i}C_{j\rangle}\mathcal{I}[C_{\langle i}C_{j\rangle}]d\mathbf{c}. \quad (3.42)$$

The integral in the right-hand side of (3.42), namely,

$$I_2 = \int C_{\langle i}C_{j\rangle}\mathcal{I}[C_{\langle i}C_{j\rangle}]d\mathbf{c} \quad (3.43)$$

is calculated by using the same methodology which was employed to determine the integral I_1. First, the integration variables are changed $(\mathbf{c}, \mathbf{c}_1) \longmapsto (\mathbf{g}, \mathbf{G})$ so that it follows from (3.13) and (3.35) that

$$I_2 = \frac{n^2}{2}\left(\frac{\beta}{\pi}\right)^3 \int e^{-2\beta G^2} e^{-\frac{\beta}{2}g^2}\left(g'_{\langle i}g'_{j\rangle} - g_{\langle i}g_{j\rangle}\right) \\ \times \left(G_{\langle i}G_{j\rangle} - G_{\langle i}g_{j\rangle} + \frac{1}{4}g_{\langle i}g_{j\rangle}\right) g\, b\, db\, d\varepsilon d\mathbf{g} d\mathbf{G}. \tag{3.44}$$

The subsequent integration of (3.44) with respect to $\mathbf{G}$, ε and to the angles of the spherical coordinates of $\mathbf{g}$ leads to

$$I_2 = -\sqrt{\pi} n^2 \left(\frac{2}{\beta}\right)^{\frac{5}{2}} \Omega^{(2,2)} = I_1. \tag{3.45}$$

At last, (3.42) and (3.45) furnish the final expression for the coefficient $\mathcal{B}$, namely,

$$\mathcal{B} = \frac{5}{16 n \Omega^{(2,2)}}\sqrt{\frac{m}{\pi k T}} = \frac{2}{3}\mathcal{A}. \tag{3.46}$$

Once the scalar coefficients are determined, the deviation ϕ of the Maxwellian distribution function is also known and expressed as

$$\phi = -\frac{15}{32 n \Omega^{(2,2)}}\sqrt{\frac{m}{\pi k T}}\left[\left(\beta C^2 - \frac{5}{2}\right)\frac{C_i}{T}\frac{\partial T}{\partial x_i} + \frac{4\beta}{3}C_i C_j \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}\right], \tag{3.47}$$

thanks to (3.29), (3.41) and (3.46).

Exercises

3.5 Show that the representation (3.29) fulfills the conditions (3.17).

3.6 Obtain the expressions (3.37), (3.38) and (3.39) for the integral I_1.

3.7 Obtain the expressions (3.44) and (3.45) for the integral I_2.

3.2.3 Constitutive Equations and Transport Coefficients

The insertion of the representation of the distribution function (3.12) together with (3.47) into the definitions of the pressure tensor and of the heat flux vector and the subsequent integration of the resulting equations leads to

$$p_{ij} = \int m C_i C_j f d\mathbf{c} = p\,\delta_{ij} - 2\mu \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \tag{3.48}$$

$$q_i = \int \frac{m}{2} C^2 C_i f d\mathbf{c} = -\lambda \frac{\partial T}{\partial x_i}. \tag{3.49}$$

The above equations represent the laws of Navier–Stokes and Fourier, respectively, where the coefficients of shear viscosity μ and thermal conductivity λ are given by

$$\mu = \frac{5}{16} \frac{1}{\Omega^{(2,2)}} \sqrt{\frac{mkT}{\pi}}, \qquad \lambda = \frac{75k}{64m} \frac{1}{\Omega^{(2,2)}} \sqrt{\frac{mkT}{\pi}}. \tag{3.50}$$

From the above equations, one can build the ratio

$$\frac{\lambda}{\mu} = \frac{15k}{4m} = \frac{5}{2} c_v = \frac{3}{2} c_p, \tag{3.51}$$

where c_v and c_p denote the specific heats at constant volume and at constant pressure, respectively.[2]

An important parameter for thermal conducting and viscous fluids is Prandtl's number,[3] defined by

$$Pr = \frac{c_p \mu}{\lambda}, \tag{3.52}$$

and which can be interpreted as the ratio of the fluid capacity to diffuse momentum to its capacity to diffuse heat. From (3.50) and (3.52), it is easy to verify that $Pr = 2/3$ for all monatomic gases whose potential functions of molecular interactions are spherically symmetric.

Table 3.2 Calculated values of Prandtl's number Pr for monatomic gases at $T =$ 273 K and $p = 1$ atm.

Gas	M	c_p J/(kgK)	μ 10^{-6}Pa s	λ 10^{-3}W/(mK)	Pr
He	4.00	5194	18.81	147.04	0.6644
Ne	20.18	1030	30.13	46.71	0.6641
Ar	39.95	520	21.08	16.46	0.6660
Kr	83.80	248	23.43	8.72	0.6662
Xe	131.30	158	21.04	5.00	0.6658

Prandtl's numbers for monatomic gases are given in Table 3.2, which were calculated by using (3.52) and the data for the coefficients of shear viscosity and thermal conductivity.[4] Note that for all ideal monatomic gases $Pr \approx 2/3$.

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[2] The specific heats at constant volume and at constant pressure are defined by $c_v = (\partial\varepsilon/\partial T)_\varrho$, $c_p = (\partial h/\partial T)_p$, respectively, where $h = \varepsilon + p/\varrho$ is the specific enthalpy. For ideal monatomic gases $p = \varrho kT/m$ and $\varepsilon = 3kT/2m$ so that $c_v = 3k/2m$ and $c_p = 5k/2m$.

[3] Ludwig Prandtl (1875–1953) German scientist.

[4] J. Kestin; K. Knierim; E. A. Mason; B. Najafi; S. T. Ro & M. Waldman, "Equilibrium and transport properties of the noble gases and their mixtures at low density", *J. Phys. Chem. Ref. Data*, **13**, 229-303 (1984).

Another important conclusion on the transport coefficients is that neither the shear viscosity nor the thermal conductivity depend on the particle number density being only functions of the temperature and of the type of the gas. This statement was previously established in Section 1.2.5 for the particular case of hard-sphere potential by using an elementary kinetic theory.

Hard-sphere Potential

For the hard-sphere potential, the viscosity cross section is given according to (1.113) by $Q^{(2)} = \mathsf{d}^2/3$. Hence, the collision integral (3.40) reduces to

$$\Omega^{(2,2)} = \frac{\mathsf{d}^2}{3}\int_0^\infty e^{-\gamma^2}\gamma^7 d\gamma = \mathsf{d}^2, \tag{3.53}$$

and the coefficients of shear viscosity and thermal conductivity, that follows from (3.50), read

$$\mu = \frac{5}{16\mathsf{d}^2}\sqrt{\frac{mkT}{\pi}}, \qquad \lambda = \frac{75k}{64m\mathsf{d}^2}\sqrt{\frac{mkT}{\pi}}. \tag{3.54}$$

Note that both coefficients—as was anticipated in Section 1.2.5—depend on the square root of the temperature.

Potential of Centers of Repulsion

The viscosity cross section for the centers of repulsion potential follows from (1.115), yielding

$$Q^{(2)} = \left(\frac{2\kappa}{m}\right)^{\frac{2}{\nu-1}} g^{-\frac{4}{\nu-1}} A_2(\nu). \tag{3.55}$$

For this case, the collision integral (3.40) reads

$$\begin{aligned}\Omega^{(2,2)} &= \left(\frac{\kappa}{2kT}\right)^{\frac{2}{\nu-1}} A_2(\nu)\int_0^\infty e^{-\gamma^2}\gamma^7\gamma^{-\frac{4}{\nu-1}}\, d\gamma \\ &= \left(\frac{\kappa}{2kT}\right)^{\frac{2}{\nu-1}} A_2(\nu)\frac{1}{2}\Gamma\left(\frac{4\nu-6}{\nu-1}\right),\end{aligned} \tag{3.56}$$

and the coefficients of shear viscosity and thermal conductivity that follows from (3.50) become

$$\mu = \frac{5}{8}\sqrt{\frac{mkT}{\pi}}\left(\frac{2kT}{\kappa}\right)^{\frac{2}{\nu-1}} \Big/ \left[A_2(\nu)\Gamma\left(\frac{4\nu-6}{\nu-1}\right)\right], \tag{3.57}$$

$$\lambda = \frac{75k}{32m}\sqrt{\frac{mkT}{\pi}}\left(\frac{2kT}{\kappa}\right)^{\frac{2}{\nu-1}} \Big/ \left[A_2(\nu)\Gamma\left(\frac{4\nu-6}{\nu-1}\right)\right]. \tag{3.58}$$

From (3.57) and (3.58), one infers that both coefficients depend only on the temperature and are proportional to $T^{(\nu+3)/2(\nu-1)}$. For the case of a Maxwellian potential where $\nu = 5$, (3.57) and (3.58) reduce to

$$\mu = \frac{2}{3\pi}\frac{kT}{A_2(5)}\sqrt{\frac{m}{2\kappa}}, \qquad \lambda = \frac{5k}{2m\pi}\frac{kT}{A_2(5)}\sqrt{\frac{m}{2\kappa}}. \tag{3.59}$$

In this latter case, the coefficients of shear viscosity and thermal conductivity are proportional to the temperature. The conclusion of Maxwell was[5]: *"Hence μ varies as the absolute temperature, and is independent of the density.... The experimental result, that the viscosity is proportional to the absolute temperature, requires us to abandon this hypothesis, which would make it vary as the square root of the absolute temperature, and to adopt the hypothesis of a repulsive force inversely as the fifth power of the distance between the molecules, which is the only law of force which gives the observed result."*

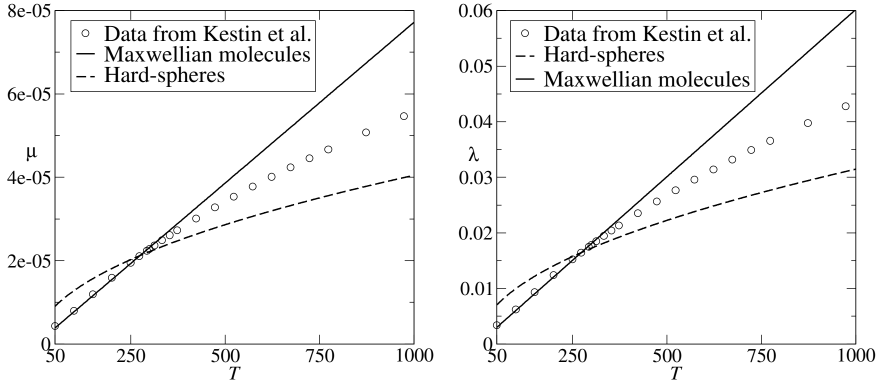

Fig. 3.1 Left frame: shear viscosity (Pa·s) as function of the temperature (K); right frame: thermal conductivity (W m^{-1} K^{-1}) as function of the temperature (K).

The coefficients of shear viscosity and thermal conductivity for argon gas are plotted as functions of the temperature in the left and right frames of Figure 3.1, respectively. In both frames, the circles represent the data taken from the work of Kestin et al., the straight lines refer to a gas of Maxwellian molecules and the dashed lines to a gas of hard spheres. The diameter of the hard spheres d and the constant κ of the Maxwellian potential were obtained from the expressions for the shear viscosity $(3.54)_1$ and $(3.59)_1$ by considering

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[5] J. C. Maxwell, "On the Dynamical Theory of Gases, *Phil. Trans. R. Soc. London*, **157**, 49-68 (1867).

$\mu = 21.08 \times 10^{-6}$ Pa·s and $T = 273$ K. Hence, for argon gas of Maxwellian particles, the coefficients of shear viscosity and thermal conductivity are given by $\mu = 7.72 \times 10^{-8} T$ and $\lambda = 6.02 \times 10^{-5} T$, respectively, whereas for the case of hard-sphere particles by $\mu = 1.28 \times 10^{-6}\sqrt{T}$ and $\lambda = 9.95 \times 10^{-4}\sqrt{T}$. Note that for temperatures in the range $50\,\mathrm{K} \leqslant T \leqslant 500\,\mathrm{K}$, the shear viscosity and thermal conductivity for a Maxwellian potential is closer to the data than those for a hard-sphere potential.

Exercises

3.8 Obtain the expressions for the pressure tensor (3.48) and for the heat flux vector (3.49).

3.9 By using the value of the shear viscosity for argon gas at $T = 273$ K given in Table 3.2 and $A_2(5) \approx 0.436$, estimate the values of κ for the Maxwellian potential and d for the hard-sphere potential.

3.3 Formal Version of the Chapman–Enskog Method

3.3.1 The dimensionless Boltzmann Equation

In the absence of external body forces, the Boltzmann equation (2.20) reduces to

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} = \int (f_1' f' - f_1 f) g\, b\, db\, d\varepsilon\, d\mathbf{c}_1. \tag{3.60}$$

The above equation can be rewritten in a dimensionless form by introducing the dimensionless variables

$$\begin{cases} t^* = t/t_c, & \mathbf{x}^* = \mathbf{x}/L_c, \quad \mathbf{c}^* = \mathbf{c}/\bar{c}, \\ \mathbf{g}^* = \mathbf{g}/\bar{g}, & b^* = b/\mathsf{d}, \quad \varepsilon^* = \varepsilon/\pi, \quad f^* = f/f_c. \end{cases} \tag{3.61}$$

In the relations (3.61), t_c and L_c are a representative time and length which characterize the fluid flow. Furthermore, d is the molecular diameter, $\bar{c}$ the mean thermal velocity and $\bar{g}$ the mean relative velocity. The characteristic value for the distribution function f_c is equal to $n/\bar{c}^3$, where n represents the particle number density of the gas. In terms of the dimensionless variables (3.61), the Boltzmann equation (3.60) becomes

$$Sr \frac{\partial f^*}{\partial t^*} + c_i^* \frac{\partial f^*}{\partial x_i^*} = \frac{1}{Kn} \int (f_1^{*\prime} f^{*\prime} - f_1^* f^*) g^*\, b^*\, db^*\, d\varepsilon^*\, dc_1^*, \tag{3.62}$$

where Sr is Strouhal's number and Kn is Knudsen's number[6], which are defined by

$$Sr = \frac{L_c}{\bar{c}\,t_c}, \qquad\qquad Kn = \frac{l}{L_c}, \tag{3.63}$$

and l is the mean free path whose expression is given by (1.3).

The Knudsen number characterizes the degree of rarefaction of a gas. When $Kn \gg 1$, the molecular collisions become negligible, the distribution function is determined via a collisionless Boltzmann equation and the regime of the gas is known as free molecular flow. Otherwise, when $Kn \ll 1$, the molecular collisions are very important, the distribution function is determined by the collision term of the Boltzmann equation and the gas is described by a continuum regime.

Exercise

3.10 Obtain the dimensionless Boltzmann equation (3.62).

3.3.2 The Integral Equations

In the method of Chapman–Enskog, the distribution function f is expanded in power series of a parameter ϵ, which is of order of the Knudsen number. The series expansion is expressed as

$$f = f^{(0)} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \ldots = \sum_{r=0}^{\infty} \epsilon^r f^{(r)}, \tag{3.64}$$

where $f^{(0)}$, $f^{(1)}$ and $f^{(2)}$ represent the first, second and third approximation to the distribution function, respectively, and so on. The parameter ϵ can be set equal to unity later, so that the proper dimensions are restored. Moreover, according to (3.14)—(3.16), the approximations must satisfy the constraints

$$\int \psi f^{(r)} d\mathbf{c} = 0, \qquad \forall\, r \geqslant 1, \tag{3.65}$$

where ψ represents the summational invariants m, mc_i and $mc^2/2$.

By inserting the series expansion of the distribution function (3.64) into the definitions of the pressure deviator and of the heat flux vector yields

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[6] Vincenc Strouhal (1850–1922) Czech physicist; Martin Hans Christian Knudsen (1871–1949) Danish physicist.

$$p_{\langle ij\rangle}=\int C_{\langle i}C_{j\rangle}\sum_{r=1}^{\infty}\epsilon^r f^{(r)}d\mathbf{c}=\sum_{r=1}^{\infty}\epsilon^r p_{\langle ij\rangle}^{(r)}, \tag{3.66}$$

$$q_i=\int\frac{m}{2}C^2C_i\sum_{r=1}^{\infty}\epsilon^r f^{(r)}d\mathbf{c}=\sum_{r=1}^{\infty}\epsilon^r q_i^{(r)}, \tag{3.67}$$

showing that both quantities are described only by the non-equilibrium distribution functions $f^{(r)}$, with $r\geqslant 1$.

From an argument based on the dimensionless expression of the Boltzmann equation of the previous section, the parameter ϵ should be introduced into the collision term of the Boltzmann equation so that it becomes

$$\mathcal{D}f+C_i\frac{\partial f}{\partial x_i}=\frac{1}{\epsilon}\mathcal{Q}(f,f). \tag{3.68}$$

Above, the collision term was expressed in terms of an integral for a bilinear quantity

$$\mathcal{Q}(F,G)=\frac{1}{2}\int(F_1'G'+F'G_1'-F_1G-FG_1)g\,b\,db\,d\varepsilon\,dc_1. \tag{3.69}$$

Furthermore, the material time derivative is also expanded in power series as

$$\mathcal{D}=\mathcal{D}_0+\epsilon\mathcal{D}_1+\epsilon^2\mathcal{D}_2+\ldots=\sum_{r=1}^{\infty}\epsilon^r\mathcal{D}_r, \tag{3.70}$$

so that the insertion of the expansions (3.66), (3.67) and (3.70) into (3.1)–(3.3) lead to the following decomposition of the balance equations

$$\mathcal{D}_0\varrho+\varrho\frac{\partial v_i}{\partial x_i}=0,\quad \mathcal{D}_r\varrho=0\quad(\forall\, r\geqslant 1), \tag{3.71}$$

$$\varrho\mathcal{D}_0v_i+\frac{\partial p}{\partial x_i}=0,\quad \varrho\mathcal{D}_rv_i+\frac{\partial p_{\langle ij\rangle}^{(r)}}{\partial x_j}=0\quad(\forall\, r\geqslant 1), \tag{3.72}$$

$$\frac{3}{2}nk\mathcal{D}_0T+p\frac{\partial v_i}{\partial x_i}=0,\quad \frac{3}{2}nk\mathcal{D}_rT+\frac{\partial q_i^{(r)}}{\partial x_i}+p_{\langle ij\rangle}^{(r)}\frac{\partial v_i}{\partial x_j}=0\quad(\forall\, r\geqslant 1). \tag{3.73}$$

The integral equations for the approximations of the distribution function are obtained from the insertion of the expansions (3.64) and (3.70) into the Boltzmann equation (3.68). By equating equal powers of ϵ, one can obtain

$$\mathcal{Q}\left(f^{(0)},f^{(0)}\right)=0, \tag{3.74}$$

$$2\mathcal{Q}\left(f^{(0)},f^{(1)}\right)=\mathcal{D}_0f^{(0)}+C_i\frac{\partial f^{(0)}}{\partial x_i}, \tag{3.75}$$

$$2\mathcal{Q}\left(f^{(0)},f^{(2)}\right)+\mathcal{Q}\left(f^{(1)},f^{(1)}\right)=\mathcal{D}_0f^{(1)}+\mathcal{D}_1f^{(0)}+C_i\frac{\partial f^{(1)}}{\partial x_i}, \tag{3.76}$$

and so on. The above equations are the three first integral equations for $f^{(0)}$, $f^{(1)}$ and $f^{(2)}$, respectively.

Exercise

3.11 Obtain the integral equations (3.74) – (3.76).

3.3.3 The Second Approximation

The first approximation to the distribution function $f^{(0)}$ is found as a solution of the integral equation (3.74). It was previously determined in Section 2.6.1 and corresponds to the Maxwellian distribution function (3.13).

For the determination of the second approximation $f^{(1)}$, the material time derivative and the gradient in the integral equation (3.75) are written as

$$\mathcal{D}_0 f^{(0)} = \frac{\partial f^{(0)}}{\partial \varrho}\mathcal{D}_0\varrho + \frac{\partial f^{(0)}}{\partial v_i}\mathcal{D}_0 v_i + \frac{\partial f^{(0)}}{\partial T}\mathcal{D}_0 T, \tag{3.77}$$

$$\frac{\partial f^{(0)}}{\partial x_i} = \frac{\partial f^{(0)}}{\partial \varrho}\frac{\partial \varrho}{\partial x_i} + \frac{\partial f^{(0)}}{\partial v_j}\frac{\partial v_j}{\partial x_i} + \frac{\partial f^{(0)}}{\partial T}\frac{\partial T}{\partial x_i}. \tag{3.78}$$

Now, by taking $f^{(1)} = f^{(0)}\phi$, the integral equation (3.75) reduces to

$$\begin{aligned}2\mathcal{Q}\left(f^{(0)}, f^{(0)}\phi\right) &= f^{(0)}\left\{\frac{1}{T}\left(\beta C^2 - \frac{5}{2}\right)C_i\frac{\partial T}{\partial x_i} + 2\beta C_i C_j \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}\right\}\\ &= \mathcal{I}[\phi] = \int f^{(0)} f_1^{(0)}\left(\phi_1' + \phi' - \phi_1 - \phi\right) g\, b\, db\, d\varepsilon\, d\mathbf{c}_1,\end{aligned} \tag{3.79}$$

by using (3.77) and (3.78) and by eliminating the material time derivatives through the use of (3.71)–(3.73). Note that the above integral equation is the same as the one given by (3.28).

The general solution of the integral equation (3.79) is given by a sum of the solution of the homogeneous integral equation plus a particular solution of it, i.e., $\phi = \phi_h + \phi_p$.

The solution of the homogeneous integral equation, namely,

$$\mathcal{I}[\phi_h] = \int f^{(0)} f_1^{(0)}(\phi_1' + \phi' - \phi_1 - \phi) g\, b\, db\, d\varepsilon\, d\mathbf{c}_1 = 0, \tag{3.80}$$

reads $\phi_h = \alpha_1 + \alpha_r^2 C_r + \alpha_3 C^2$, where α_1 and α_3 are scalar functions, whereas α_r^2 is a vector function. These functions do not depend on the peculiar velocity $\mathbf{C}$, so that the solution of the homogeneous equation is a summational invariant.

The particular solution of the integral equation is expressed as

$$\phi_p = -\frac{A_i}{T}\frac{\partial T}{\partial x_i} - 2\beta B_{ij}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}. \tag{3.81}$$

Hence, ϕ_p is a linear combination of the temperature gradient and of the velocity gradient deviator, with A_i and B_{ij} being, respectively, a vector function and a tensor function of $(\mathbf{C}, \varrho, T)$. Furthermore, it is easy to show that the representations of the vector and tensor functions in terms of the peculiar velocity $\mathbf{C}$ are given by $A_i = \mathcal{A}^\star C_i$ and $B_{ij} = \mathcal{B} C_i C_j$, where the scalar functions $\mathcal{A}^\star$ and $\mathcal{B}$ depend only on (C^2, ϱ, T).

Therefore, the solution of the non-homogeneous integral equation (3.79) reads

$$\phi = -\mathcal{A}^\star \frac{C_i}{T}\frac{\partial T}{\partial x_i} - 2\beta\mathcal{B}C_iC_j\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} + \alpha_1 + \alpha_r^2 C_r + \alpha_3 C^2. \tag{3.82}$$

The second approximation $f^{(1)} = f^{(0)}\phi$ must satisfy the constraints (3.65), which lead to the following equations

$$\alpha_1 + \frac{3kT}{m}\alpha_3 = 0, \qquad \alpha_1 + \frac{5kT}{m}\alpha_3 = 0, \tag{3.83}$$

$$\int mC^2\left[-\frac{\mathcal{A}^\star}{T}\frac{\partial T}{\partial x_j} + \alpha_j^2\right] f^{(0)} d\mathbf{c} = 0. \tag{3.84}$$

From (3.83), one infers that $\alpha_1 = \alpha_3 = 0$, whereas equation (3.84) shows that α_j^2 must be proportional to $\partial T/\partial x_j$. By writing the proportionality factor of α_j^2 as α/T, the constraint (3.84) reduces to

$$\int C^2 \mathcal{A} f^{(0)} d\mathbf{c} = 0, \tag{3.85}$$

where $\mathcal{A} = \mathcal{A}^\star - \alpha$ is a new scalar function of (C^2, ϱ, T).

From the above results, one obtains that the distribution function (3.64) up to the second approximation and with $\epsilon = 1$ can be written as

$$f = f^{(0)}(1+\phi) = f^{(0)}\left\{1 - \frac{\mathcal{A}}{T}C_i\frac{\partial T}{\partial x_i} - 2\beta\mathcal{B}C_iC_j\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}\right\}. \tag{3.86}$$

The scalar coefficients $\mathcal{A}$ and $\mathcal{B}$ in the distribution function (3.86) are obtained as solutions of the integral equations that follows from (3.79), namely,

$$f^{(0)}\left[\beta C^2 - \frac{5}{2}\right] C_i = -\mathcal{I}[\mathcal{A}C_i], \tag{3.87}$$

$$f^{(0)} C_{\langle i}C_{j\rangle} = -\mathcal{I}[\mathcal{B}C_{\langle i}C_{j\rangle}]. \tag{3.88}$$

In the following section, the integral equations (3.87) and (3.88) will be solved by expanding the scalar coefficients $\mathcal{A}(C^2, \varrho, T)$ and $\mathcal{B}(C^2, \varrho, T)$ in series of Sonine polynomials (see the appendix to this chapter).

Exercises

3.12 Obtain the constraints (3.83) and (3.84).

3.13 Show that the integral equations (3.87) and (3.88) follow from (3.79).

3.3.4 Expansion of the Scalar Coefficients $\mathcal{A}$ and $\mathcal{B}$

In terms of the Sonine polynomials, (3.152), (3.87) and (3.88) become

$$f^{(0)} S^{(1)}_{3/2}(\beta C^2) C_i = \mathcal{I}\left[\mathcal{A} C_i\right], \tag{3.89}$$

$$f^{(0)} S^{(0)}_{5/2}(\beta C^2) C_{\langle i} C_{j\rangle} = -\mathcal{I}\left[\mathcal{B} C_{\langle i} C_{j\rangle}\right]. \tag{3.90}$$

Furthermore, the expansions of the scalar coefficients $\mathcal{A}(C^2, \varrho, T)$ and $\mathcal{B}(C^2, \varrho, T)$ in series of Sonine polynomials read

$$\mathcal{A}(C^2, \varrho, T) = -\sum_{r=0}^{\infty} a^{(r)} S^{(r)}_{3/2}(\beta C^2), \tag{3.91}$$

$$\mathcal{B}(C^2, \varrho, T) = \sum_{r=0}^{\infty} b^{(r)} S^{(r)}_{5/2}(\beta C^2). \tag{3.92}$$

where the scalar coefficients $a^{(r)}$ and $b^{(r)}$ are only functions of (ϱ, T). From this point on, the dependence of the Sonine polynomials in the variable βC^2 is omitted.

The coefficient $\mathcal{A}$ must satisfy the constraint (3.85), hence by using its representation (3.91) yields

$$\begin{aligned} 0 &= -\int C^2 f^{(0)} \sum_{r=0}^{\infty} a^{(r)} S^{(r)}_{3/2} d\mathbf{c} \\ &= -4\pi n \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \sum_{r=0}^{\infty} a^{(r)} \int_0^{\infty} S^{(0)}_{3/2} S^{(r)}_{3/2} C^4 e^{-\beta C^2} dC = -\frac{3}{2}\frac{n}{\beta} a^{(0)}, \end{aligned} \tag{3.93}$$

thanks to (3.151) and $(3.153)_1$. From (3.93), it follows that $a^{(0)} = 0$, and the scalar coefficient $\mathcal{A}$ reduces to

$$\mathcal{A}(C^2, \varrho, T) = -\sum_{r=1}^{\infty} a^{(r)} S_{3/2}^{(r)}. \tag{3.94}$$

The insertion of the expressions (3.94) and (3.92) into their respective integral equations (3.89) and (3.90) leads to

$$f^{(0)} S_{3/2}^{(1)} C_i = -\sum_{r=1}^{\infty} a^{(r)} \mathcal{I}\left[S_{3/2}^{(r)} C_i\right], \tag{3.95}$$

$$f^{(0)} S_{5/2}^{(0)} C_{\langle i} C_{j\rangle} = -\sum_{r=0}^{\infty} b^{(r)} \mathcal{I}\left[S_{5/2}^{(r)} C_{\langle i} C_{j\rangle}\right]. \tag{3.96}$$

The determination of the coefficients $a^{(r)}$ e $b^{(r)}$ from (3.95) and (3.96) proceeds as follows. First, the integral equation (3.95) is multiplied by $\beta S_{3/2}^{(s)} C_i$ and the resulting equation is integrated over all values of $\mathbf{C}$. By using (3.151) one can get

$$\frac{15}{4} \frac{n}{\beta^2} \delta^{(1,r)} = \sum_{s=1}^{\infty} \alpha^{(r,s)} a^{(s)}, \qquad \alpha^{(r,s)} = -\frac{1}{\beta} \int S_{3/2}^{(r)} C_i \mathcal{I}[S_{3/2}^{(s)} C_i] d\mathbf{C}. \tag{3.97}$$

where $\delta^{(1,r)}$ represents Kronecker's symbol. Following the same methodology, the multiplication of the integral equation (3.96) by $\beta^2 S_{5/2}^{(s)} C_{\langle i} C_{j\rangle}$ and the subsequent integration of the resulting equation leads to

$$\frac{5}{2} \frac{n}{\beta^2} \delta^{(0,r)} = \sum_{s=0}^{\infty} \beta^{(r,s)} b^{(s)}, \qquad \beta^{(r,s)} = -\int S_{5/2}^{(r)} C_{\langle i} C_{j\rangle} \mathcal{I}[S_{5/2}^{(s)} C_{\langle i} C_{j\rangle}] d\mathbf{C}. \tag{3.98}$$

The integrals $(3.97)_2$ and $(3.98)_2$ depend on the fields (ϱ, T) and on the molecular interaction potential. Furthermore, from (3.24), one can infer that

$$\alpha^{(r,s)} = \alpha^{(s,r)}, \qquad \beta^{(r,s)} = \beta^{(s,r)} \qquad \text{and} \qquad \alpha^{(r,0)} = \alpha^{(0,r)} = 0. \tag{3.99}$$

One concludes that $(3.97)_1$ represents an infinite system of algebraic equations for the coefficients $a^{(n)}$, and $(3.98)_1$ represents an infinite system of algebraic equations for the coefficients $b^{(n)}$.

In the following section, it will be shown that the transport coefficients of shear viscosity and thermal conductivity are functions only of the coefficients $a^{(1)}$ and $b^{(0)}$, respectively. These coefficients are obtained from the system of equations $(3.97)_1$ and $(3.98)_1$ and read

$$a^{(1)} = \lim_{n\to\infty} \frac{\mathcal{A}'_{nn}}{\mathcal{A}_{nn}}, \qquad b^{(0)} = \lim_{n\to\infty} \frac{\mathcal{B}'_{nn}}{\mathcal{B}_{nn}}, \tag{3.100}$$

where

$$\mathcal{A}'_{nn} = \det\begin{vmatrix} \frac{15}{4}\frac{n}{\beta^2} & \alpha^{(1,2)} & \dots & \alpha^{(1,n)} \\ 0 & \alpha^{(2,2)} & \dots & \alpha^{(2,n)} \\ \vdots & \vdots & \ddots & \vdots \\ 0 & \alpha^{(n,2)} & \dots & \alpha^{(n,n)} \end{vmatrix}, \quad \mathcal{A}_{nn} = \det\begin{vmatrix} \alpha^{(1,1)} & \dots & \alpha^{(1,n)} \\ \vdots & \ddots & \vdots \\ \alpha^{(n,1)} & \dots & \alpha^{(n,n)} \end{vmatrix}, \tag{3.101}$$

$$\mathcal{B}'_{nn} = \det\begin{vmatrix} \frac{5}{2}\frac{n}{\beta^2} & \beta^{(0,1)} & \dots & \beta^{(0,n)} \\ 0 & \beta^{(1,1)} & \dots & \beta^{(1,n)} \\ \vdots & \vdots & \ddots & \vdots \\ 0 & \beta^{(n,1)} & \dots & \beta^{(n,n)} \end{vmatrix}, \quad \mathcal{B}_{nn} = \det\begin{vmatrix} \beta^{(0,0)} & \dots & \beta^{(0,n)} \\ \vdots & \ddots & \vdots \\ \beta^{(n,0)} & \dots & \beta^{(n,n)} \end{vmatrix}. \tag{3.102}$$

The coefficients $a^{(1)}$ and $b^{(0)}$ are determined through a method of successive approximations. In this method, the approximation of order p for the coefficients $a^{(1)}$ and $b^{(0)}$, denoted by $[a^{(1)}]_p$ and $[b^{(0)}]_p$, is given by the subdeterminant of order p. Hence, the first two approximations for the coefficients $a^{(1)}$ and $b^{(0)}$ are

$$[a^{(1)}]_1 = \frac{15}{4}\frac{n}{\beta^2}\frac{1}{\alpha^{(1,1)}}, \qquad [b^{(0)}]_1 = \frac{5}{2}\frac{n}{\beta^2}\frac{1}{\beta^{(0,0)}}, \tag{3.103}$$

$$[a^{(1)}]_2 = \frac{15}{4}\frac{n}{\beta^2}\frac{\alpha^{(2,2)}}{\alpha^{(1,1)}\alpha^{(2,2)} - {\alpha^{(1,2)}}^2}, \qquad [b^{(0)}]_2 = \frac{5}{2}\frac{n}{\beta^2}\frac{\beta^{(1,1)}}{\beta^{(0,0)}\beta^{(1,1)} - {\beta^{(0,1)}}^2}. \tag{3.104}$$

The determination of the integrals $\alpha^{(r,s)}$ and $\beta^{(r,s)}$ follows the same methodology used to calculate the integrals I_1 and I_2 in Section 3.2.2. Indeed, from $(3.97)_2$, $(3.98)_2$ and (3.152), one obtains

$$\alpha^{(1,1)} = \sqrt{\pi}\left(\frac{2}{\beta}\right)^{\frac{5}{2}} n^2 \Omega^{(2,2)} = \beta^{(0,0)}. \tag{3.105}$$

One can also introduce the integrals $\alpha_\star^{(r,s)}$ and $\beta_\star^{(r,s)}$ that depend only on the collision integrals $\Omega^{(l,r)}$, by writing

$$\alpha_\star^{(r,s)} = \frac{\beta^{\frac{5}{2}}}{n^2\sqrt{2\pi}}\alpha^{(r,s)}, \qquad \beta_\star^{(r,s)} = \frac{\beta^{\frac{5}{2}}}{n^2\sqrt{2\pi}}\beta^{(r,s)}, \tag{3.106}$$

so that

$$\alpha_\star^{(1,1)} = 4\Omega^{(2,2)} = \beta_\star^{(0,0)}. \tag{3.107}$$

By following the same methodology, one can obtain the expressions

$$\alpha_\star^{(1,2)} = 7\Omega^{(2,2)} - 2\Omega^{(2,3)}, \qquad \alpha_\star^{(2,2)} = \frac{77}{4}\Omega^{(2,2)} - 7\Omega^{(2,3)} + \Omega^{(2,4)}, \tag{3.108}$$

$$\beta_\star^{(0,1)} = \alpha_\star^{(1,2)}, \qquad \beta_\star^{(1,1)} = \frac{301}{12}\Omega^{(2,2)} - 7\Omega^{(2,3)} + \Omega^{(2,4)} = \alpha_\star^{(2,2)} + \frac{35}{24}\alpha_\star^{(1,1)}. \tag{3.109}$$

Exercises

3.14 Show that the constraint (3.85) leads to (3.93).

3.15 Prove that the relationships (3.99) hold.

3.16 Show that $\alpha_\star^{(1,2)} = \beta_\star^{(0,1)} = 7\Omega^{(2,2)} - 2\Omega^{(2,3)}$.

3.3.5 Transport Coefficients

The determination of the constitutive equations for the pressure tensor and for the heat flux vector proceeds as follows. The insertion of the non-equilibrium distribution function (3.86) together with the representations of $\mathcal{A}$ and $\mathcal{B}$—given by (3.94) and (3.92), respectively—into the definitions of the pressure tensor and heat flux vector leads to

$$p_{ij} = \int mC_iC_jf d\mathbf{c} = p\,\delta_{ij} - \int 2m\beta C_iC_jS_{5/2}^{(0)}f^{(0)}\sum_{r=0}^{\infty} b^{(r)}S_{5/2}^{(r)}C_{\langle p}C_{q\rangle}\frac{\partial v_p}{\partial x_q}d\mathbf{c}, \tag{3.110}$$

$$q_i = \int \frac{m}{2}C^2C_if d\mathbf{c} = \int \frac{m}{2T\beta}\left[\frac{5}{2}S_{3/2}^{(0)} - S_{3/2}^{(1)}\right]C_if^{(0)}\sum_{r=1}^{\infty} a^{(r)}S_{3/2}^{(r)}C_p\frac{\partial T}{\partial x_p}d\mathbf{c}. \tag{3.111}$$

In (3.111), the relationship $\beta C^2 = \left[\frac{5}{2}S_{3/2}^{(0)} - S_{3/2}^{(1)}\right]$ was used, which follows from $(3.153)_2$.

The substitution of the Maxwellian distribution function (3.13) into (3.110) and (3.111) and the subsequent integration of the resulting equations over all values of the peculiar velocity $\mathbf{C}$ yield

$$p_{ij} = p\,\delta_{ij} - 2\mu\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \qquad \text{where} \qquad \mu = \frac{\varrho}{2\beta}b^{(0)}, \tag{3.112}$$

$$q_i = -\lambda\frac{\partial T}{\partial x_i}, \qquad \text{where} \qquad \lambda = \frac{5k}{4m}\frac{\varrho}{\beta}a^{(1)}, \tag{3.113}$$

thanks to the orthogonality condition of the Sonine polynomials (3.151).

Since the coefficients $b^{(0)}$ and $a^{(1)}$ are determined through a method of successive approximations, so are the transport coefficients μ and λ due to the above equations. Hence, it follows from (3.103), (3.104), $(3.112)_2$ and $(3.113)_2$ that the two first approximations to the coefficients of shear viscosity and thermal conductivity read

$$[\mu]_1 = \frac{5}{4}\sqrt{\frac{mkT}{\pi}}\frac{1}{\beta_\star^{(0,0)}} = \frac{5}{16}\sqrt{\frac{mkT}{\pi}}\frac{1}{\Omega^{(2,2)}}, \tag{3.114}$$

$$[\lambda]_1 = \frac{75k}{16m}\sqrt{\frac{mkT}{\pi}}\frac{1}{\alpha_\star^{(1,1)}} = \frac{75}{64}\frac{k}{m}\sqrt{\frac{mkT}{\pi}}\frac{1}{\Omega^{(2,2)}}, \tag{3.115}$$

$$[\mu]_2 = \frac{5}{4}\sqrt{\frac{mkT}{\pi}}\frac{\beta_\star^{(1,1)}}{\beta_\star^{(0,0)}\beta_\star^{(1,1)} - {\beta_\star^{(1,2)}}^2}, \tag{3.116}$$

$$[\lambda]_2 = \frac{75k}{16m}\sqrt{\frac{mkT}{\pi}}\frac{\alpha_\star^{(2,2)}}{\alpha_\star^{(1,1)}\alpha_\star^{(2,2)} - {\alpha_\star^{(1,2)}}^2}. \tag{3.117}$$

Equations (3.114) and (3.115) are identical to the corresponding expressions in (3.50).

Now, from (3.114)–(3.117), one can build the ratios

$$\frac{[\lambda]_1}{[\mu]_1} = \frac{5}{2}c_v, \tag{3.118}$$

$$\frac{[\lambda]_2}{[\lambda]_1} = \left(1 - \frac{{\alpha_\star^{(1,2)}}^2}{\alpha_\star^{(1,1)}\alpha_\star^{(2,2)}}\right)^{-1} > \left(1 - \frac{{\beta_\star^{(0,1)}}^2}{\beta_\star^{(0,0)}\beta_\star^{(1,1)}}\right)^{-1} = \frac{[\mu]_2}{[\mu]_1}. \tag{3.119}$$

One infers from (3.118) that the ratio of the first approximations to the coefficients of thermal conductivity and shear viscosity of monatomic ideal gases is equal to $5c_v/2$ for all types of spherically symmetrical molecular interaction potentials. Furthermore, from the relationship (3.119), it follows that $[\lambda]_2/[\mu]_2 > [\lambda]_1/[\mu]_1 = 5c_v/2$, i.e., the ratio of the second approximations is larger than the ratio of the first ones.

In the following, the second approximation to the transport coefficients will be determined for the hard-sphere potential and for the potential of centers of repulsion.

Hard-sphere Potential

For the hard-sphere potential, the viscosity cross section is given by $Q^{(2)} = \frac{1}{3}\mathsf{d}^2$ so that according to (3.40), the collision integral $\Omega^{(2,r)}$ reads

$$\Omega^{(2,r)} = \int_0^\infty e^{-\gamma^2}\gamma^{2r+3}\frac{1}{3}\mathsf{d}^2 d\gamma = \frac{\mathsf{d}^2}{6}\Gamma\left(\frac{2r+4}{2}\right). \tag{3.120}$$

Hence, it follows from (3.107)–(3.109) and (3.120) that

$$\alpha_\star^{(1,1)} = \beta_\star^{(0,0)} = 4\mathsf{d}^2, \qquad \alpha_\star^{(1,2)} = \beta_\star^{(0,1)} = -\mathsf{d}^2, \tag{3.121}$$

$$\alpha_\star^{(2,2)} = \frac{45}{4}\mathsf{d}^2, \qquad \beta_\star^{(1,1)} = \frac{205}{12}\mathsf{d}^2, \tag{3.122}$$

and the two first approximations (3.114)–(3.117) to the coefficients of shear viscosity and thermal conductivity for the hard-sphere potential become

$$[\mu]_1 = \frac{5}{16\mathsf{d}^2}\sqrt{\frac{mkT}{\pi}}, \qquad [\lambda]_1 = \frac{5}{2}c_v\,[\mu]_1\,, \tag{3.123}$$

$$[\mu]_2 = \frac{205}{202}\,[\mu]_1 \approx 1.01485\,[\mu]_1\,, \qquad [\lambda]_2 = \frac{45}{44}\,[\lambda]_1 \approx 1.02273\,[\lambda]_1\,. \tag{3.124}$$

Note that the second approximations to the transport coefficients is a small correction to the first ones, so is the ratio $[\lambda]_2/[\mu]_2 \approx 1.00776[\lambda]_1/[\mu]_1$.

Potential of Centers of Repulsion

The viscosity cross section for the centers of repulsion potential is given by (3.55), and the expression for the integral $\Omega^{(2,r)}$, which follows from (3.40), reduces to

$$\begin{aligned}\Omega^{(2,r)} &= \int_0^\infty e^{-\gamma^2}\gamma^{2r+3}\left(\frac{\kappa}{2kT}\right)^{\frac{2}{\nu-1}}\gamma^{-\frac{4}{\nu-1}}A_2(\nu)\,d\gamma\\ &= \left(\frac{\kappa}{2kT}\right)^{\frac{2}{\nu-1}}A_2(\nu)\frac{1}{2}\Gamma\left(r+2-\frac{2}{\nu-1}\right).\end{aligned} \tag{3.125}$$

For the centers of repulsion potential, one obtains from (3.107)–(3.109) and (3.125):

$$\alpha_\star^{(1,1)} = \beta_\star^{(0,0)} = 2\left(\frac{\kappa}{2kT}\right)^{\frac{2}{\nu-1}}A_2(\nu)\Gamma\left(\frac{4\nu-6}{\nu-1}\right), \tag{3.126}$$

$$\alpha_\star^{(1,2)} = \beta_\star^{(0,1)} = -\frac{1}{4}\left(\frac{\nu-5}{\nu-1}\right)\alpha_\star^{(1,1)}, \tag{3.127}$$

$$\alpha_\star^{(2,2)} = \frac{45}{16}\frac{1}{(\nu-1)^2}\left(\nu^2-\frac{106}{45}\nu+\frac{77}{45}\right)\alpha_\star^{(1,1)}, \tag{3.128}$$

$$\beta_\star^{(1,1)} = \frac{205}{48}\frac{1}{(\nu-1)^2}\left(\nu^2-\frac{458}{205}\nu+\frac{301}{205}\right)\alpha_\star^{(1,1)}. \tag{3.129}$$

For this case, the first two approximations to the transport coefficients of shear viscosity and thermal conductivity become

$$[\mu]_1 = \frac{5}{8}\sqrt{\frac{mkT}{\pi}}\left(\frac{2kT}{\kappa}\right)^{\frac{2}{\nu-1}}\bigg/\left[A_2(\nu)\Gamma\left(\frac{4\nu-6}{\nu-1}\right)\right], \tag{3.130}$$

$$[\lambda]_1 = \frac{5}{2}c_v\,[\mu]_1\,, \qquad [\mu]_2 = \left(1+\frac{3(\nu-5)^2}{2(\nu-1)(101\nu-113)}\right)[\mu]_1\,, \tag{3.131}$$

$$[\lambda]_2 = \left(1+\frac{(\nu-5)^2}{4(\nu-1)(11\nu-13)}\right)[\lambda]_1\,. \tag{3.132}$$

One can verify from (3.131) and (3.132) that the second approximations to the transport coefficients of shear viscosity and thermal conductivity are equal to the first ones for the case of Maxwellian molecules, where $\nu = 5$. This conclusion is also valid for all successive approximations to the transport coefficients of a gas of Maxwellian molecules (see Section 4.2).

Exercises

3.17 Show that the inequality $[\lambda]_2/[\mu]_2 > [\lambda]_1/[\mu]_1 = 5c_v/2$ holds.

3.18 Obtain the approximations (3.124) for the hard-sphere potential and (3.131) and (3.132) for the centers of repulsion potential.

3.4 The BGK Model

One of the main difficulties to deal with the Boltzmann equation is the one associated with the expression of the collision term, since it depends on the product of two distribution functions, namely,

$$\mathcal{Q}(f,f) = \int (f_1'f' - f_1 f)\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1. \tag{3.133}$$

With the aim of simplifying the structure of the collision term but maintaining its basic properties, simpler expressions for the collision term were introduced in the literature, which are known generically as kinetic models. One of the oldest model—known as the BGK model—was formulated independently by Bhatnagar, Gross and Krook and by Welander.[7]

The collision model $\mathcal{J}(f)$ must fulfill the same properties of the true collision term $\mathcal{Q}(f,f)$ of the Boltzmann equation. The properties are

(**a**) for all summational invariants $\psi = m, mc_i$ and $mc^2/2$, $\mathcal{Q}(f,f)$ and $\mathcal{J}(f)$ must satisfy the conditions

$$\int \psi \mathcal{Q}(f,f) d\mathbf{c} = 0, \qquad \text{and} \qquad \int \psi \mathcal{J}(f) d\mathbf{c} = 0; \tag{3.134}$$

(**b**) the tendency of the distribution function to equilibrium—or equivalently the $\mathcal{H}$-theorem—must hold, i.e.,

$$\int \ln f\, \mathcal{Q}(f,f) d\mathbf{c} \leqslant 0 \qquad \text{and} \qquad \int \ln f\, \mathcal{J}(f) d\mathbf{c} \leqslant 0. \tag{3.135}$$

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[7] P. L. Bhatnagar, E. P. Gross and M. Krook, “A Model for Collision Processes in Gases. Small Amplitude Processes in Charged and Neutral One-component Systems”, *Phys. Rev.*, **94** 511-525 (1954); P. Welander, “On the Temperature Jump in a Rarefied Gas”, *Arkiv för Fysik*, **7** 507-553 (1954).

In the BGK model, the expression for $\mathcal{J}(f)$ is given by

$$\mathcal{J}(f) = \nu(f^{(0)} - f), \tag{3.136}$$

where $f^{(0)}$ is the Maxwellian distribution function (3.13) and ν represents a frequency which is of order of the collision frequency. Under this circumstance, the Boltzmann equation (2.20) becomes

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} + F_i \frac{\partial f}{\partial c_i} = \nu(f^{(0)} - f). \tag{3.137}$$

Due to (3.136), it is easy to verify that the condition $(3.134)_2$ is identically satisfied. For the proof of the second condition $(3.135)_2$, consider the simple case where the distribution function does not depend on the spatial coordinates and that the external forces are absent. In this case, (3.137) reads

$$\frac{\partial f}{\partial t} = \nu(f^{(0)} - f). \tag{3.138}$$

The multiplication of the above equation by $\ln \mathtt{b} f$ and the integration of the resulting equation over all values of $\mathbf{c}$ leads to

$$\frac{\partial}{\partial t}\int f(\ln \mathtt{b} f) d\mathbf{c} - \int \frac{\partial f}{\partial t} d\mathbf{c} = \nu \int (f^{(0)} - f)(\ln \mathtt{b} f) d\mathbf{c}. \tag{3.139}$$

By taking into account (3.138), it is easy to verify that the second term on the left-hand side of the above equation vanishes. Furthermore, one may write (3.139) as

$$\frac{\partial}{\partial t}\int f(\ln \mathtt{b} f) d\mathbf{c} = \nu \int f^{(0)} \left(1 - \frac{f}{f^{(0)}}\right) \ln \frac{f}{f^{(0)}} d\mathbf{c}, \tag{3.140}$$

since $\ln \mathtt{b} f^{(0)}$ is a summational invariant and the following relationship holds

$$\int f^{(0)} \ln \mathtt{b} f^{(0)} d\mathbf{c} = \int f \ln \mathtt{b} f^{(0)} d\mathbf{c}. \tag{3.141}$$

From the inequality $(1 - x)\ln x \leqslant 0$, which is valid for all $x > 0$, it follows the $\mathcal{H}$-theorem for the BGK model:

$$\frac{\partial \mathcal{H}}{\partial t} \leqslant 0, \qquad \text{where} \qquad \mathcal{H} = \int_V \left(\int f(\ln \mathtt{b} f) d\mathbf{c}\right) d\mathbf{x}. \tag{3.142}$$

Here V denotes the volume of the receipt where the gas is confined.

The non-equilibrium distribution function can be obtained from the model equation (3.137) by using the Chapman–Enskog method. For that end, one may write

$$f(\mathbf{x},\mathbf{c},t)=f^{(0)}(\mathbf{x},\mathbf{c},t)\,[1+\phi(\mathbf{x},\mathbf{c},t)]\,, \tag{3.143}$$

where ϕ is the deviation from the equilibrium state of the Maxwellian distribution function.

The substitution of the Maxwellian distribution function $f^{(0)}$ into the left-hand side of the model equation (3.137) and the representation (3.143) into its right-hand side yields

$$\frac{\partial f^{(0)}}{\partial t}+c_i\frac{\partial f^{(0)}}{\partial x_i}+F_i\frac{\partial f^{(0)}}{\partial c_i}=\nu(f^{(0)}-f)=-\nu f^{(0)}\phi. \tag{3.144}$$

Now, one proceeds as follows. First, the Maxwellian distribution function (3.13) is inserted into the above equation and the derivatives are performed. Next, the elimination of the time derivatives of the fields ϱ, v_i and T—by taking into account the field equations of an Eulerian fluid (3.26)—leads to the determination of the non-equilibrium distribution function, namely,

$$f=f^{(0)}\left\{1-\frac{1}{\nu}\left[\frac{1}{T}\left(\frac{mC^2}{2kT}-\frac{5}{2}\right)C_k\frac{\partial T}{\partial x_k}+\frac{m}{kT}C_kC_l\frac{\partial v_{\langle k}}{\partial x_{l\rangle}}\right]\right\}. \tag{3.145}$$

The Navier–Stokes and Fourier laws may be obtained by inserting the distribution function (3.145) into the definitions of the pressure tensor and of the heat flux vector and the subsequent integration of the resulting equations over all values of $\mathbf{c}$, yielding

$$p_{ij}=p\,\delta_{ij}-2\mu\frac{\partial v_{\langle i}}{\partial x_{j\rangle}},\qquad q_i=-\lambda\frac{\partial T}{\partial x_i}. \tag{3.146}$$

The coefficients of shear viscosity and thermal conductivity in this case are given by

$$\mu=\frac{p}{\nu},\qquad \lambda=\frac{5}{2}\frac{k}{m}\frac{p}{\nu}. \tag{3.147}$$

Although it is very simple to obtain the non-equilibrium distribution function from the BGK model, it does not furnish the right ratio for the transport coefficients. Indeed, on the basis of the results (3.147), it follows that $\lambda/\mu=5k/(2m)$, i.e., the Prandtl number is equal to $Pr=1$ instead of the corrected value of $Pr=2/3$ (see Section 3.2.3).

Exercises

3.19 Obtain the inequality $(3.142)_1$ from (3.138).

3.20 Show that the non-equilibrium distribution function is given by (3.145).

3.5 Appendix

The solution of the associated Laguerre differential equation

$$x\frac{d^2y}{dx^2}+(m+1-x)\frac{dy}{dx}+ny=0, \tag{3.148}$$

is given in terms of the associated Laguerre polynomials $L_n^m(x)$.[8]

According to the reference of the footnote, the associated Laguerre polynomials were called Sonine polynomials $S_m^{(n)}(x)$ in the older literature. The Sonine polynomials constitute a set of orthogonal functions with respect to the weight function $e^{-x}x^m$ in the interval $0<x<\infty$, i.e.,

$$\int_0^\infty e^{-x}x^m S_m^{(n)}(x)S_m^{(p)}(x)dx=\frac{(n+m)!}{n!}\delta_{np}. \tag{3.149}$$

Furthermore, the Sonine polynomials are given by the formula

$$S_m^{(n)}(x)=\sum_{k=0}^{n}\frac{(n+m)!}{k!(n-k)!(k+m)!}(-x)^k. \tag{3.150}$$

In kinetic theory of gases, it is common to use Sonine polynomials of order n and index $(l+1/2)$ in the variable $\beta C^2=mC^2/2kT$. In this case, (3.149) and (3.150) are rewritten as

$$\int_0^\infty e^{-\beta C^2}C^{2l+2}S_{l+1/2}^{(n)}(\beta C^2)S_{l+1/2}^{(p)}(\beta C^2)\beta^{l+3/2}dC=\frac{1}{2}\frac{\Gamma(n+l+3/2)}{n!}\delta_{np}, \tag{3.151}$$

$$S_{l+1/2}^{(n)}(\beta C^2)=\sum_{k=0}^{n}\frac{\Gamma(n+l+3/2)}{k!(n-k)!\Gamma(k+l+3/2)}(-\beta C^2)^k, \tag{3.152}$$

where $\Gamma(n)$ denotes the gamma function.

From (3.152), one can obtain the first three Sonine polynomials, which read

$$S_{l+1/2}^{(0)}(\beta C^2)=1, \qquad S_{l+1/2}^{(1)}(\beta C^2)=l+\frac{3}{2}-\beta C^2, \tag{3.153}$$

$$S_{l+1/2}^{(2)}(\beta C^2)=\frac{1}{2}\Big(l+\frac{5}{2}\Big)\Big(l+\frac{3}{2}\Big)-\Big(l+\frac{5}{2}\Big)\beta C^2+\frac{1}{2}\beta^2C^4. \tag{3.154}$$

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[8] See e.g. http://mathworld.wolfram.com/LaguerrePolynomial.html

Chapter 4
Moment Methods

4.1 Grad's Moment Method

4.1.1 Balance Equations

The macroscopic description of a rarefied gas within Grad's moment method[1] is based on thirteen scalar fields, namely, mass density $\varrho(\mathbf{x},t)$, hydrodynamic velocity $v_i(\mathbf{x},t)$, pressure tensor $p_{ij}(\mathbf{x},t)$ and heat flux vector $q_i(\mathbf{x},t)$.

The balance equations for these fields are given by

$$\frac{\partial \varrho}{\partial t}+\frac{\partial \varrho v_i}{\partial x_i}=0, \tag{4.1}$$

$$\frac{\partial \varrho v_i}{\partial t}+\frac{\partial\left(\varrho v_i v_j+p_{ij}\right)}{\partial x_j}=\varrho F_i, \tag{4.2}$$

$$\frac{\partial p_{ij}}{\partial t}+\frac{\partial\left(p_{ijk}+p_{ij}v_k\right)}{\partial x_k}+p_{ki}\frac{\partial v_j}{\partial x_k}+p_{kj}\frac{\partial v_i}{\partial x_k}=P_{ij}, \tag{4.3}$$

$$\frac{\partial q_i}{\partial t}+\frac{\partial\left(q_{ij}+q_i v_j\right)}{\partial x_j}+p_{ijk}\frac{\partial v_j}{\partial x_k}+q_j\frac{\partial v_i}{\partial x_j}-\frac{p_{ki}}{\varrho}\frac{\partial p_{kj}}{\partial x_j}-\frac{1}{2}\frac{p_{rr}}{\varrho}\frac{\partial p_{ij}}{\partial x_j}=Q_i. \tag{4.4}$$

The above first two equations represent the balance equations of mass density (2.97) and moment density (2.98). The balance equation for the pressure tensor (4.3) was obtained from (2.100) by taking $N=2$. For the determination of the balance equation for the heat flux vector (4.4) it was considered $N=3$ in (2.100), two indices were contracted and the resulting equation was divided by 2. Furthermore, the following definitions were introduced in (4.3) and (4.4):

$$p_{ijk}=\int mC_iC_jC_kf\,d\mathbf{c},\quad P_{ij}=\int m\left(C_i'C_j'-C_iC_j\right)ff_1g\,b\,db\,d\varepsilon\,d\mathbf{c}_1d\mathbf{c}, \tag{4.5}$$

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[1] H. Grad, "On the Kinetic Theory of Rarefied Gases", *Commun. Pure Appl. Math.*, **2**, 331-407 (1949).

$$q_{ij} = \int \frac{m}{2} C^2 C_i C_j f d\mathbf{c}, \quad Q_i = \int \frac{m}{2} \left(C'^2 C'_i - C^2 C_i \right) f f_1 g \, b \, db \, d\varepsilon \, d\mathbf{c}_1 d\mathbf{c}. \tag{4.6}$$

The tensors p_{ijk} and P_{ij} represent the non-convective flux and the production term of the pressure tensor, respectively, while the tensors q_{ij} and Q_i refer to analogous quantities for the heat flux vector.

By analyzing the system of partial differential equations (4.1)–(4.4) one concludes that it cannot be considered a system of field equations for the basic fields ϱ, v_i, p_{ij} and q_i. Indeed, in order to obtain a closed system of differential equations, the non-convective fluxes p_{ijk}, q_{ij} and the production terms P_{ij}, Q_i must be expressed in terms of the basic fields. For this end—which will be the aim of the next section—the distribution function must be expressed in terms of the thirteen scalar fields of mass density ϱ, hydrodynamic velocity v_i, pressure tensor p_{ij} and heat flux vector q_i.

Exercise

4.1 Determine the balance equations for the pressure tensor (4.3) and for the heat flux vector (4.4).

4.1.2 Grad's Distribution Function

According to Grad's moment method the distribution function is expanded in series of tensorial Hermite polynomials[2] $H_{i_1 i_2 \ldots i_N}$ $(N = 0, 1, 2, \ldots)$ as follows:

$$f = f^{(0)} \left(aH + a_i H_i + \frac{1}{2!} a_{ij} H_{ij} + \ldots + \frac{1}{N!} a_{i_1 i_2 \ldots i_N} H_{i_1 i_2 \ldots i_N} + \ldots \right), \tag{4.7}$$

where $a_{i_1 i_2 \ldots i_N}$ $(N = 0, 1, 2, \ldots)$ are tensorial coefficients that depend on $\mathbf{x}$ and t. The Maxwellian distribution function $f^{(0)}$ is written as

$$f^{(0)} = n \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-mC^2/(2kT)} = n \left(\frac{m}{kT} \right)^{\frac{3}{2}} \omega(\boldsymbol{\xi}). \tag{4.8}$$

In the above equation $\omega(\boldsymbol{\xi})$ is the weight function

$$\omega(\boldsymbol{\xi}) = \frac{1}{(2\pi)^{\frac{3}{2}}} e^{-\xi^2/2}, \qquad \text{with} \qquad \xi_i = \sqrt{\frac{m}{kT}} C_i. \tag{4.9}$$

The tensorial Hermite polynomials are defined on the basis of the weight function, namely,

---

[2] H. Grad, "Note on N-dimensional Hermite polynomials", *Commun. Pure Appl. Math.*, **2**, 325-330 (1949).

$$H_{i_1 i_2 \dots i_N}(\boldsymbol{\xi}) = \frac{(-1)^N}{\omega} \frac{\partial^N \omega}{\partial \xi_{i_1} \partial \xi_{i_2} \dots \partial \xi_{i_N}}, \tag{4.10}$$

and are orthogonal with respect to it, i.e.,

$$\int \omega(\boldsymbol{\xi}) H_{i_1 i_2 \dots i_N}(\boldsymbol{\xi}) H_{j_1 j_2 \dots j_M}(\boldsymbol{\xi}) d\boldsymbol{\xi} = \delta_{MN}\, \Delta_{i_1 j_1 i_2 j_2 \dots i_N j_N}. \tag{4.11}$$

In (4.11), δ_{MN} is Kronecker's symbol and $\Delta_{i_1 j_1 i_2 j_2 \dots i_N j_N}$ represents the sum $\Delta_{i_1 j_1 i_2 j_2 \dots i_N j_N} = \delta_{i_1 j_1} \delta_{i_2 j_2} \dots \delta_{i_N j_N} +$ (all permutations of the $j's$ indices).

The first four tensorial Hermite polynomials that can be obtained from (4.10) read

$$H(\boldsymbol{\xi}) = 1, \qquad H_i(\boldsymbol{\xi}) = \xi_i, \qquad H_{ij}(\boldsymbol{\xi}) = \xi_i \xi_j - \delta_{ij}, \tag{4.12}$$

$$H_{ijk}(\boldsymbol{\xi}) = \xi_i \xi_j \xi_k - (\xi_i \delta_{jk} + \xi_j \delta_{ik} + \xi_k \delta_{ij}). \tag{4.13}$$

As was previously commented, the basic fields of this theory are the following thirteen scalar fields[3]:

$$\varrho = \int m f d\mathbf{c} \text{ – mass density}, \tag{4.14}$$

$$\varrho v_i = \int m c_i f d\mathbf{c} \text{ – momentum density}, \tag{4.15}$$

$$T = \frac{m}{3k\varrho} \int m C^2 f d\mathbf{c} \text{ – temperature}, \tag{4.16}$$

$$p_{\langle ij \rangle} = \int m C_{\langle i} C_{j \rangle} f d\mathbf{c} \text{ – pressure tensor deviator}, \tag{4.17}$$

$$q_i = \int \frac{m}{2} C^2 C_i f d\mathbf{c} \text{ – heat flux vector}. \tag{4.18}$$

In terms of the tensorial Hermite polynomials, the above moments of the distribution function can be written as

$$\varrho = \int m \left(\frac{kT}{m}\right)^{\frac{3}{2}} f H d\boldsymbol{\xi}, \qquad 0 = \int m \left(\frac{kT}{m}\right)^2 f H_i d\boldsymbol{\xi}, \tag{4.19}$$

$$T = \frac{m}{3k\varrho} \int m \left(\frac{kT}{m}\right)^{\frac{5}{2}} f (H_{ii} + 3H) d\boldsymbol{\xi}, \tag{4.20}$$

$$p_{\langle ij \rangle} = \int m \left(\frac{kT}{m}\right)^{\frac{5}{2}} f \left(H_{ij} - \frac{1}{3} H_{rr} \delta_{ij}\right) d\boldsymbol{\xi}, \tag{4.21}$$

$$q_i = \int \frac{m}{2} \left(\frac{kT}{m}\right)^3 f \left(H_{ijj} + 5H_i\right) d\boldsymbol{\xi}. \tag{4.22}$$

---

[3] Note that the trace of the pressure tensor is given by $p_{rr} = 3p = 3kT\varrho/m$, so that one can use instead of the pressure, the temperature as a variable.

The coefficients $a_{i_1 i_2 \dots i_N}$ that appear in the distribution function (4.7) are determined from the definition of the moments of the distribution function. For a thirteen-moment theory—described by the fields of mass density ϱ, hydrodynamic velocity v_i, pressure tensor p_{ij} and heat flux vector q_i—the distribution function (4.7) is written as[4]

$$f = f^{(0)} \left(aH + a_i H_i + \frac{1}{2} a_{ij} H_{ij} + \frac{1}{10} a_{rri} H_{ssi} \right), \tag{4.23}$$

where a, a_i, a_{ij} and a_{rri} represent thirteen scalar coefficients to be determined.

The insertion of the distribution function (4.23) into the definitions of the moments of the distribution function (4.19)–(4.22) and the subsequent integration of the resulting equations using the orthogonality properties of the tensorial Hermite polynomials (4.11) leads to a complete determination of the thirteen scalar coefficients, namely

$$a = 1, \qquad a_i = 0, \qquad a_{rr} = 0, \qquad a_{\langle ij \rangle} = \frac{p_{\langle ij \rangle}}{p}, \qquad a_{rri} = \frac{2q_i}{p}\sqrt{\frac{m}{kT}}. \tag{4.24}$$

On the basis of (4.12), (4.13) and (4.24) the distribution function of the thirteen moments (4.23)—with $\beta = m/2kT$—becomes

$$f = f^{(0)} \left\{ 1 + \frac{2\beta^2}{\varrho} \left[p_{\langle ij \rangle} C_i C_j + \frac{4}{5} q_i C_i \left(\beta C^2 - \frac{5}{2} \right) \right] \right\}, \tag{4.25}$$

which is known as Grad's distribution function.

Exercises

4.2 Show that the first four tensorial Hermite polynomials are given by (4.12) and (4.13).

4.3 Obtain the expressions for the thirteen scalar coefficients a, a_i, a_{ij} and a_{rri} given in (4.24).

4.4 Consider that the distribution function has the following representation

$$f = f^{(0)} \left(a + a_i C_i + a_{ij} C_i C_j + a_{rri} C^2 C_i \right),$$

where the thirteen coefficients a, a_i, a_{ij} and a_{rri} do not depend on the peculiar velocity C_i. Determine the scalar coefficients from the definitions

---

[4] The term $\frac{1}{3!} a_{ijk} H_{ijk}$ was decomposed according to

$$\frac{1}{6} \left[a_{\langle ijk \rangle} + \frac{1}{5} \left(a_{rri} \delta_{jk} + a_{rrj} \delta_{ik} + a_{rrk} \delta_{ij} \right) \right] H_{ijk} = \frac{1}{6} a_{\langle ijk \rangle} H_{ijk} + \frac{1}{10} a_{rri} H_{ssi},$$

and the part associated with the third-order tensor $\frac{1}{6} a_{\langle ijk \rangle} H_{ijk}$ was not taken into account.

(4.14)–(4.18) and show that the resulting distribution function is Grad's distribution function.

4.1.3 Grad's Distribution from Entropy Maximization

Another way to determine Grad's distribution function is through the maximization of the entropy density (2.144) subjected to thirteen constraints which are the moments of the distribution functions (4.14)–(4.18).[5] This method is an extension of the one used in statistical mechanics to determine the equilibrium distribution functions for classical and quantum gases, where the entropy is maximized subjected to the constraints of fixed number of the molecules, fixed volume and fixed energy of the system.

According to the variational calculus, the search for the extremum value of the functional (2.144) subjected to the constraints (4.14)–(4.18) is equivalent to look for the extremum value of the following non-constrained functional:

$$
\begin{aligned}
F = -k\int (f\ln \mathsf{b}f)\,d\mathbf{c} - \Lambda\int mf d\mathbf{c} - \Lambda_i\int mc_i f d\mathbf{c} \\
-\lambda\frac{m}{3k\varrho}\int mC^2 f d\mathbf{c} - \lambda_{\langle ij\rangle}\int mC_iC_j f d\mathbf{c} - \lambda_i\int \frac{m}{2}C^2C_i f d\mathbf{c}.
\end{aligned}
\tag{4.26}
$$

The thirteen unknown quantities Λ, Λ_i, λ, $\lambda_{\langle ij\rangle}$ and λ_i, which do not depend on the peculiar velocity $\mathbf{C}$, are the Lagrange multipliers.

For the functional (4.26) the Euler–Lagrange equation reduces to $\partial F/\partial f = 0$, yielding

$$
f = \exp\left[-\ln\mathsf{b} - 1 - \frac{m}{k}\left(\Lambda + \Lambda_i c_i + \lambda\frac{mC^2}{3k\varrho} + \lambda_{\langle ij\rangle}C_iC_j + \lambda_i\frac{C^2}{2}C_i\right)\right].
\tag{4.27}
$$

The above distribution function leads to a big problem, since the largest power of the peculiar velocity is an odd function and its integration in the range $(-\infty, +\infty)$ diverges. However, for processes close to equilibrium the distribution function must be represented by a Maxwellian distribution function plus a deviation, so that one may consider the Lagrange multipliers Λ_i, $\lambda_{\langle ij\rangle}$ and λ_i as small quantities. In this case one may use the approximation $\exp(-x) \approx 1 - x$ which is valid for all $x \ll 1$, and get

$$
\begin{aligned}
f = \exp\left[-\ln\mathsf{b} - 1 - \frac{m}{k}\Lambda - \lambda\frac{m^2C^2}{3k^2\varrho}\right]\Bigg\{1 - \frac{m}{k}\Lambda_i v_i \\
-\frac{m}{k}\left[\Lambda_i C_i + \Lambda_{\langle ij\rangle}C_iC_j + \frac{1}{2}\lambda_i C^2 C_i\right]\Bigg\}.
\end{aligned}
\tag{4.28}
$$

---

[5] M. N. Kogan, "On the principle of maximum entropy" in *Rarefied Gas Dynamics*, Vol. I, pp. 359-368 (Academic Press, New York, 1967).

One may infer that the above distribution function does not diverge in the range $(-\infty, +\infty)$.

The Lagrange multipliers are determined from the definitions of the constraints (4.14)–(4.18). First, the substitution of the distribution function (4.28) into the definition of the mass density (4.14) and the integration of the resulting equation lead to

$$\exp\left[-\ln \mathsf{b} - 1 - \frac{m}{k}\Lambda\right]\left[1 - \frac{m}{k}\Lambda_i v_i\right] = \frac{\varrho}{m}\left(\frac{\lambda m^2}{3\pi k^2 \varrho}\right)^{\frac{3}{2}}. \tag{4.29}$$

Next, using the relationship (4.29), the remaining constraints (4.15)–(4.18) provide the following system of equations for the determination of the Lagrange multipliers:

$$\Lambda_i + \frac{5}{4}\left(\frac{3k^2\varrho}{\lambda m^2}\right)\lambda_i = 0, \qquad \lambda = \frac{3}{2}\frac{k}{m}\frac{\varrho}{T}, \tag{4.30}$$

$$\lambda_{\langle ij\rangle} = -\frac{2p_{\langle ij\rangle}}{\varrho}\left(\frac{k}{m}\right)\left(\frac{\lambda m^2}{3k^2\varrho}\right)^2, \tag{4.31}$$

$$\Lambda_i + \frac{7}{4}\left(\frac{3k^2\varrho}{\lambda m^2}\right)\lambda_i = -\frac{8}{5}\frac{q_i}{\varrho}\left(\frac{k}{m}\right)\left(\frac{\lambda m^2}{3k^2\varrho}\right)^2. \tag{4.32}$$

Indeed, from the system of equations (4.30)–(4.32) it follows that

$$\Lambda_i = \frac{m}{kT^2}\frac{q_i}{\varrho}, \qquad \lambda = \frac{3}{2}\frac{k}{m}\frac{\varrho}{T}, \qquad \lambda_{\langle ij\rangle} = -\frac{p_{\langle ij\rangle}}{2\varrho}\frac{m}{kT^2}, \qquad \lambda_i = -\frac{2}{5}\frac{m^2}{k^2T^3}\frac{q_i}{\varrho}. \tag{4.33}$$

Now, the insertion of (4.29) and (4.33) into the expression (4.28) leads to Grad's distribution function (4.25).

Exercise

4.5 Obtain (4.29)–(4.32).

4.1.4 Determination of the Non-convective Fluxes, Production Terms, Entropy Density and Entropy Flux

The insertion of Grad's distribution function (4.25) into the definitions $(4.5)_1$ and $(4.6)_1$ of the non-convective fluxes p_{ijk} and q_{ij}, and the subsequent integration of the resulting equations lead to

$$p_{ijk} = \frac{2}{5}\left(q_i\delta_{jk} + q_j\delta_{ik} + q_k\delta_{ij}\right), \qquad q_{ij} = \frac{5p^2}{2\varrho}\delta_{ij} + \frac{7p}{2\varrho}p_{\langle ij\rangle}. \tag{4.34}$$

For the determination of the production terms P_{ij} and Q_i one changes the integration variables $(\mathbf{c},\mathbf{c}_1)\longmapsto(\mathbf{g},\mathbf{G})$ using the relationships (3.35), so that in these new variables equations $(4.5)_2$ and $(4.6)_2$ become

$$P_{ij}=\int\frac{m}{2}\Big[\frac{1}{2}\left(g_i'g_j'-g_ig_j\right)-G_i\left(g_j'-g_j\right)-G_j\left(g_i'-g_i\right)\Big]ff_1 g\,b\,db\,d\varepsilon\,d\mathbf{g}\,d\mathbf{G},\tag{4.35}$$

$$Q_i=\int\frac{m}{2}\left[\frac{1}{2}G_r\left(g_r'g_i'-g_rg_i\right)-\frac{1}{2}\left(G^2+\frac{1}{4}g^2\right)\left(g_i'-g_i\right)-G_iG_r\left(g_r'-g_r\right)\right]\times ff_1 g\,b\,db\,d\varepsilon\,d\mathbf{g}\,d\mathbf{G}.\tag{4.36}$$

Furthermore, in terms of the new variables the product of Grad's distribution functions—which follows from (4.25)—is written as

$$ff_1=n^2\left(\frac{\beta}{\pi}\right)^3e^{-\left(2\beta G^2+\frac{\beta}{2}g^2\right)}\left\{1+\frac{4\beta^2}{\varrho}p_{\langle kl\rangle}\left[G_kG_l+\frac{1}{4}g_kg_l\right]+\frac{8\beta^2}{5\varrho}q_j\left[2G_j\left(\beta G^2+\frac{\beta}{4}g^2-\frac{5}{2}\right)+\beta g_jG_kg_k\right]\right\}.\tag{4.37}$$

In the above equation, the non-linear terms in the pressure deviator $p_{\langle ij\rangle}$ and heat flux vector q_i were not taken into account, since only a linearized theory will be analyzed in this section.

The determination of the production terms P_{ij} and Q_i proceeds as follows. First, one inserts the product of the distribution functions (4.37) into equations (4.35) and (4.36). Next, using the relationships (4.114) and (4.116) of the appendix to this chapter, one can integrate the resulting equations with respect to the azimuthal angle ε, yielding

$$P_{ij}=\frac{\pi}{4}\frac{\varrho^2}{m}\left(\frac{\beta}{\pi}\right)^3\int\left\{1+\frac{4\beta^2}{\varrho}p_{\langle kl\rangle}\left[G_kG_l+\frac{1}{4}g_kg_l\right]\right\}\times e^{-\left(2\beta G^2+\frac{\beta}{2}g^2\right)}\sin^2\chi\left(g^2\delta_{ij}-3g_ig_j\right)g\,b\,db\,d\mathbf{g}\,d\mathbf{G},\tag{4.38}$$

$$Q_i=\frac{\pi}{4}\frac{\varrho^2}{m}\left(\frac{\beta}{\pi}\right)^3\int\frac{8\beta^2}{5\varrho}q_j\left[2G_j\left(\beta G^2+\frac{\beta}{4}g^2-\frac{5}{2}\right)+\beta g_jG_kg_k\right]\times e^{-\left(2\beta G^2+\frac{\beta}{2}g^2\right)}\sin^2\chi G_r\left(g^2\delta_{ir}-3g_ig_r\right)g\,b\,db\,d\mathbf{g}\,d\mathbf{G}.\tag{4.39}$$

In the above equations, it was not considered the odd integrals in $\mathbf{g}$ and $\mathbf{G}$, because they vanish identically.

The subsequent integration of the last two equations in $\mathbf{G}$ and in the spherical angles of $\mathbf{g}$ leads to

$$P_{ij} = -\frac{p_{\langle ij\rangle}}{\tau_r}, \qquad Q_i = -\frac{2q_i}{3\tau_r}. \tag{4.40}$$

Above, τ_r denotes the relaxation time of the pressure deviator, which is given by

$$\tau_r = \frac{5}{16n}\sqrt{\frac{m}{\pi kT}}\frac{1}{\varOmega^{(2,2)}}, \tag{4.41}$$

where $\varOmega^{(2,2)}$ is the collision integral defined by (3.40).

The calculation of the production terms including non-linear terms is a hard task, which leads to

$$\begin{aligned} P_{ij} &= -\frac{p_{\langle ij\rangle}}{\tau_r} - \frac{1}{7p\tau_r}\left(\frac{\varOmega^{(2,3)}}{\varOmega^{(2,2)}} - \frac{7}{2}\right)\left(p_{\langle ir\rangle}p_{\langle rj\rangle} - \frac{1}{3}p_{\langle rs\rangle}p_{\langle rs\rangle}\delta_{ij}\right) \\ &\quad + \frac{\varrho}{25p^2\tau_r}\left(\frac{\varOmega^{(2,4)}}{\varOmega^{(2,2)}} - 9\frac{\varOmega^{(2,3)}}{\varOmega^{(2,2)}} + \frac{63}{4}\right)q_{\langle i}q_{j\rangle}, \end{aligned} \tag{4.42}$$

$$Q_i = -\frac{2q_i}{3\tau_r} - \frac{1}{5p\tau_r}\left(\frac{\varOmega^{(2,3)}}{\varOmega^{(2,2)}} - \frac{7}{2}\right)p_{\langle ij\rangle}q_j. \tag{4.43}$$

It is interesting to note that the above equations for the production terms in a non-linear theory reduce to the linear expressions (4.40) for the case of a Maxwellian potential. Indeed, as it will be shown in Section 4.2, the expressions for the production terms (4.40) are exact for Maxwellian potentials.

In Section 2.7 the entropy density ϱs and the entropy flux φ_i were defined in terms of the distribution function as

$$\varrho s = \int(-kf\ln \mathtt{b}f)d\mathbf{c}, \qquad \varphi_i = \int(-kf\ln \mathtt{b}f)C_i d\mathbf{c}. \tag{4.44}$$

One can calculate these two quantities as a function of the thirteen scalar fields of mass density, momentum density, temperature, pressure deviator and heat flux vector using Grad's distribution function. Indeed, the insertion of Grad's distribution function (4.25) into (4.44) and the integration of the resulting equations lead to

$$\varrho s = kn\left[\ln\frac{T^{\frac{3}{2}}}{\varrho} + \frac{3}{2} - \ln\left(\mathtt{b}\sqrt{\frac{m}{(2\pi k)^3}}\right)\right] - \frac{1}{4pT}p_{\langle rs\rangle}p_{\langle rs\rangle} - \frac{\varrho}{5p^2T}q_r q_r, \tag{4.45}$$

$$\varphi_i = \frac{q_i}{T} - \frac{2}{5pT}p_{\langle ij\rangle}q_j. \tag{4.46}$$

In the above equations, the approximation $\ln(1+x) \approx x - x^2/2$ was employed, which is valid for all $|x| \ll 1$ and considered up to quadratic terms in the pressure deviator and heat flux vector. The first term on the right-hand side of (4.45) is the equilibrium value of the entropy density for a monatomic ideal gas, while the last two terms are non-linear contributions related to the pressure deviator and heat flux vector. From (4.46) one infers that the entropy flux is equal to the heat flux vector divided by the temperature plus a non-linear term proportional to the product of the pressure deviator and heat flux vector. In a linear theory this equation reduces to $\varphi_i = q_i/T$, which is one of the premises of the thermodynamic theory of irreversible processes (see Section 3.1).

Exercises

4.6 Determine the constitutive equations for the non-convective fluxes (4.34).

4.7 Obtain the final expressions (4.40) for the production terms.

4.8 Show that the relaxation time of the pressure deviator (4.41), for the hard-sphere potential where $\Omega^{(2,2)} = \mathsf{d}^2$, is related with the mean free time τ (equation (1.2)) by $\tau_r = 5\tau/4$. [Note that $\bar{g} = 4\sqrt{kT/(\pi m)}$.]

4.9 Show that the production terms (4.42) and (4.43) reduce to (4.40) for a gas of Maxwellian molecules. Hint, calculate the collision integrals $\Omega^{(2,r)}$ for $r = 2, 3, 4$ using (3.40).

4.10 Determine the expressions for the entropy density (4.45) and for the entropy flux (4.46).

4.1.5 Field Equations

Once the constitutive equations for the non-convective fluxes and production terms are known functions of the basic fields, a system of thirteen scalar field equations can be obtained. This system is composed by the equations of the five scalar fields of mass density, momentum density and temperature which follows from (4.1), (4.2) and the trace of equation (4.3), respectively, i.e.,

$$\mathcal{D}\varrho + \varrho\frac{\partial v_i}{\partial x_i} = 0, \tag{4.47}$$

$$\varrho\mathcal{D}v_i + \frac{\partial p}{\partial x_i} + \frac{\partial p_{\langle ij\rangle}}{\partial x_j} = \varrho F_i, \tag{4.48}$$

$$\frac{3}{2}nk\mathcal{D}T + \frac{\partial q_i}{\partial x_i} + p\frac{\partial v_i}{\partial x_i} + p_{\langle ij\rangle}\frac{\partial v_i}{\partial x_j} = 0, \tag{4.49}$$

together with the equations for the eight scalar fields which represent the pressure deviator and the heat flux vector. The eight scalar equations are obtained from the traceless part (4.3) and (4.4) through the insertion of the constitutive equations of the non-convective fluxes (4.34) and production terms (4.42) and (4.43), resulting

$$\begin{aligned}
&\mathcal{D}p_{\langle ij\rangle}+\frac{5}{3}p_{\langle ij\rangle}\frac{\partial v_k}{\partial x_k}+\frac{4}{5}\frac{\partial q_{\langle i}}{\partial x_{j\rangle}}+p_{\langle ki\rangle}\frac{\partial v_{\langle j}}{\partial x_{k\rangle}}+p_{\langle kj\rangle}\frac{\partial v_{\langle i}}{\partial x_{k\rangle}}-\frac{2}{3}p_{\langle kr\rangle}\frac{\partial v_{\langle r}}{\partial x_{k\rangle}}\delta_{ij}\\
&+p_{\langle ki\rangle}\frac{\partial v_{[j}}{\partial x_{k]}}+p_{\langle kj\rangle}\frac{\partial v_{[i}}{\partial x_{k]}}+\underline{2p\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}}=-\underline{\frac{p_{\langle ij\rangle}}{\tau_r}}+\frac{\varrho}{25p^2\tau_r}\left(\frac{\varOmega^{(2,4)}}{\varOmega^{(2,2)}}-9\frac{\varOmega^{(2,3)}}{\varOmega^{(2,2)}}\right.\\
&\left.+\frac{63}{4}\right)q_{\langle i}q_{j\rangle}-\frac{1}{7p\tau_r}\left(\frac{\varOmega^{(2,3)}}{\varOmega^{(2,2)}}-\frac{7}{2}\right)\left(p_{\langle ir\rangle}p_{\langle rj\rangle}-\frac{1}{3}p_{\langle rs\rangle}p_{\langle rs\rangle}\delta_{ij}\right),
\end{aligned}\tag{4.50}$$

$$\begin{aligned}
&\mathcal{D}q_i+2q_i\frac{\partial v_k}{\partial x_k}+\left(\frac{p}{\varrho}\delta_{ij}-\frac{p_{\langle ij\rangle}}{\varrho}\right)\frac{\partial p_{\langle jk\rangle}}{\partial x_k}+\frac{p}{\varrho}p_{\langle ik\rangle}\left(\frac{7}{2T}\frac{\partial T}{\partial x_k}-\frac{1}{p}\frac{\partial p}{\partial x_k}\right)\\
&+\frac{9}{5}q_j\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}+q_j\frac{\partial v_{[i}}{\partial x_{j]}}+\underline{\frac{5}{2}\frac{k}{m}p\frac{\partial T}{\partial x_i}}=-\underline{\frac{2q_i}{3\tau_r}}-\frac{1}{5p\tau_r}\left(\frac{\varOmega^{(2,3)}}{\varOmega^{(2,2)}}-\frac{7}{2}\right)p_{\langle ij\rangle}q_j.
\end{aligned}\tag{4.51}$$

In a five-field theory described by the fields of mass density, momentum density and temperature, the balance equations are given by (4.47)–(4.49), but the pressure deviator and the heat flux vector are no longer variables, just constitutive quantities. One may use the remaining eight equations (4.50) and (4.51) to obtain the constitutive equations for the pressure deviator and for the heat flux vector. Indeed, by neglecting all non-linear terms on the right-hand sides of both equations and by considering only the equilibrium values of the pressure deviator $p_{\langle ij\rangle}=0$ and of the heat flux vector $q_i=0$ on the left-hand sides of (4.50) and (4.51), only the underlined terms remain, yielding

$$p_{\langle ij\rangle}=-2\mu\frac{\partial v_{\langle i}}{\partial x_{j\rangle}},\quad\text{where}\quad\mu=p\tau_r=\frac{5}{16}\sqrt{\frac{mkT}{\pi}}\frac{1}{\varOmega^{(2,2)}},\tag{4.52}$$

$$q_i=-\lambda\frac{\partial T}{\partial x_i},\quad\text{where}\quad\lambda=\frac{15k}{4m}p\tau_r=\frac{75k}{64m}\sqrt{\frac{mkT}{\pi}}\frac{1}{\varOmega^{(2,2)}}.\tag{4.53}$$

Above, it was used the expression (4.41) for the relaxation time of the pressure deviator. Equations (4.52) and (4.53) represent the laws of Navier–Stokes and Fourier, respectively, where the coefficients of shear vicosity and thermal conductivity have the same expressions as those found by applying the Chapman–Enskog method (see (3.50)).

Exercise

4.11 Obtain (4.50) and (4.51).

4.2 The Method of Maxwell and Ikenberry–Truesdell

4.2.1 Calculation of the Production Terms

The method that will be analyzed in this section is restricted to molecules which interact according to the Maxwellian potential. It was proposed by Maxwell[6] and developed by Ikenberry and Truesdell[7], and its advantage is that it is not necessary to develop the distribution function in polynomials of the peculiar velocity.

Here, only a sketch of the method is presented, and the main objective of this section is to obtain Navier–Stokes and Fourier laws from a method known in the literature as Maxwellian iteration.

The starting point are the thirteen moment equations (4.1)–(4.4) for the fields of mass density, momentum density, pressure deviator and heat flux vector.

The determination of the production terms for the pressure deviator $(4.5)_2$ and for the heat flux vector $(4.6)_2$ proceeds as follows. First, for Maxwellian molecules, where $\nu = 5$, one can get from (1.101) that

$$g\, b\, db = \sqrt{\frac{2\kappa}{m}} s_0 ds_0, \tag{4.54}$$

by writing the reduced mass as $\mu = m/2$. Next, by using the relationships

$$C_i^1 + C_i = C_i^{1\prime} + C_i', \quad g_i' = C_i^{1\prime} - C_i' \quad \text{and} \quad C_i' = \frac{1}{2}\left(C_i + C_i^1 - g_i'\right), \tag{4.55}$$

one can write the production term of the pressure tensor $(4.5)_2$ as

$$\begin{aligned} P_{ij} &= \frac{m}{4}\sqrt{\frac{2\kappa}{m}} \int \Big[(C_i + C_i^1)(C_j + C_j^1) - g_i'(C_j + C_j^1) \\ &\quad - g_j'(C_i + C_i^1) + g_i' g_j' - 4C_iC_j\Big] f f_1 s_0 ds_0\, d\varepsilon\, d\mathbf{c}_1 d\mathbf{c} \\ &= \frac{m\pi}{4}\sqrt{\frac{2\kappa}{m}} \int \Big[2(C_i + C_i^1)(C_j + C_j^1) - 2(C_i^1 - C_i)(C_j + C_j^1)\cos\chi \\ &\quad - 2(C_j^1 - C_j)(C_i + C_i^1)\cos\chi + (C^2 - 2C_rC_r^1 + C_1^2)\sin^2\chi\delta_{ij} \\ &\quad + (3\cos^2\chi - 1)(C_i^1 - C_i)(C_j^1 - C_j) - 8C_iC_j\Big] f f_1 s_0\, ds_0\, d\mathbf{c}_1 d\mathbf{c}. \end{aligned} \tag{4.56}$$

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[6] J. C. Maxwell, “On the Dynamical Theory of Gases”, *Phil. Trans. R. Soc. London*, **157**, 49-68 (1867).

[7] E. Ikenberry & C. Truesdell, “On the Pressures and the Flux of Energy in a Gas According to Maxwell’s Kinetic Theory, I.”, *J. Rational Mech. Anal.*, **5**, 1-54 (1956).

The last equality was obtained by integrating over the azimuthal angle ε using the formulas (4.114) and (4.116) of the appendix to this chapter. Finally, the integration of (4.56) over all values of the velocities $\mathbf{c}$ and $\mathbf{c}_1$ leads to

$$P_{ij} = -\frac{3\pi}{2} n p_{\langle ij\rangle} \sqrt{\frac{2\kappa}{m}} \int_0^\infty (1-\cos^2\chi) s_0 \, ds_0 = -\frac{3\pi}{2} n \sqrt{\frac{2\kappa}{m}} A_2(5) p_{\langle ij\rangle}, \quad (4.57)$$

by taking into account the definitions of the moments of the distribution function (4.14)–(4.18). Above, $A_l(\nu)$ represents the integral defined by (1.116). Note that $(4.40)_1$ reduces to (4.57) for the case of Maxwellian molecules, since according to (3.56) the collision integral reads

$$\Omega^{(2,2)} = \frac{15}{16} \sqrt{\frac{\kappa\pi}{2kT}} A_2(5). \quad (4.58)$$

The integration of the production term $(4.6)_2$ for the heat flux vector proceeds in the same manner, yielding

$$Q_i = -\pi n \sqrt{\frac{2\kappa}{m}} A_2(5) q_i. \quad (4.59)$$

It is important to call attention to the fact that the results for the production terms (4.57) and (4.59) are exact, since none approximation to the distribution function was done, whereas those given in (4.40) were obtained by approximating the distribution function in polynomials of the peculiar velocity.

Exercise

4.12 Obtain the expressions (4.57) and (4.59) for the the pressure tensor and heat flux vector production terms.

4.2.2 The Maxwellian Iteration

The substitution of the production terms (4.57) and (4.59) into the balance equations for the traceless part of the pressure tensor (4.3) and for the heat flux vector (4.4) leads to

$$\mathcal{D}p_{\langle ij\rangle} + p_{\langle ij\rangle}\frac{\partial v_k}{\partial x_k} + \frac{\partial p_{ijk}}{\partial x_k} - \frac{2}{3}\frac{\partial q_k}{\partial x_k}\delta_{ij} + p_{ki}\frac{\partial v_j}{\partial x_k} + p_{kj}\frac{\partial v_i}{\partial x_k} - \frac{2}{3}p_{kr}\frac{\partial v_r}{\partial x_k}\delta_{ij}$$
$$= -\frac{3\pi}{2} n \sqrt{\frac{2\kappa}{m}} A_2(5) p_{\langle ij\rangle}, \quad (4.60)$$

$$\mathcal{D}q_i + q_i\frac{\partial v_j}{\partial x_j} + \frac{\partial q_{ij}}{\partial x_j} + p_{ijk}\frac{\partial v_j}{\partial x_k} + q_j\frac{\partial v_i}{\partial x_j} - \frac{p_{ki}}{\varrho}\frac{\partial p_{kj}}{\partial x_j} - \frac{1}{2}\frac{p_{rr}}{\varrho}\frac{\partial p_{ij}}{\partial x_j}$$
$$= -\pi n\sqrt{\frac{2\kappa}{m}}A_2(5)q_i. \tag{4.61}$$

Hence, the above equations together with (4.47)–(4.49) become a system of thirteen field equations for the fields of mass density, hydrodynamic velocity, temperature, pressure deviator and heat flux vector, once the constitutive equations for the non-convective terms p_{ijk} and q_{ij} are known functions of the formers.

By following the same methodology of Section 4.1.4 one may consider a five-field theory described by the balance equations (4.47)–(4.49) for the mass density, hydrodynamic velocity and temperature, respectively, and determine the constitutive equations for the pressure deviator and heat flux vector from the remaining eight equations (4.60) and (4.61).

The method used here to obtain the constitutive equations is known in the literature as Maxwellian iteration. In this method, the equilibrium values of the moments of the distribution function—calculated using the Maxwellian distribution function—are inserted into the left-hand sides of (4.60) and (4.61) and it follows from their right-hand sides the first iteration values for the pressure deviator and for the heat flux vector.

The equilibrium values of the moments of the distribution function read

$$p_{ij}^{(0)} = \int mC_iC_jf^{(0)}d\mathbf{c} = p\,\delta_{ij}, \quad p_{ijk}^{(0)} = \int mC_iC_jC_kf^{(0)}d\mathbf{c} = 0, \tag{4.62}$$

$$q_i^{(0)} = \int \frac{m}{2}C^2C_if^{(0)}d\mathbf{c} = 0, \quad q_{ij}^{(0)} = \int \frac{m}{2}C^2C_iC_jf^{(0)}d\mathbf{c} = \frac{5p^2}{2\varrho}\delta_{ij}, \tag{4.63}$$

so that the first iteration values obtained from (4.60) and (4.61) through the use of the Maxwellian iteration method become

$$p_{\langle ij\rangle}^{(1)} = -2\mu\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \qquad q_i^{(1)} = -\lambda\frac{\partial T}{\partial x_i}. \tag{4.64}$$

The above equations are Navier–Stokes and Fourier laws, respectively, where the coefficients of shear viscosity and thermal conductivity are given by

$$\mu = \frac{2}{3\pi}\frac{kT}{A_2(5)}\sqrt{\frac{m}{2\kappa}}, \qquad \lambda = \frac{5}{2\pi}\frac{k^2T}{mA_2(5)}\sqrt{\frac{m}{2\kappa}}. \tag{4.65}$$

These expressions for the transport coefficients were previously determined in Section 3.2.3 (see (3.59)).

For the determination of the second iterated values for the pressure deviator $p_{\langle ij\rangle}$ and heat flux vector q_i—known in the literature as Burnett equations—it is necessary to know the first iterated values of the moments of the distribution function, p_{ijk} and q_{ij}. They follow by using the Maxwellian iteration method for the balance equations of p_{ijk} and q_{ij} and one is referred to the work by Ikenberry and Truesdell to a complete determination of the second iterated values for the pressure deviator and for the heat flux vector. By considering only linear terms in the gradients, the Burnett equations read

$$p^{(2)}_{\langle ij\rangle} = -2\mu\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} + \frac{\mu^2}{\varrho T}\frac{\partial^2 T}{\partial x_{\langle i}\partial x_{j\rangle}} - 2\frac{\mu^2}{\varrho^2}\frac{\partial^2 \varrho}{\partial x_{\langle i}\partial x_{j\rangle}}, \tag{4.66}$$

$$q^{(2)}_i = -\lambda\frac{\partial T}{\partial x_i} - \frac{15}{4}\frac{\mu^2}{\varrho}\frac{\partial}{\partial x_i}\left(\frac{\partial v_k}{\partial x_k}\right) + 3\frac{\mu^2}{\varrho}\frac{\partial}{\partial x_j}\left(\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}\right). \tag{4.67}$$

Hence, in a linearized theory the second iterated value for the pressure deviator depends on the second gradients of the mass density and temperature, while the one for the heat flux vector depends on the second gradients of the hydrodynamical velocity. According to $(4.52)_2$ and $(4.53)_2$, the transport coefficients of shear viscosity and thermal conductivity are proportional to relaxation time of the pressure deviator, which in turn is of the order of the mean free time. In this sense the contributions to the pressure deviator and the heat flux vector due to the second gradients are smaller than those related to the first gradients, since the coefficients of the second gradient terms are proportional to the square of the relaxation time of the pressure deviator.

Exercises

4.13 Obtain the expressions for the moments of the distribution function (4.62) and (4.63).

4.14 Obtain the linearized Burnett equations (4.66) and (4.67) by using the Maxwellian iteration method and by considering the first iterated values (4.64) together with

$$p^{(1)}_{ijk} = \frac{2}{5}\left(q^{(1)}_i\delta_{jk} + q^{(1)}_j\delta_{ik} + q^{(1)}_k\delta_{ij}\right), \qquad q^{(1)}_{ij} = \frac{5p^2}{2\varrho}\delta_{ij} + \frac{7p}{2\varrho}p^{(1)}_{\langle ij\rangle}.$$

4.3 The Chapman–Enskog–Grad Combined Method

In this section a method to obtain the constitutive equations for the pressure deviator and for the heat flux vector is developed by combining the features of Chapman–Enskog and Grad's methods. In this method neither a solution of the integral equation is needed—as in the Chapman–Enskog method—nor the field equations for the moments of the distribution function are used—as in Grad's method.[8]

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[8] A. G. Bezerra Jr.; S. Reinecke & G. M. Kremer, "A Combined Chapman-Enskog and Grad Method. I. Monatomic Gases and Mixtures", *Continuum Mech. Thermodyn.*, **6**, 149-160 (1994).

The starting point in this method is to observe that the deviation of the Maxwellian distribution function in the Chapman–Enskog method ϕ, which is a unknown quantity, can be written in terms of known quantities. These known quantities can be chosen as the thirteen scalar fields of mass density, hydrodynamic velocity, temperature, pressure deviator and heat flux vector which appear in Grad's distribution function (4.25), i.e.,

$$\phi = \frac{2\beta^2}{\varrho}\left[p_{\langle ij\rangle}C_iC_j + \frac{4}{5}q_iC_i\left(\beta C^2 - \frac{5}{2}\right)\right]. \tag{4.68}$$

In the Chapman–Enskog–Grad combined method one inserts the representation (4.68) into the non-homogeneous integral equation of the Chapman–Enskog method (3.28), so that it becomes an equation for the determination of the pressure deviator $p_{\langle ij\rangle}$ and of the heat flux vector q_i. This equation reads

$$\begin{aligned} f^{(0)}\left\{\frac{1}{T}\left(\beta C^2 - \frac{5}{2}\right)C_k\frac{\partial T}{\partial x_k} + 2\beta C_kC_l\frac{\partial v_{\langle k}}{\partial x_{l\rangle}}\right\} &= \frac{2\beta^2}{\varrho}p_{\langle kl\rangle}\,\mathcal{I}[C_kC_l] \\ &+\frac{8\beta^2}{5\varrho}q_k\,\mathcal{I}\left[\left(\beta C^2 - \frac{5}{2}\right)C_k\right]. \end{aligned} \tag{4.69}$$

Above, $\mathcal{I}$ denotes the integral (3.22).

For the determination of the pressure deviator, one multiplies (4.69) by $C_{\langle i}C_{j\rangle}$ and integrates the resulting equation over all values of $\mathbf{c}$, yielding

$$2\frac{p}{m}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} = \frac{2\beta^2}{\varrho}p_{\langle kl\rangle}\int C_{\langle i}C_{j\rangle}\mathcal{I}[C_kC_l]d\mathbf{c}. \tag{4.70}$$

In order to solve the above equation for the pressure deviator $p_{\langle kl\rangle}$, let I_{ijkl} denote the integral

$$I_{ijkl} = \int C_iC_j\mathcal{I}[C_kC_l]d\mathbf{c}. \tag{4.71}$$

The representation of I_{ijkl} in terms of Kronecker's symbol is

$$I_{ijkl} = A_1\delta_{ij}\delta_{kl} + A_2(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \tag{4.72}$$

since it is symmetric in the indexes (i,j) and (k,l). Above, A_1 and A_2 are two scalar coefficients which can be determined from the following system of equations obtained by contracting the integral I_{ijkl} in two different manners, namely,

$$I_{rrss} = 9A_1 + 6A_2, \qquad I_{rsrs} = 3A_1 + 12A_2. \tag{4.73}$$

Hence, one can write the expressions

$$I_{ijkl} = \frac{2I_{rrss} - I_{rsrs}}{15}\delta_{ij}\delta_{kl} + \frac{3I_{rsrs} - I_{rrss}}{30}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \tag{4.74}$$

$$I_{\langle ij\rangle kl} = \frac{3I_{rsrs} - I_{rrss}}{15}\delta_{k\langle i}\delta_{j\rangle l}. \tag{4.75}$$

Now using the relationship (4.75), (4.70) can be rewritten as

$$2\frac{p}{m}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} = \frac{2\beta^2}{5\varrho}p_{\langle ij\rangle}\int C_{\langle r}C_{s\rangle}\mathcal{I}[C_{\langle r}C_{s\rangle}]d\mathbf{c} = \frac{2\beta^2}{5\varrho}p_{\langle ij\rangle}I_2, \tag{4.76}$$

where I_2 is the integral defined by (3.43) and whose value is given by (3.45). Hence, it follows from (4.76) Navier–Stokes' law

$$p_{\langle ij\rangle} = -2\mu\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \qquad \text{where} \qquad \mu = \frac{5}{16}\sqrt{\frac{mkT}{\pi}}\frac{1}{\Omega^{(2,2)}}, \tag{4.77}$$

is the coefficient of shear viscosity.

The determination of the heat flux vector follows the same methodology. Indeed, the multiplication of (4.69) by C^2C_i and the integration of the resulting equation over all values of $\mathbf{c}$ yield

$$\begin{aligned}5\frac{kp}{m^2}\frac{\partial T}{\partial x_i} &= \frac{8\beta^2}{5\varrho}q_k\int C^2C_i\mathcal{I}\left[\left(\beta C^2 - \frac{5}{2}\right)C_k\right]d\mathbf{c} \\ &= \frac{8\beta^2}{15\varrho}q_i\int C^2C_k\mathcal{I}\left[\left(\beta C^2 - \frac{5}{2}\right)C_k\right]d\mathbf{c} = \frac{8\beta^2}{15\varrho}q_iI_1.\end{aligned} \tag{4.78}$$

In the above equation, the following relationship was used:

$$I_{ik} = \int C^2C_i\mathcal{I}\left[\left(\beta C^2 - \frac{5}{2}\right)C_k\right]d\mathbf{c} = \frac{I_{rr}}{3}\delta_{ik}. \tag{4.79}$$

Moreover, in the last equality of (4.78), I_1 is the integral (3.33) which is expressed by (3.39). Fourier's law follows from (4.78), namely,

$$q_i = -\lambda\frac{\partial T}{\partial x_i}, \qquad \text{where} \qquad \lambda = \frac{75}{64}\frac{k}{m}\sqrt{\frac{mkT}{\pi}}\frac{1}{\Omega^{(2,2)}}, \tag{4.80}$$

is the coefficient of thermal conductivity.

Exercises

4.15 Obtain (4.70) from (4.69).

4.16 Determine the representations (4.74) and (4.75).

4.4 Non-inertial Reference Frames

4.4.1 Objective Tensors

An orthogonal matrix $\mathbf{Q}$ preserves the scalar product of two vectors $\mathbf{u}$ and $\mathbf{v}$, i.e,

$$\mathbf{Q}\,\mathbf{u}\cdot\mathbf{Q}\,\mathbf{v}=\mathbf{u}\cdot\mathbf{v} \qquad \text{or} \qquad Q_{ij}u_jQ_{ik}v_k=u_iv_i=\delta_{jk}u_jv_k. \tag{4.81}$$

From the above equation it follows that $Q_{ij}Q_{ik}=\delta_{jk}$, or by introducing the unity matrix $\mathbf{1}$, $\mathbf{Q}^T\mathbf{Q}=\mathbf{Q}\mathbf{Q}^T=\mathbf{1}$. Hence, its transpose is equal to its inverse $\mathbf{Q}^T=\mathbf{Q}^{-1}$ and $\det\mathbf{Q}=\pm 1$.

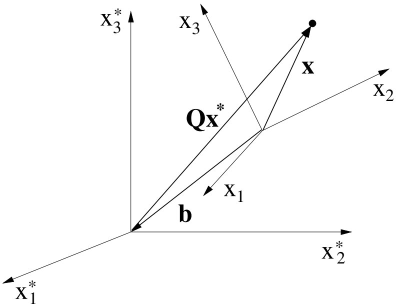

Fig. 4.1 Transformation of two frames of Cartesian coordinates x_i^* and x_i

An Euclidean transformation from a Cartesian frame of coordinates x_i^* to a Cartesian frame of coordinates x_i—represented in Figure 4.1—is defined by

$$x_i=O_{ij}(t)x_j^*+b_i(t) \qquad \Rightarrow \qquad x_j^*=O_{ij}(t)\left[x_i-b_i(t)\right]. \tag{4.82}$$

In the above equation, $O_{ij}(t)$ is an orthogonal matrix that depends on time and determines the directions of the $\mathbf{x}$ frame with respect to the $\mathbf{x}^*$ frame. The vector $b_i(t)$, which is also time dependent, represents the position of the $\mathbf{x}$ frame origin to the corresponding one in the $\mathbf{x}^*$ frame. The time transformation is simply $t=t^*+\alpha$, where α is a constant.

A Galilean transformation is a particular case of the Euclidean transformation, where the orthogonal matrix O_{ij} does not depend on time and $b_i(t)=-V_it$ with V_i being a constant translational velocity of the $\mathbf{x}$ frame with respect to the $\mathbf{x}^*$ frame, i.e., $x_i=O_{ij}x_j^*-V_it$.

An objective tensor $\mathbf{T}$ of rank N is defined as a quantity whose components $T^*_{i_1i_2\ldots i_N}$ in one coordinate frame transform into a quantity with components

$T_{i_1 i_2 \dots i_N}$ relative to another coordinate frame under an Euclidean transformation according to

$$T_{i_1 i_2 \dots i_N} = (\det \mathbf{O})^p O_{i_1 j_1} O_{i_2 j_2} \dots O_{i_N j_N} T^*_{j_1 j_2 \dots j_N}, \tag{4.83}$$

where $\mathbf{O}$ denotes the orthogonal matrix of the Euclidean transformation. If $p = 0$, $\mathbf{T}$ is called an absolute objective tensor and if $p = 1$ as an axial objective tensor. From now on, the adjectives absolute and axial will be dropped. Objective tensors of rank zero are called scalars, of rank one vectors and of second rank simply tensors.

The fields of mass density ϱ and temperature T are objective scalars, while the heat flux vector q_i and the pressure tensor p_{ij} are objective vector and tensor, respectively. Hence, their transformations read

$$\varrho = \varrho^*, \qquad T = T^*, \qquad q_i = O_{ij} q_j^*, \qquad p_{ij} = O_{ik} O_{jl} p^*_{kl}. \tag{4.84}$$

The velocity is not an objective vector, since the time derivative of $(4.82)_1$ leads to

$$v_i = O_{ij} v_j^* + \dot{O}_{ij} x_j^* + \dot{b}_i, \qquad \text{or} \qquad v_i = O_{ij} v_j^* + W_{ik}(x_k - b_k) + \dot{b}_i, \tag{4.85}$$

using $(4.82)_2$. The matrix $W_{ik} = \dot{O}_{ij} O_{kj}$ is an anti-symmetric matrix and represents the angular velocity matrix of the $\mathbf{x}$ frame with respect to the $\mathbf{x}^*$ frame. If $\mathbf{w}$ denotes the axial vector associated with the matrix of angular velocity, i.e., $W_{ij} = \varepsilon_{ikj} w_k$, (4.85) may be rewritten as

$$\mathbf{v} - \mathbf{O}\mathbf{v}^* = \mathbf{w} \times (\mathbf{x} - \mathbf{b}) + \dot{\mathbf{b}}. \tag{4.86}$$

The two terms on the right-hand side of the above equation represent, respectively, the rotational and the translational velocities of the $\mathbf{x}$ frame with respect to the $\mathbf{x}^*$ frame.

If $\mathbf{v}_1$ and $\mathbf{v}_2$ denote two velocity vectors, their difference is an objective vector, i.e.,

$$\mathbf{v}_1 - \mathbf{v}_2 = \mathbf{O}(\mathbf{v}_1^* - \mathbf{v}_2^*). \tag{4.87}$$

Furthermore, it is easy to prove from (4.85) that the Jacobian of the transformation of the velocities is given by

$$J = \frac{\partial(v_1, v_2, v_3)}{\partial(v_1^*, v_2^*, v_3^*)} = \det \mathbf{O} = \pm 1, \tag{4.88}$$

so that the transformation of the volume elements in the velocity space is $d\mathbf{v} = |J| d\mathbf{v}^* = d\mathbf{v}^*$.

The temperature gradient is an objective vector, because

$$\frac{\partial T}{\partial x_i} = \frac{\partial T}{\partial x_j^*} \frac{\partial x_j^*}{\partial x_i} = O_{ij} \frac{\partial T}{\partial x_j^*}. \tag{4.89}$$

However, the gradient of velocity is not an objective tensor, since from (4.85) one can obtain

$$\frac{\partial v_i}{\partial x_j} = O_{ik}\frac{\partial v_k^*}{\partial x_j} + \dot{O}_{ik}\frac{\partial x_k^*}{\partial x_j} = O_{ik}O_{jl}\frac{\partial v_k^*}{\partial x_l^*} + W_{ij}. \tag{4.90}$$

By taking the symmetric and the antisymmetric parts of the above equation, yields

$$\frac{\partial v_{(i}}{\partial x_{j)}} = O_{ik}O_{jl}\frac{\partial v_{(k}^*}{\partial x_{l)}^*}, \qquad \frac{\partial v_{[i}}{\partial x_{j]}} = O_{ik}O_{jl}\frac{\partial v_{[k}^*}{\partial x_{l]}^*} + W_{ij}, \tag{4.91}$$

respectively. Hence, the symmetric part of the gradient of velocity is an objective tensor whereas its antisymmetric part is not.

The acceleration is not an objective vector, since the time derivative of $(4.85)_1$ leads to

$$a_i = O_{ij}a_j^* + 2\dot{O}_{ij}v_j^* + \ddot{O}_{ij}x_j^* + \ddot{b}_i. \tag{4.92}$$

The elimination of x_j^* and v_j^* from the above equation by using $(4.82)_2$ and $(4.85)_2$, yields (see exercise 4.18)

$$a_i - O_{ij}a_j^* = 2W_{ij}(v_j - \dot{b}_j) - \mathbf{W}_{ij}^2(x_j - b_j) + \dot{W}_{ij}(x_j - b_j) + \ddot{b}_i, \tag{4.93}$$

or by introducing the angular velocity vector it may be written as

$$\mathbf{a} - \mathbf{O}\mathbf{a}^* = 2\mathbf{w}\times(\mathbf{v} - \dot{\mathbf{b}}) - \mathbf{w}\times[\mathbf{w}\times(\mathbf{x} - \mathbf{b})] + \dot{\mathbf{w}}\times(\mathbf{x} - \mathbf{b}) + \ddot{b}. \tag{4.94}$$

One can identify on the right-hand side of the above equation the following terms:

$$\begin{cases} 2\mathbf{w}\times(\mathbf{v} - \dot{\mathbf{b}}) & \text{– Coriolis acceleration,} \\ -\mathbf{w}\times[\mathbf{w}\times(\mathbf{x} - \mathbf{b})] & \text{– centrifugal acceleration,} \\ \dot{\mathbf{w}}\times(\mathbf{x} - \mathbf{b}) & \text{– Euler acceleration,} \\ \ddot{\mathbf{b}} & \text{– acceleration of relative translation.} \end{cases} \tag{4.95}$$

Exercises

4.17 Show that the matrix W_{ij} is anti-symmetric. Hint: take the time derivative of $\mathbf{Q}^T\mathbf{Q} = \mathbf{Q}\mathbf{Q}^T = \mathbf{1}$.

4.18 Show that $\ddot{O}_{ij}O_{kj} = \dot{W}_{ik} - W_{ir}W_{kr}$.

4.19 Obtain the transformations of the velocity and acceleration under a Galilean transformation. If $V_i = O_{ij}V_j^*$ defines a Galilean vector under a Galilean transformation, show that the acceleration is a Galilean vector but the velocity is not.

4.4.2 The Boltzmann Equation in Non-inertial Reference Frames

The Boltzmann equation (2.20) for monatomic gases in an inertial reference frame reads

$$\frac{\partial f^*}{\partial t^*}+c_i^*\frac{\partial f^*}{\partial x_i^*}+F_i^*\frac{\partial f^*}{\partial c_i^*}=\int\left(f_1'^*f'^*-f_1^*f^*\right)g^*b^*db^*d\varepsilon^*d\mathbf{c}_1^*. \tag{4.96}$$

In the above equation, the stars denote the coordinates of a molecule in an inertial reference frame $(\mathbf{x}^*,\mathbf{c}^*,t^*)$. The coordinates of a molecule in a non-inertial reference frame, denoted by $(\mathbf{x},\mathbf{c},t)$, are related with the coordinates of the inertial one by the transformations

$$x_i=O_{ij}(t)x_j^*+b_i(t),\qquad c_i=O_{ij}c_j^*+\dot{O}_{ij}x_j^*+\dot{b}_i,\qquad t=t^*+\alpha. \tag{4.97}$$

The distribution function is considered as an objective scalar under an Euclidean transformation, i.e., $f^*\equiv f(\mathbf{x}^*,\mathbf{c}^*,t^*)=f(\mathbf{x},\mathbf{c},t)$.

The right-hand side of the Boltzmann equation has the same form in inertial and non-inertial reference frames, e.g.,

$$\int(f_1'^*f'^*-f_1^*f^*)g^*b^*db^*d\varepsilon^*d\mathbf{c}_1^*=\int(f_1'f'-f_1f)g\,b\,db\,d\varepsilon\,d\mathbf{c}_1, \tag{4.98}$$

because b and ε are objective scalars, $d\mathbf{c}_1^*=d\mathbf{c}_1$ and $g=|\mathbf{c}_1-\mathbf{c}|=|\mathbf{O}(\mathbf{c}_1^*-\mathbf{c}^*)|=|\mathbf{c}_1^*-\mathbf{c}^*|=g^*$.

For the transformation of the left-hand side of the Boltzmann equation, the use of the chain rule implies

$$\frac{\partial f^*}{\partial t^*}=\frac{\partial f}{\partial t}+\frac{\partial f}{\partial x_i}\left(\dot{O}_{ij}x_j^*+\dot{b}_i\right)+\frac{\partial f}{\partial c_i}\left(\dot{O}_{ij}c_j^*+\ddot{O}_{ij}x_j^*+\ddot{b}_i\right), \tag{4.99}$$

$$\frac{\partial f^*}{\partial x_j^*}=\frac{\partial f}{\partial x_i}O_{ij}+\frac{\partial f}{\partial c_i}\dot{O}_{ij},\qquad\frac{\partial f^*}{\partial c_j^*}=\frac{\partial f}{\partial c_i}O_{ij}. \tag{4.100}$$

The Boltzmann equation in a non-inertial reference frame follows from (4.96), (4.98)–(4.100), yielding

$$\begin{aligned}\frac{\partial f}{\partial t}+c_i\frac{\partial f}{\partial x_i}+\Big\{F_i+2W_{ij}(c_j-\dot{b}_j)-W_{ij}^2(x_j-b_j)\\+\dot{W}_{ij}(x_j-b_j)+\ddot{b}_i\Big\}\frac{\partial f}{\partial c_i}=\int(f_1'f'-f_1f)g\,b\,db\,d\varepsilon\,d\mathbf{c}_1.\end{aligned} \tag{4.101}$$

Above, it was assumed that the external body force is an objective vector, i.e., $F_i=O_{ij}F_j^*$.

By using the same procedure as that employed in Section 2.3, one can obtain the transfer equation for an arbitrary function $\psi(\mathbf{x},\mathbf{c},t)$ in a non-inertial reference frame, namely,

$$\begin{aligned}\frac{\partial}{\partial t}\int \psi f d\mathbf{c} + \frac{\partial}{\partial x_i}\int \psi c_i f d\mathbf{c} - \int \Bigg\{\frac{\partial \psi}{\partial t} + c_i\frac{\partial \psi}{\partial x_i} + \frac{\partial \psi}{\partial c_i}\Bigg[F_i \\ + 2W_{ij}(c_j - \dot{b}_j) - W_{ij}^2(x_j - b_j) + \dot{W}_{ij}(x_j - b_j) + \ddot{b}_i\Bigg]\Bigg\} f\, d\mathbf{c} \\ = \int \psi(f_1'f' - f_1 f) g\, b\, db\, d\varepsilon\, d\mathbf{c}_1 d\mathbf{c}. \qquad (4.102)\end{aligned}$$

Now from the transfer equation (4.102) it follows the balance equations for the mass density, momentum density, pressure tensor and heat flux vector in a non-inertial reference frame:

$$\mathcal{D}\varrho + \varrho\frac{\partial v_i}{\partial x_i} = 0, \qquad (4.103)$$

$$\begin{aligned}\varrho\mathcal{D}v_i + \frac{\partial p_{ij}}{\partial x_j} &= \varrho\{F_i + 2W_{ij}(v_j - \dot{b}_i) - W_{ij}^2(x_j - b_j) \\ &+ \dot{W}_{ij}(x_j - b_j) + \ddot{b}_i\}, \qquad (4.104)\end{aligned}$$

$$\begin{aligned}\mathcal{D}p_{ij} + p_{ij}\frac{\partial v_k}{\partial x_k} + \frac{\partial p_{ijk}}{\partial x_k} - p_{kj}\frac{\partial v_i}{\partial x_k} - p_{ki}\frac{\partial v_j}{\partial x_k} \\ - 2W_{ik}p_{jk} - 2W_{jk}p_{ik} = P_{ij}, \qquad (4.105)\end{aligned}$$

$$\begin{aligned}\mathcal{D}q_i + q_i\frac{\partial v_j}{\partial x_j} + \frac{\partial q_{ij}}{\partial x_j} - \frac{p_{ij}}{\varrho}\frac{\partial p_{jk}}{\partial x_k} - \frac{p_{rr}}{2\varrho}\frac{\partial p_{ij}}{\partial x_j} + p_{rij}\frac{\partial v_r}{\partial x_j} \\ + q_j\frac{\partial v_i}{\partial x_j} - 2W_{ij}q_j = Q_i, \qquad (4.106)\end{aligned}$$

by choosing ψ equal to m, mc_i, mC_iC_j and $mC^2C_i/2$, respectively. In the above equations, the material time derivative $\mathcal{D} = \partial/\partial t + v_i\partial/\partial x_i$ was introduced.

Exercises

4.20 Obtain (4.99) and (4.100).

4.21 Show that $\partial[W_{ij}(c_j - b_j)]/\partial c_i = 0$ and obtain the transfer equation (4.102).

4.22 Obtain the balance equations in a non-inertial reference frame (4.103)–(4.106).

4.4.3 Frame Dependence of the Heat Flux Vector

One of the main principles of continuum mechanics is the so-called principle of material frame indifference which states that the constitutive equations for objective constitutive quantities must be the same in all frames of references, i.e., they must be the same in inertial as well as in non-inertial frames of reference.

The validity of this principle was questioned by Müller[9] who showed—from a kinetic theory of gases—that the stress deviator and the heat flux vector depend on the frame of reference.

Here, only the frame dependence of the heat flux vector will be analyzed by following the arguments of Müller. Consider a gas enclosed by two infinite concentric cylinders which are rotating with the same angular velocity w, the outer cylinder at a temperature which is larger than the temperature of the inner one (see Figure 4.2). It is assumed that the material time derivative of the temperature vanishes $\mathcal{D}T = 0$ and that the gas performs a rigid rotation, i.e.,

$$v_i = \Omega_{ij} x_j, \qquad \text{hence} \qquad \frac{\partial v_{(i}}{\partial x_{j)}} = 0, \qquad \frac{\partial v_{[i}}{\partial x_{j]}} = \Omega_{ij}, \tag{4.107}$$

were $\Omega_{ij} = -\Omega_{ji}$ is an antisymmetric matrix.

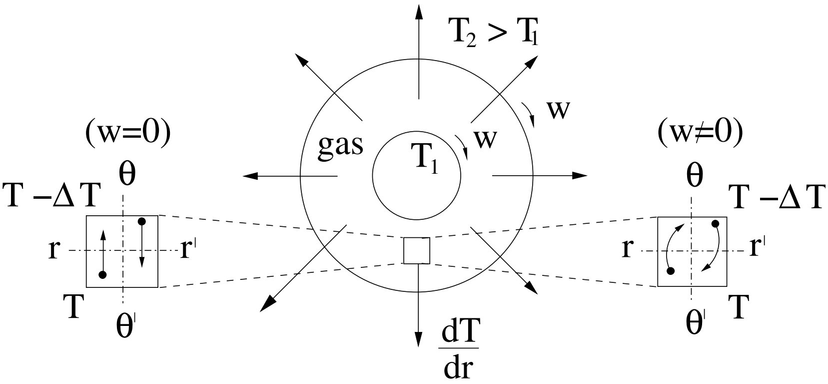

Fig. 4.2 Gas enclosed by two infinite concentric rotating cylindes.

In order to determine the constitutive equation for the heat flux vector one proceeds as follows. First, the balance equation for the heat flux vector (4.106) is written as

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[9] I. Müller, "On the frame dependence of stress and heat flux", *Arch. Rational Mech. Anal.* **45**, 241-250 (1972).

$$\begin{aligned}\mathcal{D}q_i + 2q_i\frac{\partial v_j}{\partial x_j} + \left(\frac{p}{\varrho}\delta_{ij} - \frac{p_{\langle ij\rangle}}{\varrho}\right)\frac{\partial p_{\langle jk\rangle}}{\partial x_k} + \frac{p}{\varrho}p_{\langle ik\rangle}\left(\frac{7}{2T}\frac{\partial T}{\partial x_k} - \frac{1}{p}\frac{\partial p}{\partial x_k}\right)\\ + \frac{9}{5}q_j\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} - \left(2W_{ij} - \frac{\partial v_{[i}}{\partial x_{j]}}\right)q_j + \frac{5}{2}\frac{k}{m}p\frac{\partial T}{\partial x_i} = -\frac{2}{3}\frac{1}{\tau_r}q_i,\end{aligned} \qquad (4.108)$$

by considering the constitutive equations for p_{ijk}, q_{ij} and Q_i given by (4.34) and $(4.40)_2$. Next, a method akin to the Maxwellian iteration procedure described in Section 4.2.2 is used. From the first iteration one obtains Fourier's law $(4.64)_2$, while from the second iteration it follows

$$q_i^{(2)} = -\lambda\left[\delta_{ij} + 3\tau_r\left(W_{ij} - \Omega_{ij}\right)\right]\frac{\partial T}{\partial x_j}, \qquad (4.109)$$

by using (4.107) and the result from exercise 4.23 (note that the first iterated value of the pressure deviator is given by $p^{(1)}_{\langle ij\rangle} = 0$).

Now by considering cylindrical coordinates (r, θ, z) and $T = T(r)$, one can rewrite the heat flux vector (4.109)—without the index relative to the iteration—in terms of the components as

$$q_r = -\lambda\frac{dT}{dr}, \qquad q_\theta = -3\lambda\tau_r\left(w - \omega\right)\frac{dT}{dr}. \qquad (4.110)$$

Above, it was introduced the axial vectors ω_k and w_k defined by $\Omega_{ij} = \varepsilon_{ikj}\omega_k$ and $W_{ij} = \varepsilon_{ikj}w_k$, respectively.

The interpretation of the above result is the following. First, consider that the cylinders are at rest—so that the system of reference is an inertial one—and fix the attention into a small area element of dimensions of a mean free path (see Figure 4.2). One verifies the existence of a radial heat flux due to the energy transfer from the molecules situated above and below the section rr'. If the cylinders are rotating, there exists a tangential heat flux which results from the energy transfer in the section $\theta\theta'$ as a consequence of a $\theta\theta'$ Coriolis acceleration acting on the molecules of the gas.

The ratio of the tangential and radial components of the heat flux vector reads

$$\frac{q_\theta}{q_r} = 3\tau_r\left(w - \omega\right). \qquad (4.111)$$

One infers from the above equation that the tangential component of the heat flux vector is very small to be detected experimentally, since τ_r is of the order of 10^{-10} s (see exercise 4.8 and Table 1.1) while the angular velocity of an ultracentrifuge is of the order of 10^5 rpm.

Exercises

4.23 Show that the following equality holds

$$\mathcal{D}\left(\frac{\partial T}{\partial x_i}\right)=\frac{\partial \mathcal{D}T}{\partial x_i}-\frac{\partial v_j}{\partial x_i}\frac{\partial T}{\partial x_j}.$$

4.24 Obtain the expressions for the heat flux vector (4.109) and (4.110).

4.5 Appendix

Without loss of generality one can orient the relative velocity $\mathbf{g}$ in the direction of the x_3-axis and write $\mathbf{g}'$ in spherical coordinates (g,χ,ε) where χ denotes the scattering angle and ε the azimuthal angle, i.e.,

$$(\mathbf{g})=g\begin{pmatrix}0\\0\\1\end{pmatrix},\qquad(\mathbf{g}')=g\begin{pmatrix}\sin\chi\cos\varepsilon\\ \sin\chi\sin\varepsilon\\ \cos\chi\end{pmatrix}.\tag{4.112}$$

The integration of the relative velocity $\mathbf{g}'$ with respect to the azimuthal angle ε yields

$$\int_0^{2\pi}g\begin{pmatrix}\sin\chi\cos\varepsilon\\ \sin\chi\sin\varepsilon\\ \cos\chi\end{pmatrix}d\varepsilon=2\pi\cos\chi\,g\begin{pmatrix}0\\0\\1\end{pmatrix}.\tag{4.113}$$

Now, by adopting the Cartesian notation, one can write the above equality as

$$\int_0^{2\pi}g_i'd\varepsilon=2\pi\cos\chi\,g_i.\tag{4.114}$$

Following the same methodology, the integration with respect to the azimuthal angle ε of the matrix elements $g_i'g_j'$ implies

$$\int_0^{2\pi}g^2\begin{pmatrix}\sin^2\chi\,\cos^2\varepsilon & \sin^2\chi\,\cos\varepsilon\,\sin\varepsilon & \sin\chi\,\cos\chi\,\cos\varepsilon\\ \sin^2\chi\,\cos\varepsilon\,\sin\varepsilon & \sin^2\chi\,\sin^2\varepsilon & \sin\chi\,\cos\chi\,\sin\varepsilon\\ \sin\chi\,\cos\chi\,\cos\varepsilon & \sin\chi\,\cos\chi\,\sin\varepsilon & \cos^2\chi\end{pmatrix}d\varepsilon$$
$$=g^2\begin{pmatrix}\pi\sin^2\chi & 0 & 0\\ 0 & \pi\sin^2\chi & 0\\ 0 & 0 & 2\pi\cos^2\chi\end{pmatrix}$$
$$=\pi\sin^2\chi g^2\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}+\pi(3\cos^2\chi-1)g^2\begin{pmatrix}0&0&0\\0&0&0\\0&0&1\end{pmatrix}.\tag{4.115}$$

Hence, by adopting the Cartesian notation for the above expression, one obtains

$$\int_0^{2\pi}g_i'g_j'd\varepsilon=\pi\sin^2\chi g^2\delta_{ij}+\pi(3\cos^2\chi-1)g_ig_j.\tag{4.116}$$

Chapter 5

Polyatomic Gases

5.1 Some Properties of Polyatomic Gases

The molecules of polyatomic gases have internal variables that are associated with their internal energy states, namely: (a) the rotational state, (b) the vibrational state, (c) the electronic state and (d) the nuclei state.

Monatomic and polyatomic gases differ from each other concerning the behaviors of the specific heat at constant volume c_v and the ratio of the coefficients of thermal conductivity and shear viscosity λ/μ. These two differences will be explained below.

At sufficiently high temperatures, the monatomic gases are treated as classical gases, and the specific heat at constant volume is practically a constant and given by $c_v = 3k/2m$. However, for polyatomic gases, the specific heat at constant volume is a function of the temperature.

In order to analyze the specific heat of diatomic gases, a schematic representation of c_v as function of T is shown in Figure 5.1. At low temperatures, where quantum effects are neglected, the specific heat of a diatomic gas is equal to the one of a monatomic gas, i.e., $c_v = 3k/2m$ and one says that the rotational and vibrational energies are still frozen. By increasing the temperature, the rotational modes are excited and the specific heat grows up to $c_v = 5k/2m$ where the rotational modes are completely excited. In the plateau corresponding to $c_v = 5k/2m$, the energy equipartition principle holds by considering three translational and two rotational degrees of freedom. The subsequent increase of the temperature excites the vibrational modes and the specific heat grows up to $c_v = 7k/2m$. The energy equipartition principle holds also in the plateau $c_v = 7k/2m$ where the vibrational modes are completely excited which corresponds to three translational, two rotational and two vibrational degrees of freedom.

The relationship λ/μ for monatomic gases is a constant since it is given by

$$\frac{\lambda}{\mu} = \frac{15}{4}\frac{k}{m} = \frac{5}{2}c_v^T, \tag{5.1}$$

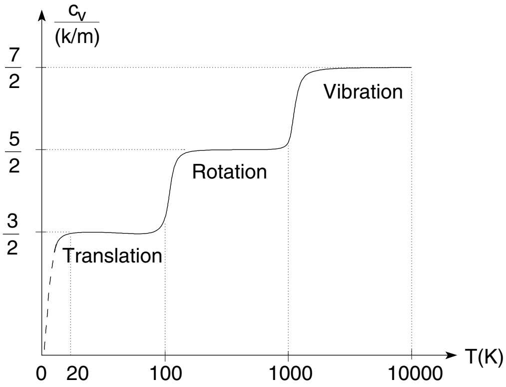

Fig. 5.1 Schematic representation of c_v versus T for H_2.

due to (3.51). Above, $c_v^T = (\partial \varepsilon^T / \partial T)_\varrho$ is the specific heat at a constant volume corresponding to the specific translational internal energy $\varepsilon^T = 3kT/2m$.

For polyatomic gases, the ratio λ/μ is a function of the temperature, and several formulas for this ratio were proposed in the literature.[1] The first proposal is due to Eucken who in 1913 wrote the thermal conductivity as a sum of two parts, namely,

$$\lambda = \mu \left(f_T c_v^T + f_I c_v^I \right). \tag{5.2}$$

The first term on the right-hand side of the above equation considers the transport of the translational energy, while the second one consider the transport of the energy of the internal variable. The specific heat at constant volume $c_v^I = (\partial \varepsilon^I / \partial T)_v$ refers to the specific energy of the internal variable ε^I. Furthermore, Eucken choose the values $f_T = 5/2$ and $f_I = 1$, such that (5.2) becomes

$$\frac{\lambda}{\mu} = \frac{5}{2} c_v^T + c_v^I = \frac{15}{4} \frac{k}{m} + c_v^I. \tag{5.3}$$

The above equation can be rewritten as

$$f_E = \frac{\lambda}{\mu c_v} = \left(\frac{9}{2 f_d} + 1 \right), \tag{5.4}$$

where f_E is known as Eucken's number. Moreover, f_d is the total number of the degrees of freedom of the molecule and

$$c_v = c_v^T + c_v^I = \frac{f_d}{2} \frac{k}{m}, \tag{5.5}$$

is the total specific heat at constant volume.

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[1] See e.g., Poling B.E., Prausnitz J.M. & O'Connell J.P.: *The Properties of Gases and Liquids* (McGraw-Hill, New York, 2000).

Eucken's number (5.5) depends only on the counting of the degrees of freedom of the molecules and is independent of the temperature. Hence, it has the same shortcomings as the models which are based on the energy equipartition principle, such as the evaluation of the specific heats of polyatomic gases.

Exercise

5.1 Experimental values of Eucken's number f_E at temperature of 300 K for nitrogen and methane gases are 1.95 and 1.81, respectively. Calculate the theoretical values of Eucken's number by assuming that $f_d = 5$ for nitrogen molecules and $f_d = 6$ for methane molecules and compare the results with the experimental values.

5.2 Semi-classical Model

The model which will be analyzed in this section was proposed independently by Wang Chang and Uhlenbeck and by de Boer in the middle of the last century and a joint paper[2] was published in 1964. It is a semi-classical model which assumes that the molecules may occupy only discrete states of internal energy, i.e., the internal degrees of freedom of the molecules are treated quantum-mechanically.

5.2.1 Boltzmann and Transfer Equations

The collision of two molecules of a polyatomic gas modify their translational energies as well as their internal energy states. Before a binary encounter, let $(\mathbf{c}, e_\alpha)$ denote the velocity and the internal energy in the quantum state α of a molecule and $(\mathbf{c}_1, e_{\alpha_1})$ denote the velocity and the internal energy in the quantum state α_1 of another molecule which participate in the collision process. After the collision, the velocities and internal energies are represented by $(\mathbf{c}', e_{\alpha'})$ and $(\mathbf{c}_1', e_{\alpha_1'})$.

The momentum and energy conservation laws for two molecules at collision reads

$$\mathbf{c}+\mathbf{c}_1 = \mathbf{c}'+\mathbf{c}_1', \quad \frac{1}{2}mc^2+e_\alpha+\frac{1}{2}mc_1^2+e_{\alpha_1} = \frac{1}{2}mc'^2+e_{\alpha'}+\frac{1}{2}mc_1'^2+e_{\alpha_1'}. \quad (5.6)$$

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[2] C. S. Wang Chang, G. E. Uhlenbeck & J. de Boer, "The heat conductivity and viscosity of polyatomic gases", in *Studies in Statistical Mechanics* Vol.II, pp. 243-268 (North-Holland, Amsterdam, 1964).

In terms of the relative velocities $\mathbf{g} = \mathbf{c}_1 - \mathbf{c}$ and $\mathbf{g}' = \mathbf{c}_1' - \mathbf{c}'$, the energy conservation law $(5.6)_2$ becomes

$$\mathcal{E} \equiv \frac{m}{4}g^2 + e_\alpha + e_{\alpha_1} = \frac{m}{4}g'^2 + e_{\alpha'} + e_{\alpha_1'}. \tag{5.7}$$

The state of the polyatomic gas in the μ-phase space will be described by a distribution function $f(\mathbf{x}, \mathbf{c}, \alpha, t)$ such that $f(\mathbf{x}, \mathbf{c}, \alpha, t)d\mathbf{x}\, d\mathbf{c}$ gives, at time t, the number of molecules in the quantum state α, in volume element within the range $\mathbf{x}$ and $\mathbf{x}+d\mathbf{x}$ and with linear velocity within the range $\mathbf{c}$ and $\mathbf{c}+d\mathbf{c}$.

In order to determine the Boltzmann equation, one considers the scattering process of two beams which before a collision are represented by the velocities and internal energy states of the molecules $(\mathbf{c}, e_\alpha)$ and $(\mathbf{c}_1, e_{\alpha_1})$ and after the encounter by $(\mathbf{c}', e_{\alpha'})$ and $(\mathbf{c}_1', e_{\alpha_1'})$. The collision is also characterized by a differential cross section, denoted by $\sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'}(\mathbf{g} \to \mathbf{g}')$. It is a function of the energy of the relative motion of the molecules $\mathcal{E}$ and represents the transition from the quantum states $\alpha\alpha_1$ to $\alpha'\alpha_1'$ of two colliding molecules whose relative velocities before and after the encounter are given by $\mathbf{g}$ and $\mathbf{g}'$, respectively.

The number of collisions per unit volume and time that changes the states of a molecular pair from $\{(\mathbf{c}, e_\alpha), (\mathbf{c}_1, e_{\alpha_1})\}$ to the states $\{(\mathbf{c}', e_{\alpha'}), (\mathbf{c}_1', e_{\alpha_1'})\}$ and with relative velocity within the element of solid angle $d\Omega$ is given by

$$f(\mathbf{x}, \mathbf{c}, \alpha, t) f(\mathbf{x}, \mathbf{c}_1, \alpha_1, t)\, \sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'}(\mathbf{g} \to \mathbf{g}')\, g\, d\Omega\, d\mathbf{c}\, d\mathbf{c}_1. \tag{5.8}$$

One may notice that the above expression is similar to the one for monatomic gases, which is given by (2.12). Hence, the total number of collisions per unit volume and time that annihilates molecules in the state $(\mathbf{c}, e_\alpha)$ of the μ-phase space is obtained by integrating over all velocities $\mathbf{c}_1$, over the solid angle $d\Omega$ and by summing over all quantum states $\alpha_1, \alpha', \alpha_1'$, yielding

$$\sum_{\alpha_1, \alpha', \alpha_1'} \int f(\mathbf{x}, \mathbf{c}, \alpha, t) f(\mathbf{x}, \mathbf{c}_1, \alpha_1, t)\, \sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'}(\mathbf{g} \to \mathbf{g}')\, g\, d\Omega\, d\mathbf{c}_1\, d\mathbf{c}. \tag{5.9}$$

Likewise, one can determine the number of collisions per unit volume and time that change the states of a molecular pair from $\{(\mathbf{c}', e_\alpha'), (\mathbf{c}_1', e_{\alpha_1'})\}$ to the states $\{(\mathbf{c}, e_\alpha), (\mathbf{c}_1, e_{\alpha_1})\}$ and with relative velocity within the element of solid angle $d\Omega$. As in the case of a monatomic gas, corresponding to a direct collision there exists a restitution collision which is obtained by reversing the direction of the relative velocities (see Figure 5.2). Hence, the number of collisions per unit volume and time that creates molecules in the state $(\mathbf{c}, e_\alpha)$ of the μ-phase space is given by

$$\sum_{\alpha_1, \alpha', \alpha_1'} \int f(\mathbf{x}, \mathbf{c}', \alpha', t) f(\mathbf{x}, \mathbf{c}_1', \alpha_1', t)\, \sigma_{\alpha'\alpha_1'}^{\alpha\alpha_1}(\mathbf{g}' \to \mathbf{g})\, g'\, d\Omega\, d\mathbf{c}_1'\, d\mathbf{c}'. \tag{5.10}$$

In order to modify the expression (5.10), it is easy to verify that the velocity transformations $\mathbf{g}' = \mathbf{c}_1' - \mathbf{c}'$ and $\mathbf{G}' = \mathbf{G} = (\mathbf{c}' + \mathbf{c}_1')/2$ imply that $d\mathbf{c}'d\mathbf{c}_1' = d\mathbf{G}d\mathbf{g}'$ and one may write

$$g\,d\mathbf{c}'\,d\mathbf{c}_1' = g\,d\mathbf{G}\,d\mathbf{g}' = g\,d\mathbf{G}\,g'^2\,dg'\,d\Omega = g'\,d\mathbf{G}\,d\mathbf{g} = g'\,d\mathbf{c}\,d\mathbf{c}_1, \tag{5.11}$$

thanks to the relationship $mg\,dg = mg'\,dg'$, which follows from (5.7) for fixed values of the internal energy of the molecules. Furthermore, a consequence of the time reversal invariance of the equations of motion (classical and quantum mechanically) is the validity of the principle of microscopic reversibility. The principle of microscopic reversibility asserts that the transition probabilities per unit time between the initial and final states are equal to each other, i.e., $\omega_{\alpha\alpha_1}^{\alpha'\alpha_1'}(\mathbf{g}\to\mathbf{g}') = \omega_{\alpha'\alpha_1'}^{\alpha\alpha_1}(\mathbf{g}'\to\mathbf{g})$. The differential cross sections are related to the flux of molecules which are scattered into the range of a solid angle $d\Omega$ per unit of the initial flux. Hence, the differential cross section is: **(a)** proportional to the transition probability times the number of final states in the solid angle $d\Omega$ within the volume element $d\mathbf{p}' = p'^2 d\Omega dp'$ around the final momentum $\mathbf{p}' = m\mathbf{g}'$ and **(b)** inversely proportional to the incoming flux which has relative velocity modulus g. On the basis of the above reasons, one may build the relationship

$$\frac{\sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'}(\mathbf{g}\to\mathbf{g}')}{\sigma_{\alpha'\alpha_1'}^{\alpha\alpha_1}(\mathbf{g}'\to\mathbf{g})} = \frac{\omega_{\alpha\alpha_1}^{\alpha'\alpha_1'}(\mathbf{g}\to\mathbf{g}')p'^2 d\Omega dp'/g}{\omega_{\alpha'\alpha_1'}^{\alpha\alpha_1}(\mathbf{g}'\to\mathbf{g})p^2 d\Omega dp/g'}, \tag{5.12}$$

which due to the relationship $gdp = g'dp'$ reduces to the following connection between the differential cross sections

$$p^2\sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'}(\mathbf{g}\to\mathbf{g}') = p'^2\sigma_{\alpha'\alpha_1'}^{\alpha\alpha_1}(\mathbf{g}'\to\mathbf{g}). \tag{5.13}$$

Hence, for non-degenerated polyatomic gases, it follows from (5.11) and (5.13) that

$$g\,\sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'}(\mathbf{g}\to\mathbf{g}')\,d\mathbf{c}_1\,d\mathbf{c} = g'\sigma_{\alpha'\alpha_1'}^{\alpha\alpha_1}(\mathbf{g}'\to\mathbf{g})\,d\mathbf{c}_1'\,d\mathbf{c}', \tag{5.14}$$

and (5.10) becomes

$$\sum_{\alpha_1,\alpha',\alpha_1'}\int f(\mathbf{x},\mathbf{c}',\alpha',t)f(\mathbf{x},\mathbf{c}_1',\alpha_1',t)\,\sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'}(\mathbf{g}\to\mathbf{g}')\,g\,d\Omega\,d\mathbf{c}_1\,d\mathbf{c}. \tag{5.15}$$

For spherical molecules, the differential cross section depends only on the energy $\mathcal{E}$ and on the scattering angle, so that the arguments $(\mathbf{g}\to\mathbf{g}')$ and $(\mathbf{g}'\to\mathbf{g})$ can be dropped out from the differential cross sections.

From the difference of (5.15) and (5.9) divided by $d\mathbf{c}$, one obtains the collision term of the Boltzmann equation. Indeed, by introducing the abbreviations $f_\alpha \equiv f(\mathbf{x},\mathbf{c},\alpha,t)$, $f_{\alpha_1} \equiv f(\mathbf{x},\mathbf{c}_1,\alpha_1,t)$, $f_{\alpha'} \equiv f(\mathbf{x},\mathbf{c}',\alpha',t)$ and

$f_{\alpha_1'} \equiv f(\mathbf{x}, \mathbf{c}_1', \alpha_1', t)$, the Boltzmann equation for the distribution function f_α becomes

$$\frac{\partial f_\alpha}{\partial t} + c_i \frac{\partial f_\alpha}{\partial x_i} + F_i \frac{\partial f_\alpha}{\partial c_i} = \sum_{\alpha_1, \alpha', \alpha_1'} \int \left(f_{\alpha'} f_{\alpha_1'} - f_\alpha f_{\alpha_1} \right) \sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'} \, g \, d\Omega d\mathbf{c}_1. \quad (5.16)$$

The transfer equation is obtained through the multiplication of the Boltzmann equation by an arbitrary function $\psi_\alpha \equiv \psi(\mathbf{x}, \mathbf{c}, \alpha, t)$, the integration over all values of $\mathbf{c}$ and addition over all internal states α. Hence, it follows

$$\begin{aligned} \frac{\partial}{\partial t} \left(\sum_\alpha \int \psi_\alpha f_\alpha d\mathbf{c} \right) + \frac{\partial}{\partial x_i} \left(\sum_\alpha \int \psi_\alpha f_\alpha c_i d\mathbf{c} \right) - \sum_\alpha \int \left[\frac{\partial \psi_\alpha}{\partial t} + c_i \frac{\partial \psi_\alpha}{\partial x_i} \right. \\ \left. + F_i \frac{\partial \psi_\alpha}{\partial c_i} \right] f_\alpha d\mathbf{c} = \sum_{\alpha' s} \int \psi_\alpha (f_{\alpha'} f_{\alpha_1'} - f_\alpha f_{\alpha_1}) \, \sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'} \, g \, d\Omega \, d\mathbf{c}_1 \, d\mathbf{c} \\ = \frac{1}{4} \sum_{\alpha' s} \int (\psi_\alpha + \psi_{\alpha_1} - \psi_{\alpha'} - \psi_{\alpha_1'})(f_{\alpha'} f_{\alpha_1'} - f_\alpha f_{\alpha_1}) \, \sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'} \, g \, d\Omega \, d\mathbf{c}_1 \, d\mathbf{c}. \quad (5.17) \end{aligned}$$

In the above equation, the sum over $\alpha' s$ corresponds to a sum over all values of of α, α_1, α' and α_1'. Moreover, to obtain the second equality, the following relationships are used, which are obtained by the changes $(\alpha, \mathbf{c}) \leftrightarrow (\alpha', \mathbf{c}')$ and $(\alpha, \mathbf{c}) \leftrightarrow (\alpha_1, \mathbf{c}_1)$:

$$\begin{aligned} & \sum_{\alpha' s} \int \psi_\alpha (f_{\alpha'} f_{\alpha_1'} - f_\alpha f_{\alpha_1}) \, \sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'} \, g \, d\Omega \, d\mathbf{c}_1 \, d\mathbf{c} \\ & = \sum_{\alpha' s} \int \psi_{\alpha'} (f_\alpha f_{\alpha_1} - f_{\alpha'} f_{\alpha_1'}) \, \sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'} \, g \, d\Omega \, d\mathbf{c}_1 \, d\mathbf{c} \\ & = \sum_{\alpha' s} \int \psi_{\alpha_1} (f_{\alpha'} f_{\alpha_1'} - f_\alpha f_{\alpha_1}) \, \sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'} \, g \, d\Omega \, d\mathbf{c}_1 \, d\mathbf{c}. \qquad (5.18) \end{aligned}$$

Exercises

5.2 Obtain the energy conservation law (5.7).

5.3 Show that the relationships (5.18) hold.

5.2.2 Macroscopic Description

The macroscopic fields associated with the mass density ϱ, momentum density ϱv_i and internal energy density $\varrho\varepsilon$ of a polyatomic gas are defined by

$$\varrho = \sum_\alpha \int m f_\alpha d\mathbf{c}, \qquad (5.19)$$

$$\varrho v_i = \sum_\alpha \int m c_i f_\alpha d\mathbf{c}, \tag{5.20}$$

$$\varrho \varepsilon = \sum_\alpha \int \left(\frac{1}{2} m C^2 + e_\alpha\right) f_\alpha d\mathbf{c}. \tag{5.21}$$

By applying the same methodology as the one used in Section 2.5.2, one obtains the following balance equations from the transfer equation (5.17):

(a) *Balance of mass density* ($\psi_\alpha = m$):

$$\frac{\partial \varrho}{\partial t} + \frac{\partial \varrho v_i}{\partial x_i} = 0, \tag{5.22}$$

(b) *Balance of momentum density* ($\psi_\alpha = m c_i$):

$$\frac{\partial \varrho v_i}{\partial t} + \frac{\partial}{\partial x_j}(\varrho v_i v_j + p_{ij}) = \varrho F_i, \tag{5.23}$$

(c) *Balance of energy density* ($\psi_\alpha = mC^2/2 + e_\alpha$):

$$\frac{\partial \varrho \varepsilon}{\partial t} + \frac{\partial}{\partial x_i}(\varrho \varepsilon v_i + q_i) + p_{ij}\frac{\partial v_j}{\partial x_i} = 0. \tag{5.24}$$

In the above equations, the pressure tensor p_{ij} and the heat flux vector q_i read

$$p_{ij} = \sum_\alpha \int m C_i C_j f_\alpha d\mathbf{c}, \qquad q_i = \sum_\alpha \int \left(\frac{1}{2} m C^2 + e_\alpha\right) C_i f_\alpha d\mathbf{c}. \tag{5.25}$$

(d) *Balance of entropy density* $\psi_\alpha = -k \ln \mathtt{b} f_\alpha$:

$$\frac{\partial \varrho s}{\partial t} + \frac{\partial}{\partial x_i}(\varrho s v_i + \varphi_i) = \varsigma, \tag{5.26}$$

where the entropy density ϱs, the entropy flux φ_i and the entropy production density ς are defined by

$$\varrho s = -k \sum_\alpha \int f_\alpha (\ln \mathtt{b} f_\alpha) d\mathbf{c}, \qquad \varphi_i = -k \sum_\alpha \int f_\alpha C_i (\ln \mathtt{b} f_\alpha) d\mathbf{c}, \tag{5.27}$$

$$\varsigma = \frac{k}{4} \sum_{\alpha' s} \int \ln \frac{f_{\alpha'} f_{\alpha'_1}}{f_\alpha f_{\alpha_1}} \left(\frac{f_{\alpha'} f_{\alpha'_1}}{f_\alpha f_{\alpha_1}} - 1\right) f_\alpha f_{\alpha_1} \, \sigma_{\alpha\alpha_1}^{\alpha'\alpha'_1} \, g \, d\Omega d\mathbf{c}_1 d\mathbf{c}. \tag{5.28}$$

One may infer that the entropy production density is a positive semi-definite quantity, i.e., $\varsigma \geqslant 0$, due the inequality $(x-1)\ln x \geqslant 0$ which holds for all $x > 0$.

Exercise

5.4 Obtain the the balance equations (5.24) and (5.26) from the transfer equation (5.17).

5.2.3 The Equilibrium Distribution Function

In equilibrium, the collision term of the Boltzmann equation (5.16) must vanish, so that

$$f_{\alpha'}^{(0)} f_{\alpha_1'}^{(0)} = f_{\alpha}^{(0)} f_{\alpha_1}^{(0)}, \qquad \text{or} \qquad \ln f_{\alpha'}^{(0)} + \ln f_{\alpha_1'}^{(0)} = \ln f_{\alpha}^{(0)} + \ln f_{\alpha_1}^{(0)}. \tag{5.29}$$

Hence, $\ln f_\alpha^{(0)}$ is a summational invariant, which according to Section 2.4, must be a combination of mass, momentum and energy, i.e.,

$$\ln f_\alpha^{(0)} = mA + m\mathbf{c}\cdot\mathbf{B} + \left(\frac{1}{2}mc^2 + e_\alpha\right)D, \tag{5.30}$$

where A, $\mathbf{B}$ and D are unknown coefficients.

Equation (5.30) can be rewritten as

$$f_\alpha^{(0)} = a\ \exp\left\{-b^\star\left[\frac{m}{2}(\mathbf{c}-\mathbf{u})^2 + e_\alpha\right]\right\}, \tag{5.31}$$

by introducing the relationships $mA = \ln a - \frac{1}{2}mb^\star u^2$, $\mathbf{B} = b^\star\mathbf{u}$ and $D = -b^\star$.

The substitution of the equilibrium distribution function (5.31) into the definitions of the basic fields (5.19) through (5.21) and the integration of the resulting equations lead to

$$\varrho = ma\left(\frac{2\pi}{mb^\star}\right)^{\frac{3}{2}} \sum_\alpha \exp(-b^\star e_\alpha), \qquad\qquad u_i = v_i, \tag{5.32}$$

$$\varepsilon = \frac{3}{2mb^\star} + \frac{1}{m}\frac{\sum_\alpha e_\alpha \exp(-b^\star e_\alpha)}{\sum_\alpha \exp(-b^\star e_\alpha)}. \tag{5.33}$$

One can infer from the above equations that it is not possible to obtain $b^\star$ explicitly. For this end, one makes use of the entropy density $(5.27)_1$, which in equilibrium reduces to

$$s\,|_E = -\frac{k}{\varrho}\sum_\alpha \int f_\alpha^{(0)}(\ln \mathsf{b} f_\alpha^{(0)})d\mathbf{c} = -\frac{k}{m}\left[\ln(a\mathsf{b}) - b^\star m\varepsilon\right]. \tag{5.34}$$

The differentiation of (5.34) yields

$$ds\,|_E = -\frac{k}{m}\left[\frac{da}{a} - mb^\star d\varepsilon - m\varepsilon db^\star\right], \tag{5.35}$$

while the differentiation of $(5.32)_1$ leads to

$$\frac{d\varrho}{\varrho} = \frac{da}{a} - m\varepsilon db^\star. \tag{5.36}$$

Hence, it follows from (5.35) and (5.36)

$$ds\,|_E = kb^\star\left\{d\varepsilon - \frac{1}{m\varrho b^\star}d\varrho\right\} \equiv \frac{1}{T}\left\{d\varepsilon - \frac{p}{\varrho^2}d\varrho\right\}, \tag{5.37}$$

where the second equality represents the Gibbs equation (2.149). Now, one identifies $kb^\star = 1/T$, and the distribution function (5.31) becomes

$$f_\alpha^{(0)} = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\frac{e^{-e_\alpha/kT}}{\mathcal{Z}}\,e^{-mC^2/2kT}, \qquad \text{where} \qquad \mathcal{Z} = \sum_\alpha e^{-e_\alpha/kT} \tag{5.38}$$

is the so-called partition function.

The specific internal energy (5.33) can be rewritten as a sum of two terms, one related with the translational energy of the molecules ε^T and another connected with the internal variables of the molecules ε^I, namely, $\varepsilon = \varepsilon^T + \varepsilon^I$, so that

$$\varepsilon^T = \frac{3}{2}\frac{k}{m}T = \frac{3}{2}\frac{p}{\varrho}, \qquad \varepsilon^I = \frac{1}{m\mathcal{Z}}\sum_\alpha e_\alpha e^{-e_\alpha/kT} = \frac{kT^2}{m}\frac{\partial \ln\mathcal{Z}}{\partial T}. \tag{5.39}$$

The corresponding specific heats at constant volume read

$$c_v^T = \left(\frac{\partial\varepsilon^T}{\partial T}\right)_v = \frac{3}{2}\frac{k}{m}, \tag{5.40}$$

$$c_v^I = \left(\frac{\partial\varepsilon^I}{\partial T}\right)_v = \frac{\partial}{\partial T}\left(\frac{kT^2}{m}\frac{\partial\ln\mathcal{Z}}{\partial T}\right) = \frac{1}{mkT^2}\left[\frac{1}{Z}\sum_\alpha e_\alpha^2 e^{-\epsilon_\alpha} - (m\varepsilon^I)^2\right]. \tag{5.41}$$

Note that the specific heat corresponding to the translational energy of the molecules does not depend on the temperature, but the one related to the internal variables of the molecules does.

It is important to determine the energy and the specific heat associated with one of the internal modes of a polyatomic molecule. The one which is easier to handle is connected with the vibrational energy of a diatomic molecule and will be analyzed below.

According to quantum mechanics, the non-degenerated energy levels of a vibrating one-dimensional harmonic oscillator with frequency ν is given by

$$e_\alpha = h\nu\left(\alpha+\frac{1}{2}\right), \tag{5.42}$$

where h is Planck's constant. In this case, the partition function reads

$$\mathcal{Z}=\sum_{\alpha=1}^{\infty}\exp\left[-\frac{h\nu}{kT}\left(\alpha+\frac{1}{2}\right)\right]=\frac{\exp(-\theta_V/2T)}{1-\exp(-\theta_V/T)}, \tag{5.43}$$

due to the relationship $\sum_{\alpha=0}^{\infty}x^\alpha = 1/(1-x)$ which is valid for all $|x|<1$. Above, a characteristic vibrational temperature $\theta_V = h\nu/k$ was introduced, and some typical values for gases of diatomic molecules are: $\theta_V = 6210$ K for H_2, $\theta_V = 3340$ K for N_2 and $\theta_V = 810$ K for Cl_2.

Once the partition function (5.43) is known it is easy to obtain from (5.41) the specific heat at constant volume corresponding to the vibrational energy, namely,

$$c_v^I = \frac{k}{m}\left[\frac{(\theta_V/2T)}{\sinh(\theta_V/2T)}\right]^2. \tag{5.44}$$

Note that the specific heat depends on the temperature. Here, two limiting cases are interesting to analyze: **(a)** when $T \ll \theta_V$, the specific heat tends to zero and **(b)** when $T \gg \theta_V$, (5.44) implies that $c_v^I = k/m$ which corresponds to the plateau where the energy equipartition principle holds.

Exercises

5.5 Obtain through integration (5.32) through (5.34).

5.6 Determine through differentiation (5.35) and (5.36).

5.7 Obtain the specific heat at constant volume related with the vibrational energy of a diatomic molecule (5.44) and show that mc_v^I/k versus $\theta_V/2T$ has the same behavior as the curve drawn in Figure 5.1 for the rise from the rotational plateau to the vibrational one.

5.2.4 Equilibrium States

The substitution of the equilibrium distribution function (5.38) into the Boltzmann equation (5.16) yields

$$f_\alpha^{(0)}\left\{\frac{\mathcal{D}\varrho}{\varrho}+\frac{\mathcal{D}T}{T}\left(\frac{mC^2}{2kT}+\frac{e_\alpha}{kT}-\frac{m(\varepsilon^T+\varepsilon^I)}{kT}\right)+\frac{m}{kT}C_i\mathcal{D}v_i+\left[\frac{m}{kT}C_j\frac{\partial v_j}{\partial x_i}\right.\right.$$
$$\left.\left.+\frac{1}{\varrho}\frac{\partial\varrho}{\partial x_i}-\frac{m}{kT}F_i+\frac{1}{T}\frac{\partial T}{\partial x_i}\left(\frac{mC^2}{2kT}+\frac{e_\alpha}{kT}-\frac{m(\varepsilon^T+\varepsilon^I)}{kT}\right)\right]C_i\right\}=0, \tag{5.45}$$

where $\mathcal{D} = \partial/\partial t + v_i\partial/\partial x_i$ is the material time derivative.

Equation (5.45) must be valid for all values of the peculiar velocity $\mathbf{C}$ and all values of the internal energy e_α. Hence, by following the same methodology of Section 2.6.2, one obtains

$$\mathcal{D}\varrho = 0, \qquad \varrho\mathcal{D}v_i + \frac{\partial p}{\partial x_i} = F_i, \qquad \mathcal{D}T = 0, \tag{5.46}$$

$$\frac{\partial T}{\partial x_i} = 0, \qquad \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} = 0. \tag{5.47}$$

Equations (5.46) represent the balance equations of an incompressible, non-viscous and non-heat conducting fluid. Furthermore, from equations (5.47), one may infer that a polyatomic gas is at equilibrium when the gradient of temperature, the velocity gradient deviator and the divergence of the velocity vanish, i.e.,

$$\frac{\partial T}{\partial x_i} = 0, \qquad \frac{\partial v_{\langle i}}{\partial x_{j\rangle}} = 0, \qquad \frac{\partial v_i}{\partial x_i} = 0. \tag{5.48}$$

Note that for monatomic gases the material time derivative of the temperature and the divergence of the velocity do not vanish at equilibrium and they are related to each other by (2.115).

Exercise

5.8 Obtain the constraints (5.46) and (5.47) from (5.45).

5.2.5 The Non-equilibrium Distribution Function

According to the analysis of the previous section, a polyatomic gas at equilibrium is characterized by (5.48) of vanishing temperature gradient, deviator of the velocity gradient and divergence of the velocity. Hence, these terms are the thermodynamic forces for a non-equilibrium state, and one may notice that besides the thermodynamic forces of monatomic gases there exists another one for polyatomic gases which corresponds to the divergence of the velocity. In this sense, there exists an additional thermodynamic flux connected with this scalar thermodynamic force. The corresponding thermodynamic flux adopted here is the dynamic pressure,[3] which is a non-equilibrium quantity previously introduced in Section 3.1. In terms of the distribution function, the trace and the traceless parts of the pressure tensor are defined by

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[3] Another equivalent description is to introduce a non-equilibrium energy density instead of a non-equilibrium pressure (see M. N. Kogan, "Molecular gas dynamics", *Ann. Rev. Fluid. Mech.,* **5** 383-404 (1973)).

$$\varpi + p = \frac{p_{rr}}{3} = \frac{1}{3}\sum_{\alpha}\int mC^2 f_\alpha d\mathbf{c}, \qquad p_{\langle ij\rangle} = \sum_{\alpha}\int mC_{\langle i}C_{j\rangle} f_\alpha d\mathbf{c}, \quad (5.49)$$

where ϖ, p and $p_{\langle ij\rangle}$ denote the dynamic pressure, the hydrostatic pressure and the pressure deviator, respectively.

In Section 5.2.3, the specific internal energy was written as a sum of one term connected with the translational energy of the molecules and another one with the internal variable of the molecules. Here, a similar decomposition is adopted for the heat flux vector by splitting it as a sum of a translational heat flux vector q_i^T and a heat flux vector of the internal variable q_i^I. In terms of the distribution function, they are given by

$$q_i^T = \sum_{\alpha}\int \frac{1}{2} mC^2 C_i f_\alpha d\mathbf{c}, \qquad q_i^I = \sum_{\alpha}\int e_\alpha C_i f_\alpha d\mathbf{c}. \quad (5.50)$$

In order determine the transport coefficients of a polyatomic gas, the Chapman–Enskog–Grad combined method will be used (see Section 4.3). For that end, one has to determine a non-equilibrium distribution function for a polyatomic gas similar to Grad's distribution function. Here, it is supposed that the basic fields are the 17 scalar fields: mass density ϱ, hydrodynamic velocity v_i, specific internal energy ε, pressure deviator $p_{\langle ij\rangle}$, dynamic pressure ϖ, translational heat flux vector q_i^T and heat flux vector of the internal variable q_i^I. By writing the non-equilibrium distribution function as

$$f_\alpha = f_\alpha^{(0)}\left(a^* + a_i^* C_i + a_{ij}^* C_i C_j + a_{rri}^* C^2 C_i + a' e_\alpha + a_i' e_\alpha C_i\right), \quad (5.51)$$

one has 17 scalar coefficients—namely, a^*, a_i^*, a_{ij}^*, a_{rri}^*, a' and a_i'—to be determined from the definitions of the basic fields. Indeed, the insertion of (5.51) into the definitions of the 17 basic fields (5.19), (5.20), (5.21), (5.49) and (5.50) yields

$$f_\alpha = f_\alpha^{(0)}\Bigg\{1 + \frac{p_{\langle ij\rangle}}{2\varrho}\left(\frac{m}{kT}\right)^2 C_i C_j + \frac{\varpi}{p}\left[\frac{mC^2}{2kT} - \frac{3}{2} - \frac{3k}{2mc_v^I}\left(\frac{e_\alpha - m\varepsilon^I}{kT}\right)\right]$$
$$+ \frac{2}{5}\frac{q_i^T}{\varrho}\left(\frac{m}{kT}\right)^2\left[\frac{mC^2}{2kT} - \frac{5}{2}\right] C_i + \frac{2}{3}\frac{q_i^I}{\varrho}\left(\frac{m}{kT}\right)^2 \frac{c_v^T}{c_v^I}\left[\frac{e_\alpha - m\varepsilon^I}{kT}\right] C_i\Bigg\}, \quad (5.52)$$

after the integration of the resulting equations over all values of $\mathbf{c}$ and the summation over all values of α. Expression (5.52) is Grad's distribution function for the 17 basic fields.

Exercise

5.9 Obtain the non-equilibrium distribution function (5.52) from the representation (5.51) by using the procedure described above.

5.2.6 The Laws of Navier–Stokes and Fourier

By following the Chapman–Enskog–Grad combined method, the insertion of the equilibrium distribution function (5.38) into the left-hand side of the Boltzmann equation (5.16) and Grad's distribution function (5.52) into its right-hand side leads to

$$f_\alpha^{(0)}\left\{\frac{\mathcal{D}\varrho}{\varrho}+\frac{\mathcal{D}T}{T}\left(\frac{mC^2}{2kT}+\frac{e_\alpha}{kT}-\frac{m(\varepsilon^T+\varepsilon^I)}{kT}\right)+\frac{m}{kT}C_i\mathcal{D}v_i+\left[\frac{1}{\varrho}\frac{\partial\varrho}{\partial x_i}\right.\right.$$
$$\left.\left.+\frac{1}{T}\frac{\partial T}{\partial x_i}\left(\frac{mC^2}{2kT}+\frac{e_\alpha}{kT}-\frac{m(\varepsilon^T+\varepsilon^I)}{kT}\right)+\frac{m}{kT}C_j\frac{\partial v_j}{\partial x_i}-\frac{m}{kT}F_i\right]C_i\right\}=\mathsf{I}_\alpha. \quad (5.53)$$

The linearized term I_α—which represents the right-hand side of the Boltzmann equation and is a function of thermodynamic fluxes $p_{\langle ij\rangle}$, ϖ, q_i^T and q_i^I—reads

$$\mathsf{I}_\alpha=\frac{p_{\langle rs\rangle}}{2\varrho}\left(\frac{m}{kT}\right)^2\mathcal{I}_\alpha\left[C_{\langle r}C_{s\rangle}\right]+\frac{\varpi}{p}\mathcal{I}_\alpha\left[\frac{mC^2}{2kT}-\frac{3}{2}-\frac{c_v^T}{c_v^I}\left(\frac{e_\alpha-m\varepsilon^I}{kT}\right)\right]$$
$$+\frac{2}{5}\frac{q_r^T}{\varrho}\left(\frac{m}{kT}\right)^2\mathcal{I}_\alpha\left[\left(\frac{mC^2}{2kT}-\frac{5}{2}\right)C_r\right]+\frac{2}{3}\frac{q_r^I}{\varrho}\left(\frac{m}{kT}\right)^2\frac{c_v^T}{c_v^I}\mathcal{I}_\alpha\left[\left(\frac{e_\alpha-m\varepsilon^I}{kT}\right)C_r\right]. \quad (5.54)$$

Above, all non-linear terms in the thermodynamic fluxes were neglected and introduced the abbreviation for any arbitrary function $\phi_\alpha\equiv\phi(\mathbf{x},\mathbf{c},\alpha,t)$:

$$\mathcal{I}_\alpha\left[\phi_\alpha\right]=\sum_{\alpha_1,\alpha',\alpha_1'}\int f_\alpha^{(0)}f_{\alpha_1}^{(0)}\left(\phi_{\alpha_1'}+\phi_{\alpha'}-\phi_{\alpha_1}-\phi_\alpha\right)\sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'}\,g\,d\Omega d\mathbf{c}_1. \quad (5.55)$$

By following a similar procedure as the one applied to obtain the right-hand side of the transfer equation (5.17), it is easy to show that

$$\sum_\alpha\int\psi_\alpha\mathcal{I}_\alpha[\phi_\alpha]d\mathbf{c}=\frac{1}{4}\sum_\alpha\int\left(\psi_{\alpha_1}+\psi_\alpha-\psi_{\alpha_1'}-\psi_{\alpha'}\right)\mathcal{I}_\alpha[\phi_\alpha]d\mathbf{c}. \quad (5.56)$$

The multiplication of (5.54) successively by m, mc_i and $(\frac{1}{2}mC^2+e_\alpha)$, the integration over all values of $\mathbf{c}$ and the summation over all values of α of the resulting equations lead to the field equations of an Eulerian fluid, namely,

$$\mathcal{D}\varrho+\varrho\frac{\partial v_i}{\partial x_i}=0,\qquad \varrho\mathcal{D}v_i+\frac{\partial p}{\partial x_i}=\varrho F_i,\qquad \varrho c_v\mathcal{D}T+p\frac{\partial v_i}{\partial x_i}=0. \quad (5.57)$$

Now, the material time derivatives of the mass density ϱ, hydrodynamic velocity v_i and temperature T are eliminated from (5.54) through the use of (5.57), yielding

$$f_\alpha^{(0)}\left\{\frac{m}{kT}C_rC_s\frac{\partial v_{\langle r}}{\partial x_{s\rangle}}+\frac{k}{m}\frac{1}{c_v}\left[\frac{c_v^I}{c_v^T}\left(\frac{mC^2}{2kT}-\frac{3}{2}\right)-\frac{e_\alpha-m\varepsilon^I}{kT}\right]\frac{\partial v_r}{\partial x_r}\right.$$
$$\left.+\left[\frac{mC^2}{2kT}-\frac{5}{2}+\frac{e_\alpha-m\varepsilon^I}{kT}\right]\frac{C_r}{T}\frac{\partial T}{\partial x_r}\right\}=\mathsf{I}_\alpha. \tag{5.58}$$

From the above equation, the constitutive equations for the pressure deviator $p_{\langle ij\rangle}$, dynamic pressure ϖ and heat flux vectors q_i^T and q_i^I will be obtained as well as the corresponding transport coefficients of shear and bulk viscosities and thermal conductivity.

In order to determine the constitutive equation for the pressure deviator, one multiplies (5.58) by $mC_{\langle i}C_{j\rangle}/nkT$ and obtains

$$2\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}=\frac{4p_{\langle ij\rangle}}{5\pi^3\mathcal{Z}^2}\frac{m^5}{(2kT)^6}\sum_{\alpha' s}\int\exp\left[-\frac{m}{2kT}(C^2+C_1^2)-\frac{e_\alpha+e_{\alpha_1}}{kT}\right]$$
$$\times\left(C^{1'}_{\langle r}C^{1'}_{s\rangle}+C'_{\langle r}C'_{s\rangle}-C^{1}_{\langle r}C^{1}_{s\rangle}-C_{\langle r}C_{s\rangle}\right)^2 g\,\sigma_{\alpha\alpha_1}^{\alpha'\alpha'_1}\,d\Omega d\mathbf{c}_1\,d\mathbf{c}$$
$$=-\frac{p_{\langle ij\rangle}}{5\pi^3\mathcal{Z}^2}\frac{m^5}{(2kT)^6}\sum_{\alpha' s}\int\exp\left[-\frac{m}{2kT}\left(2G^2+\frac{g^2}{2}\right)-\frac{e_\alpha+e_{\alpha_1}}{kT}\right]$$
$$\times\left(g'_{\langle r}g'_{s\rangle}-g_{\langle r}g_{s\rangle}\right)^2 g\,\sigma_{\alpha\alpha_1}^{\alpha'\alpha'_1}\,d\Omega\,d\mathbf{g}\,d\mathbf{G}, \tag{5.59}$$

by integrating the resulting equation over all values of $\mathbf{c}$ and by summing over all values of α. In the first equality of the above equation, (5.56) and (4.75) were used, while in the second one, the integration variables $(\mathbf{C},\mathbf{C}_1)\rightarrow(\mathbf{g},\mathbf{G})$ were changed. Now, by taking into account (3.34) and (3.35) and the relationship $\mathbf{g}\cdot\mathbf{g}'=g\,g'\cos\chi$, one can integrate (5.59) with respect to $\mathbf{G}$ and the angular coordinates of $\mathbf{g}$. Hence, it follows the constitutive equation for the pressure deviator as function of the velocity gradient deviator, i.e.,

$$p_{\langle ij\rangle}=-2\mu\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \tag{5.60}$$

where the coefficient of shear viscosity reads

$$\mu=\frac{5}{8}\sqrt{\pi kTm}\mathcal{Z}^2\left\{\sum_{\alpha' s}\int\left[\gamma^4\sin^2\chi-\gamma^2\Delta\epsilon\,\sin^2\chi+\frac{1}{3}(\Delta\epsilon)^2\right]\right.$$
$$\left.\times\;e^{-(\gamma^2+\epsilon_\alpha+\epsilon_{\alpha_1})}\gamma^3\sigma_{\alpha\alpha_1}^{\alpha'\alpha'_1}\,d\Omega d\gamma\right\}^{-1}. \tag{5.61}$$

In the expression for the coefficient of shear viscosity (5.61), the dimensionless quantities were introduced:

$$\gamma^2 = \frac{mg^2}{4kT}, \qquad \gamma'^2 = \frac{mg'^2}{4kT}, \tag{5.62}$$

$$\epsilon_\alpha = \frac{e_\alpha}{kT}, \quad \epsilon_{\alpha_1} = \frac{e_{\alpha_1}}{kT}, \quad \epsilon_{\alpha'} = \frac{e_{\alpha'}}{kT}, \quad \epsilon_{\alpha'_1} = \frac{e_{\alpha'_1}}{kT}. \tag{5.63}$$

Furthermore, the dimensionless modulus of the relative velocity γ' was replaced by the relationship that follows from (5.7), namely,

$$\gamma'^2 = \gamma^2 - \varDelta\epsilon, \qquad \text{where} \qquad \varDelta\epsilon \equiv \epsilon_{\alpha'} + \epsilon_{\alpha'_1} - \epsilon_\alpha - \epsilon_{\alpha_1}. \tag{5.64}$$

The constitutive equation for the dynamic pressure is obtained by using the same methodology employed for the determination of the pressure deviator. The multiplication of (5.58) by the expression

$$\left[\frac{mC^2}{2kT} - \frac{3}{2} - \frac{c_v^T}{c_v^I}\left(\frac{e_\alpha - m\varepsilon^I}{kT}\right)\right],$$

the integration over all values of **c** and the summation over all values of α of the resulting equation leads to

$$\varpi = -\eta \frac{\partial v_i}{\partial x_i}, \tag{5.65}$$

where the coefficient of bulk viscosity is given by

$$\eta = \frac{1}{2}\left(\frac{c_v^I}{c_v}\right)^2 \sqrt{\pi k T m}\,\mathcal{Z}^2 \left\{ \sum_{\alpha' s} \int (\varDelta\epsilon)^2\, e^{-(\gamma^2 + \epsilon_\alpha + \epsilon_{\alpha_1})} \gamma^3 \sigma_{\alpha\alpha_1}^{\alpha'\alpha'_1}\, d\varOmega d\gamma \right\}^{-1}. \tag{5.66}$$

Now, by combining the two constitutive equations (5.60) and (5.65), one obtains the Navier–Stokes law, namely,

$$p_{ij} = \left(p - \eta \frac{\partial v_r}{\partial x_r}\right)\delta_{ij} - 2\mu \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}. \tag{5.67}$$

For the determination of Fourier's law, one multiplies (5.58) by

$$\left(\frac{mC^2}{2kT} - \frac{5}{2}\right) C_i \qquad \text{and} \qquad \left(\frac{e_\alpha - m\varepsilon^I}{kT}\right) C_i,$$

and by applying the same procedure described above, one obtains the following algebraic system of equations for the heat flux vectors q_i^T and q_i^I:

$$\frac{5}{3} c_v^T \frac{\partial T}{\partial x_i} = -\frac{4}{15} \varUpsilon_1\, q_i^T - \frac{4}{9}\frac{c_v^T}{c_v^I} \varUpsilon_2\, q_i^I, \tag{5.68}$$

$$c_v^I \frac{\partial T}{\partial x_i} = -\frac{4}{15} \widetilde{\varUpsilon}_2\, q_i^T - \frac{4}{9}\frac{c_v^T}{c_v^I} \varUpsilon_3\, q_i^I. \tag{5.69}$$

where $\varUpsilon_1$, $\varUpsilon_2$, $\widetilde{\varUpsilon}_2$ and $\varUpsilon_3$ represent the integrals:

$$\varUpsilon_1 = \frac{4}{\sqrt{\pi kTm}}\frac{1}{\mathcal{Z}^2}\sum_{\alpha' s}\int\left[\gamma^4\sin^2\chi - \gamma^2\Delta\epsilon\,\sin^2\chi + \frac{11}{8}(\Delta\epsilon)^2\right]$$
$$\times\; e^{-(\gamma^2+\epsilon_\alpha+\epsilon_{\alpha_1})}\gamma^3\sigma_{\alpha\alpha_1}^{\alpha'\alpha'_1}\,d\Omega d\gamma, \tag{5.70}$$

$$\varUpsilon_2 = \widetilde{\varUpsilon}_2 = -\frac{5}{2}\frac{1}{\sqrt{\pi kTm}}\frac{1}{\mathcal{Z}^2}\sum_{\alpha' s}\int(\Delta\epsilon)^2\,e^{-(\gamma^2+\epsilon_\alpha+\epsilon_{\alpha_1})}\gamma^3\sigma_{\alpha\alpha_1}^{\alpha'\alpha'_1}\,d\Omega d\gamma, \tag{5.71}$$

$$\varUpsilon_3 = \frac{1}{\sqrt{\pi kTm}}\frac{1}{\mathcal{Z}^2}\sum_{\alpha' s}\int\left\{\left[\gamma'_r(\epsilon_{\alpha'_1}-\epsilon_{\alpha'}) - \gamma_r(\epsilon_{\alpha_1}-\epsilon_\alpha)\right]^2 + \frac{3}{2}(\Delta\epsilon)^2\right\}$$
$$\times\; e^{-(\gamma^2+\epsilon_\alpha+\epsilon_{\alpha_1})}\gamma^3\sigma_{\alpha\alpha_1}^{\alpha'\alpha'_1}\,d\Omega d\gamma. \tag{5.72}$$

By solving the system of equations (5.68) and (5.69), it follows the constitutive equations for the translational heat flux vector q_i^T and for the heat flux vector of the internal variable q_i^I, namely,

$$q_i^T = -\lambda^T\frac{\partial T}{\partial x_i}, \qquad q_i^I = -\lambda^I\frac{\partial T}{\partial x_i} \tag{5.73}$$

where the coefficients of thermal conductivity λ^T and λ^I read

$$\lambda^T = \frac{25c_v^T}{4\varUpsilon_1}\left(1 - \frac{3c_v^I\varUpsilon_2}{5c_v^T\varUpsilon_3}\right)\Bigg/\left(1 - \frac{\varUpsilon_2\widetilde{\varUpsilon}_2}{\varUpsilon_1\varUpsilon_3}\right), \tag{5.74}$$

$$\lambda^I = \frac{9(c_v^I)^2}{4c_v^T\varUpsilon_3}\left(1 - \frac{5c_v^T\widetilde{\varUpsilon}_2}{3c_v^I\varUpsilon_1}\right)\Bigg/\left(1 - \frac{\varUpsilon_2\widetilde{\varUpsilon}_2}{\varUpsilon_1\varUpsilon_3}\right). \tag{5.75}$$

The total heat flux vector is the sum of the translational and of the internal variable heat flux vectors, so that Fourier's law becomes

$$q_i = -(\lambda^T + \lambda^I)\frac{\partial T}{\partial x_i} = -\lambda\frac{\partial T}{\partial x_i}. \tag{5.76}$$

From (5.74) and (5.75), one obtains that the coefficient of thermal conductivity λ is given by

$$\lambda = \frac{25c_v^T}{4\varUpsilon_1}\left[1 - \frac{3}{5}\frac{c_v^I}{c_v^T}\frac{\varUpsilon_2+\widetilde{\varUpsilon}_2}{\varUpsilon_3} + \frac{9}{25}\left(\frac{c_v^I}{c_v^T}\right)^2\frac{\varUpsilon_1}{\varUpsilon_3}\right]\Bigg/\left(1 - \frac{\varUpsilon_2\widetilde{\varUpsilon}_2}{\varUpsilon_1\varUpsilon_3}\right). \tag{5.77}$$

Exercises

5.10 Obtain the relationship (5.56).

5.11 Determine the coefficients of shear viscosity (5.61) and bulk viscosity (5.66).

5.12 Obtain the system of algebraic equations (5.68) and (5.69). Hint: use the relationship (4.79).

5.2.7 A Limiting Case

One interesting case to analyze is when the exchange from the translational energy to the energy of the internal variable of the molecules proceeds very slowly. In this case, the following conditions hold:

$$g = g', \qquad \varDelta\epsilon = 0, \qquad \epsilon_{\alpha_1'} - \epsilon_{\alpha'} \approx \epsilon_{\alpha_1} - \epsilon_\alpha. \tag{5.78}$$

Moreover, the sums over the states α' and α_1' of the differential cross section is only a function of the relative velocity and of the scattering angle, i.e.,

$$\sum_{\alpha',\alpha_1'} \sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'}\, d\varOmega \equiv \sigma(\chi, g)\sin\chi d\chi d\varepsilon = b\, db\, d\varepsilon. \tag{5.79}$$

In the last equality above, the relationship (1.109) was used.

In this limiting case, the coefficient of shear viscosity (5.61) becomes

$$\mu = \frac{5}{8}\sqrt{\pi kTm}\mathcal{Z}^2\left\{\sum_{\alpha,\alpha_1}\int e^{-(\gamma^2+\epsilon_\alpha+\epsilon_{\alpha_1})}\gamma^7 \mathrm{sen}^2\chi\, b\, db\, d\varepsilon\, d\gamma\right\}^{-1}, \tag{5.80}$$

so that the sum over all values of α and α_1 and the integration over all values of the azimuthal angle ε leads to

$$\mu = \frac{5}{16}\frac{1}{\varOmega^{(2,2)}}\sqrt{\frac{kTm}{\pi}}. \tag{5.81}$$

where $\varOmega^{(l,r)}$ denote the collision integral (3.40). One may note that (5.81) for the coefficient of shear viscosity is the same as the one for a monatomic gas $(3.50)_1$.

Likewise, one can obtain from (5.71) that $\varUpsilon_2 = \widetilde{\varUpsilon}_2 = 0$, while (5.70) and (5.72) become

$$\varUpsilon_1 = \frac{4}{\sqrt{\pi kTm}}\frac{1}{\mathcal{Z}^2}\sum_{\alpha,\alpha_1}\int e^{-(\gamma^2+\epsilon_\alpha+\epsilon_{\alpha_1})}\gamma^7\mathrm{sen}^2\chi\, b\, db\, d\varepsilon\, d\gamma$$

$$= 8\sqrt{\frac{\pi}{kTm}}\varOmega^{(2,2)}, \tag{5.82}$$

$$\varUpsilon_3 = \frac{2}{\sqrt{\pi kTm}}\frac{1}{\mathcal{Z}^2}\sum_{\alpha,\alpha_1}\int e^{-(\gamma^2+\epsilon_\alpha+\epsilon_{\alpha_1})}\gamma^5(\epsilon_{\alpha_1}-\epsilon_\alpha)^2(1-\cos\chi) b\, db\, d\varepsilon\, d\gamma$$

$$= 8\frac{m}{k}c_v^I\sqrt{\frac{\pi}{kTm}}\varOmega^{(1,1)}, \tag{5.83}$$

respectively. Hence, the coefficient of thermal conductivity (5.77) reduces to

$$\lambda = \frac{25}{32}\sqrt{\frac{kTm}{\pi}}\frac{c_v^T}{\Omega^{(2,2)}} + \frac{3}{16}\sqrt{\frac{kTm}{\pi}}\frac{c_v^I}{\Omega^{(1,1)}} = \left(\frac{5}{2}\,c_v^T + \frac{3}{5}\frac{\Omega^{(2,2)}}{\Omega^{(1,1)}}\,c_v^I\right)\mu. \quad (5.84)$$

The second equality above represents Eucken's formula (5.2) with

$$f_T = \frac{5}{2}, \qquad \text{and} \qquad f_I = \frac{3}{5}\frac{\Omega^{(2,2)}}{\Omega^{(1,1)}}. \quad (5.85)$$

For the hard-sphere potential, the collision integrals become $\Omega^{(1,1)} = \mathsf{d}^2/2$ and $\Omega^{(2,2)} = \mathsf{d}^2$, so that $f_I = 1.2$. For the centers of repulsion potential, the collision integral $\Omega^{(2,2)}$ is given by (3.56), while

$$\Omega^{(1,1)} = \left(\frac{\kappa}{2kT}\right)^{\frac{2}{\nu-1}} A_1(\nu)\frac{1}{2}\Gamma\left(\frac{3\nu-5}{\nu-1}\right). \quad (5.86)$$

In this case, one obtains that

$$f_I = \frac{3}{5}\frac{A_2(\nu)}{A_1(\nu)}\frac{\Gamma\left(\frac{4\nu-6}{\nu-1}\right)}{\Gamma\left(\frac{3\nu-5}{\nu-1}\right)}. \quad (5.87)$$

For Maxwellian molecules $\nu = 5$ and by using (1.122), it follows that $f_I \approx 1.55$.

One may rewrite (5.84) as

$$\frac{\lambda}{\mu} = \frac{5}{2}c_v^T + \frac{\varrho D}{\mu}c_v^I, \qquad \text{where} \qquad D = \frac{3}{16n}\sqrt{\frac{kT}{m\pi}}\frac{1}{\Omega^{(1,1)}} \quad (5.88)$$

is the self-diffusion coefficient (see $(8.153)_1$). The ratio λ/μ given by $(5.88)_1$ can be interpreted as a sum of two contributions: one owing to the transfer of translational energy of the molecules and another due to the transfer of internal energy of the molecules and associated to a diffusion process.

The dynamic pressure is responsible for the relaxation processes that correspond to the transfer of the translational and internal energies of the molecules. In the limiting case when the exchange from the translational energy to the energy of the internal variable of the molecules proceeds very slowly, no information about the dynamic pressure may be obtained, once the term $\frac{\varpi}{p}\mathcal{I}_\alpha\left[\frac{mC^2}{2kT} - \frac{3}{2} - \frac{c_v^T}{c_v^I}\left(\frac{e_\alpha - m\varepsilon^I}{kT}\right)\right]$ in (5.54) vanishes when the relationships (5.78) hold. Note also that $\eta \to \infty$, when $\Delta\epsilon \to 0$.

Exercises

5.13 Determine (5.82) and (5.83).

5.14 Obtain the relationship $(5.88)_1$.

5.3 Classical Model

In this section, a model for a polyatomic gas will be analyzed, in which the internal states of the molecules are treated classically. A classical representation of the internal states of the molecules may be considered, a good approximation for the investigation of the transport properties of polyatomic gases of heavy molecules over a wide range of the temperature. The model investigated here is based on a work proposed by Taxman[4], and an application of this theory will be described in Section 5.4 where the internal states of the molecules are represented by their rotational energy.

5.3.1 Basic Fields

The internal energy of a molecule will be represented by e_ω, where ω stands for the classical internal states of a molecule like its rotational energy with respect to the molecular center of mass.

Some definitions and results of Section 5.2 can be used here by replacing the sums by integrals, i.e., for any discrete function $\mathcal{F}_\alpha$, one may replace it by a continuous function $\mathcal{F}$ according to $\sum_\alpha \mathcal{F}_\alpha \to \int \mathcal{F} d\omega$. Furthermore, the distribution function is written as $f \equiv f(\mathbf{x}, \mathbf{c}, \omega, t)$ and the fields of mass density (5.19), momentum density (5.20), internal energy density (5.21), pressure tensor (5.49) and heat flux vectors (5.50) read

$$\varrho = \int m f d\mathbf{c}\, d\omega, \quad \varrho v_i = \int m c_i f d\mathbf{c}\, d\omega, \quad \varrho\varepsilon = \int \left(\frac{1}{2}mC^2 + e_\omega\right) f d\mathbf{c}\, d\omega, \tag{5.89}$$

$$\varpi + p = \frac{1}{3}\int mC^2 f d\mathbf{c}\, d\omega, \qquad p_{\langle ij\rangle} = \int mC_{\langle i}C_{j\rangle} f d\mathbf{c}\, d\omega, \tag{5.90}$$

$$q_i^T = \int \frac{1}{2}mC^2 C_i f d\mathbf{c}\, d\omega, \qquad q_i^I = \int e_\omega C_i f d\mathbf{c}\, d\omega. \tag{5.91}$$

In this case, the equilibrium distribution function and the partition function (5.38) become

$$f^{(0)} = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \frac{e^{-e_\omega/kT}}{\mathcal{Z}}\, e^{-mC^2/2kT}, \qquad \text{and} \qquad \mathcal{Z} = \int e^{-e_\omega/kT} d\omega. \tag{5.92}$$

Exercise

5.15 Assume that the internal energy state of a molecule corresponds to its rotational energy , i.e., $e_\omega = Iw^2/2$, where I denotes the moment of inertia

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[4] N. Taxman, “Classical theory of transport phenomena in dilute polyatomic gases”, *Phys. Rev.*, **110** 1235-1239 (1958).

of the molecule and $w = \sqrt{\mathbf{w}\cdot\mathbf{w}}$ represents the modulus of the rotational velocity with respect to its center of mass. Show that the equilibrium distribution function $(5.92)_1$ and the specific internal energy $(5.39)_2$ corresponding to the rotational energy are given by

$$f^{(0)} = n\left(\frac{\sqrt{mI}}{2\pi kT}\right)^3 e^{-(mC^2+Iw^2)/2kT}, \qquad \varepsilon^I = \frac{3}{2}\frac{k}{m}T,$$

respectively. Note that in this case the rotational specific heat c_v^I does not depend on the temperature.

5.3.2 Boltzmann and Transfer Equations

The Boltzmann equation does not follow in a straightforward manner as the one presented in Section 5.2.1 because generally classical inverse collisions do not exist. This can be understood by the schematic representation in Figure 5.2, where a direct ($\mathbf{g} \to \mathbf{g}'$) and a restitution ($-\mathbf{g}' \to -\mathbf{g}$) collision are represented for the semi-classical case and a direct ($\mathbf{g} \to \mathbf{g}'$) and a restitution ($\mathbf{g}^* \to \mathbf{g}$) collision are shown for the classical case.

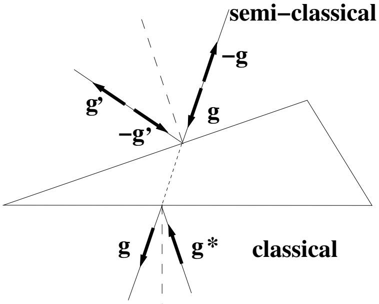

Fig. 5.2 Schematic representation of a direct and a restitution collision in the semi-classical and classical cases.

In order to obtain the Boltzmann equation, one may start with the expressions (5.9) and (5.10) by replacing

$$\sum_{\alpha_1,\alpha',\alpha_1'} \int f(\mathbf{x},\mathbf{c},\alpha,t) f(\mathbf{x},\mathbf{c}_1,\alpha_1,t)\, \sigma_{\alpha\alpha_1}^{\alpha'\alpha_1'}(\mathbf{g}\to\mathbf{g}')\, g\, d\Omega'\, d\mathbf{c}_1\, d\mathbf{c} \qquad \longmapsto$$

$$\int f(\mathbf{x},\mathbf{c},\omega,t) f(\mathbf{x},\mathbf{c}_1,\omega_1,t)\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\mathbf{c}\, d\omega_1\, d\omega, \tag{5.93}$$

$$\sum_{\alpha_1,\alpha',\alpha_1'} \int f(\mathbf{x},\mathbf{c}',\alpha',t) f(\mathbf{x},\mathbf{c}_1',\alpha_1',t)\, \sigma^{\alpha\alpha_1}_{\alpha'\alpha_1'}(\mathbf{g}'\to\mathbf{g})\, g'\, d\Omega\, d\mathbf{c}_1'\, d\mathbf{c}' \qquad \longmapsto$$
$$\int f(\mathbf{x},\mathbf{c}^*,\omega^*,t) f(\mathbf{x},\mathbf{c}_1^*,\omega_1^*,t)\, g^*\, b^*\, db^*\, d\varepsilon^*\, d\mathbf{c}_1^*\, d\mathbf{c}^*\, d\omega_1{}^*\, d\omega^*$$
$$= \int f(\mathbf{x},\mathbf{c}^*,\omega^*,t) f(\mathbf{x},\mathbf{c}_1^*,\omega_1^*,t)\, g\, b\, db\, d\varepsilon\, d\mathbf{c}\, d\mathbf{c}_1\, d\omega\, d\omega_1. \tag{5.94}$$

In (5.94), the following relationship was used:

$$g^*\, b^*\, db^*\, d\varepsilon^*\, d\mathbf{c}^*\, d\mathbf{c}_1^*\, d\omega^*\, d\omega_1{}^* = g\, b\, db\, d\varepsilon\, d\mathbf{c}\, d\mathbf{c}_1\, d\omega\, d\omega_1, \tag{5.95}$$

which is a consequence of the Liouville theorem. In other words, Liouville's theorem asserts that if one follows the evolution of a volume element in the phase space its volume does not change in the course of time.

Now, by following the same methodology of Section 5.2.1, one may obtain the Boltzmann equation for a polyatomic gas, in which the internal states of the molecules are classically treated, namely,

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} + F_i \frac{\partial f}{\partial c_i} = \int \left(f^* f_1^* - f f_1\right)\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\omega_1, \tag{5.96}$$

where $f(\mathbf{x},\mathbf{c}_1^*,\omega_1^*,t) \equiv f_1^*$ and so on.

For the determination of the transfer equation, one multiplies the Boltzmann equation (5.96) by an arbitrary function $\psi \equiv \psi(\mathbf{x},\mathbf{c},\omega,t)$ and integrates the resulting equation over all values of $\mathbf{c}$ and ω, yielding

$$\frac{\partial}{\partial t}\int \psi f d\mathbf{c}\, d\omega + \frac{\partial}{\partial x_i}\int \psi f c_i d\mathbf{c}\, d\omega - \int \left[\frac{\partial \psi}{\partial t} + c_i \frac{\partial \psi}{\partial x_i} + F_i \frac{\partial \psi}{\partial c_i}\right] f d\mathbf{c}\, d\omega$$
$$= \int \psi (f^* f_1^* - f f_1)\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\omega_1\, d\mathbf{c}\, d\omega$$
$$= \frac{1}{2}\int (\psi_1' + \psi' - \psi_1 - \psi) f f_1\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\omega_1\, d\mathbf{c}\, d\omega. \tag{5.97}$$

The last equality on the right-hand side of the above equation is obtained by noting that one may write

$$\int \psi(\mathbf{x},\mathbf{c},\omega,t) f^* f_1^*\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\omega_1\, d\mathbf{c}\, d\omega$$
$$= \int \psi(\mathbf{x},\mathbf{c},\omega,t) f^* f_1^*\, g^*\, b^*\, db^*\, d\varepsilon^*\, d\mathbf{c}_1^*\, d\omega_1{}^*\, d\mathbf{c}^*\, d\omega^*$$
$$= \int \psi(\mathbf{x},\mathbf{c}',\omega',t) f f_1\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\omega_1\, d\mathbf{c}\, d\omega, \tag{5.98}$$

by renaming the pre-collisional velocities $(\mathbf{c}^*,\mathbf{c}_1^*,\omega^*,\omega_1^*)$ as $(\mathbf{c},\mathbf{c}_1,\omega,\omega_1)$ and the post-collisional velocities $(\mathbf{c},\mathbf{c}_1,\omega,\omega_1)$ as $(\mathbf{c}',\mathbf{c}_1',\omega',\omega_1')$. Furthermore, one may change the role of the colliding molecules $(\mathbf{c},\omega) \to (\mathbf{c}_1,\omega_1)$, so that

$$\begin{aligned}
&\int \psi(\mathbf{x},\mathbf{c},\omega,t)(f^* f_1^* - f f_1)\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\omega_1\, d\mathbf{c}\, d\omega \\
&= \int [\psi(\mathbf{x},\mathbf{c}',\omega',t) - \psi(\mathbf{x},\mathbf{c},\omega,t)]\, f f_1\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\omega_1\, d\mathbf{c}\, d\omega \\
&= \int [\psi(\mathbf{x},\mathbf{c}_1',\omega_1',t) - \psi(\mathbf{x},\mathbf{c}_1,\omega_1,t)]\, f f_1\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\omega_1\, d\mathbf{c}\, d\omega. \qquad (5.99)
\end{aligned}$$

From the transfer equation (5.97), one can obtain the balance equations for the mass density (5.22), momentum density (5.23) and energy density (5.24).

The determination of the balance equation for the entropy density is more involved. Indeed, the choosing of $\psi = -k \ln \mathtt{b} f$ into the transfer equation (5.97) leads to (5.26) where the entropy density ϱs, the entropy flux φ_i and the entropy production density ς are given by

$$\varrho s = -k \int f(\ln \mathtt{b} f) d\mathbf{c}\, d\omega, \qquad \varphi_i = -k \int f C_i (\ln \mathtt{b} f) d\mathbf{c}\, d\omega, \qquad (5.100)$$

$$\varsigma = -\frac{k}{2} \int \ln \frac{f' f_1'}{f f_1} f f_1\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\omega_1\, d\mathbf{c}\, d\omega. \qquad (5.101)$$

One may observe from the expression for the entropy production density (5.101) that it is not possible to infer the positiveness of this quantity. However, one can prove that the relationship holds

$$\int f f_1\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\omega_1\, d\mathbf{c}\, d\omega = \int f' f_1'\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\omega_1\, d\mathbf{c}\, d\omega, \qquad (5.102)$$

by following the same arguments of renaming the velocities. Hence, one can build the relationship

$$-\frac{k}{2} \int \left(\frac{f' f_1'}{f f_1} - 1 \right) f f_1\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\omega_1\, d\mathbf{c}\, d\omega = 0, \qquad (5.103)$$

so that the entropy production density (5.101) becomes

$$\varsigma = -\frac{k}{2} \int \left[\ln \frac{f' f_1'}{f f_1} - \left(\frac{f' f_1'}{f f_1} - 1 \right) \right] f f_1\, g\, b\, db\, d\varepsilon\, d\mathbf{c}_1\, d\omega_1\, d\mathbf{c}\, d\omega. \qquad (5.104)$$

Now, one may conclude that the entropy density production is a positive semi-definite quantity due to the inequality $[\ln x - (x-1)] \leqslant 0$, which is valid for all $x > 0$.

Exercise

5.16 Show that (5.102) is valid.

5.3.3 Transport Coefficients

In order to determine the transport coefficients, one has to replace the integrals $\mathcal{I}_\alpha\left[\phi_\alpha\right]$ in (5.55) by

$$\mathcal{I}^*\left[\phi\right]=\int f^{(0)}f_1^{(0)}\left(\phi_1^*+\phi^*-\phi_1-\phi\right)\,g\,b\,db\,d\varepsilon\,d\mathbf{c}_1\,d\omega_1. \tag{5.105}$$

Relationship (5.56) does not hold, but if one makes use of the same arguments of the previous section, it is easy to prove that

$$\begin{aligned}\int\psi\mathcal{I}^*[\phi]d\omega\,d\mathbf{c}&=\int f^{(0)}f_1^{(0)}\psi'\left(\phi_1+\phi-\phi_1'-\phi'\right)\,g\,b\,db\,d\varepsilon\,d\mathbf{c}_1\,d\omega_1\,d\mathbf{c}\,d\omega\\&=-\int\psi'\mathcal{I}[\phi]d\omega\,d\mathbf{c}=\int\phi\mathcal{I}[\psi]d\omega\,d\mathbf{c}.\end{aligned} \tag{5.106}$$

The transport coefficients are obtained by following the same methodology used in Section 5.2.6, so that the coefficients of shear viscosity and bulk viscosity read

$$\begin{aligned}\mu=\frac{5}{8}\sqrt{\pi kTm}\mathcal{Z}^2\Bigg\{\int&\left[\gamma^4\sin^2\chi-\left(\frac{2}{3}\gamma'^2+\gamma^2\sin^2\chi\right)\Delta\epsilon\right]\\&\times\;e^{-(\gamma^2+\epsilon_\omega+\epsilon_{\omega_1})}\gamma^3\,b\,db\,d\varepsilon\,d\gamma\,d\omega_1\,d\omega\Bigg\}^{-1},\end{aligned} \tag{5.107}$$

$$\begin{aligned}\eta=\frac{1}{4}\frac{m{c_v^I}^2}{kc_v}\sqrt{\pi kTm}\mathcal{Z}^2\Bigg\{\int&\Delta\epsilon\left[3\left(\epsilon_{\omega'}-\frac{m\varepsilon^I}{kT}\right)+\frac{mc_v^I}{k}\left(\frac{3}{2}-\gamma'^2\right)\right]\\&\times\;e^{-(\gamma^2+\epsilon_\omega+\epsilon_{\omega_1})}\gamma^3\,b\,db\,d\varepsilon\,d\gamma\,d\omega_1\,d\omega\Bigg\}^{-1}.\end{aligned} \tag{5.108}$$

Furthermore, the integrals $\varUpsilon_1$, $\varUpsilon_2$, $\widetilde{\varUpsilon}_2$ and $\varUpsilon_3$, which define the coefficient of thermal conductivity (5.77), become

$$\begin{aligned}\varUpsilon_1=\frac{4}{\sqrt{\pi kTm}}\frac{1}{\mathcal{Z}^2}\int&\left[\gamma^4\sin^2\chi+\left(\gamma^2\cos^2\chi+\frac{25}{8}-\frac{15}{4}\gamma^2\right)\Delta\epsilon\right.\\&\left.+\;\frac{11}{4}(\Delta\epsilon)^2\right]e^{-(\gamma^2+\epsilon_\omega+\epsilon_{\omega_1})}\gamma^3\,b\,db\,d\varepsilon\,d\gamma\,d\omega_1\,d\omega,\end{aligned} \tag{5.109}$$

$$\varUpsilon_2=\frac{-5}{\sqrt{\pi kTm}}\frac{1}{\mathcal{Z}^2}\int\left(\frac{3}{2}-\gamma^2+\Delta\epsilon\right)\Delta\epsilon\,e^{-(\gamma^2+\epsilon_\omega+\epsilon_{\omega_1})}\gamma^3\,b\,db\,d\varepsilon\,d\gamma\,d\omega_1\,d\omega, \tag{5.110}$$

$$\widetilde{\varUpsilon}_2 = \frac{-10}{\sqrt{\pi kTm}}\frac{1}{\mathcal{Z}^2}\int\left(\epsilon_{\omega'} - \frac{m\varepsilon^I}{kT}\right)\varDelta\epsilon\, e^{-(\gamma^2+\epsilon_\omega+\epsilon_{\omega_1})}\gamma^3\, b\,db\,d\varepsilon\,d\gamma\,d\omega_1\,d\omega, \tag{5.111}$$

$$\begin{aligned}\varUpsilon_3 = \frac{4}{\sqrt{\pi kTm}}\frac{1}{\mathcal{Z}^2}\int\left(\epsilon_{\omega'} - \frac{m\varepsilon^I}{kT}\right)\Bigg[\frac{3}{2}\varDelta\epsilon - (\epsilon_{\omega_1'} - \epsilon_{\omega'})\gamma'^2 \\ - (\epsilon_{\omega_1} - \epsilon_\omega)\gamma'\gamma\cos\chi\Bigg]\, e^{-(\gamma^2+\epsilon_\omega+\epsilon_{\omega_1})}\gamma^3\, b\,db\,d\varepsilon\,d\gamma\,d\omega_1\,d\omega.\end{aligned} \tag{5.112}$$

Note that in the classical case, the symmetry of the integrals $\varUpsilon_2 = \widetilde{\varUpsilon}_2$ is lost.

Exercises

5.17 Prove (5.106).

5.18 Determine the coefficients of shear viscosity (5.107) and bulk viscosity (5.108).

5.4 Rough Spherical Molecules

The molecular model which will be analyzed in this section for the description of a polyatomic gas was proposed by Bryan,[5] who wrote *"The cases of perfectly rough spheres or circular disks having both their normal and tangential coefficients of restitution unity furnish interesting examples for solution. We may imagine the spheres and disks covered over with perfectly elastic fine teeth, or minute projections by whose action the tangential components of the relative velocity are reversed at impact,... "*. The corresponding transport coefficients for a polyatomic gas of rough spheres were calculated by Pidduck.[6] In this model, the spherical molecules interact according to a hard-sphere potential but are considered as perfectly rough. In elastic binary collisions, the perfectly rough sphere molecules grip to each other without slipping so that there is a total conversion of the deformation energy at collision into translational and rotational energies of the molecules. As a consequence of this hypothesis, the relative velocity of the points of the spheres which are in contact during the encounter is reversed. Furthermore, the internal energy of the molecules is characterized just by a rotational energy and the principal advantage of this model is that it is not necessary to specify the space orientation of the molecules.

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[5] G. H. Bryan, *Brit. Ass. Rep.* p. 83 (1894).

[6] F. B. Pidduck, “The kinetic theory of a special type of rigid molecule”, *Proc. Roy. Soc. A*, **101** 101-112 (1922).

Here, a rarefied polyatomic gas of rough spherical molecules without spin will be analyzed, since the inclusion of the spin is only important for the case of dense polyatomic gases.

This model has some shortcomings, the principal being that even the slightest grazing collision leads to a large deflection of the molecules. However, its simplicity allows to determine explicitly the transport coefficients.

5.4.1 Dynamics of a Binary Collision

The collision of two identical rough spherical molecules with mass m, diameter d and moment of inertia I is represented in Figure 5.3. In this figure, $\mathbf{k}$ denotes the unit vector directed along the line which joins the molecules centers and pointing from center of the molecule labeled by the index 1 to the center of the molecule without label. The collision process is characterized by the pre-collisional linear $(\mathbf{c}, \mathbf{c}_1)$ and angular $(\mathbf{w}, \mathbf{w}_1)$ velocities and post-collisional linear $(\mathbf{c}', \mathbf{c}_1')$ and angular $(\mathbf{w}', \mathbf{w}_1')$ velocities.

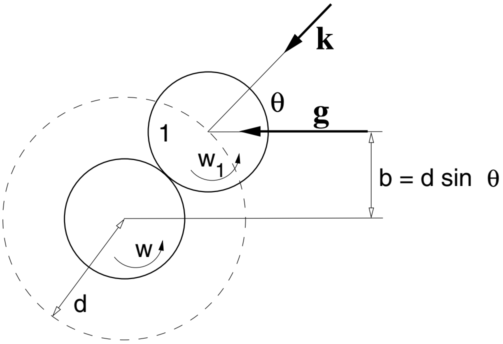

Fig. 5.3 Collision of two rough spherical molecules.

If $\mathbf{J}$ denotes the impulse exerted by the molecule without the label on the labeled molecule, the equations which relate the post-collisional velocities to the pre-collisional velocities read

$$m\mathbf{c}' = m\mathbf{c} - \mathbf{J}, \qquad I\mathbf{w}' = I\mathbf{w} + \frac{\mathsf{d}}{2}\mathbf{k} \times \mathbf{J}, \tag{5.113}$$

$$m\mathbf{c}_1' = m\mathbf{c}_1 + \mathbf{J}, \qquad I\mathbf{w}_1' = I\mathbf{w}_1 + \frac{\mathsf{d}}{2}\mathbf{k} \times \mathbf{J}. \tag{5.114}$$

Furthermore, the pre- and post-collisional relative velocities of the points of the spheres which are in contact during the encounter are given by

$$\mathbf{u} = \mathbf{g} - \frac{\mathsf{d}}{2}\mathbf{k} \times (\mathbf{w} + \mathbf{w}_1), \qquad \mathbf{u}' = \mathbf{g}' - \frac{\mathsf{d}}{2}\mathbf{k} \times (\mathbf{w}' + \mathbf{w}_1'), \tag{5.115}$$

respectively. As usual, $\mathbf{g} = \mathbf{c}_1 - \mathbf{c}$ and $\mathbf{g}' = \mathbf{c}_1' - \mathbf{c}'$ denote the pre- and post-collisional linear relative velocities.

Since for rough spherical molecules the relative velocity is reversed after the encounter, the relationship $\mathbf{u} = -\mathbf{u}'$ holds and one obtains from the subtraction of the two equations in (5.115) that

$$2\mathbf{u} = -\frac{2}{m}\mathbf{J} + \frac{\mathsf{d}^2}{2I}\left[(\mathbf{k}\cdot\mathbf{J})\,\mathbf{k} - \mathbf{J}\right], \tag{5.116}$$

thanks to (5.113) and (5.114). From the above equation, it is easy to verify that $\mathbf{k}\cdot\mathbf{u} = -\mathbf{k}\cdot\mathbf{J}/m$ so that one may solve it for $\mathbf{J}$, yielding

$$\mathbf{J} = -\frac{m\kappa}{(\kappa+1)}\left[\mathbf{u} + \frac{1}{\kappa}(\mathbf{u}\cdot\mathbf{k})\mathbf{k}\right]. \tag{5.117}$$

In (5.117), the dimensionless moment of inertia defined by $\kappa = 4I/m\mathsf{d}^2$ was introduced, which may vary from zero to a maximum value of $2/3$, the former corresponding to a concentration of the mass at the center of the sphere, while the latter to a concentration of the mass on the surface of the sphere. The value $\kappa = 2/5$ refers to a uniform distribution of the mass on the sphere.

The determination of the equations that relate the post- to the pre-collisional velocities can now be obtained from (5.113) through (5.115) and (5.117), yielding

$$\mathbf{c}' = \mathbf{c} + \frac{\kappa}{(\kappa+1)}\left[\mathbf{g} - \frac{\mathsf{d}}{2}\mathbf{k}\times(\mathbf{w}_1+\mathbf{w}) + \frac{1}{\kappa}(\mathbf{k}\cdot\mathbf{g})\mathbf{k}\right], \tag{5.118}$$

$$\mathbf{c}_1' = \mathbf{c}_1 - \frac{\kappa}{(\kappa+1)}\left[\mathbf{g} - \frac{\mathsf{d}}{2}\mathbf{k}\times(\mathbf{w}_1+\mathbf{w}) + \frac{1}{\kappa}(\mathbf{k}\cdot\mathbf{g})\mathbf{k}\right], \tag{5.119}$$

$$\mathbf{w}' = \mathbf{w} - \frac{2}{\mathsf{d}(\kappa+1)}\mathbf{k}\times\left[\mathbf{g} - \frac{\mathsf{d}}{2}\mathbf{k}\times(\mathbf{w}_1+\mathbf{w})\right], \tag{5.120}$$

$$\mathbf{w}_1' = \mathbf{w}_1 - \frac{2}{\mathsf{d}(\kappa+1)}\mathbf{k}\times\left[\mathbf{g} - \frac{\mathsf{d}}{2}\mathbf{k}\times(\mathbf{w}_1+\mathbf{w})\right]. \tag{5.121}$$

As was pointed out in the previous section, classical inverse collisions generally do not exist (see Figure 5.2). Hence, the restitution collision will be represented by the pre-collisional velocities $(\mathbf{c}^*, \mathbf{c}_1^*, \mathbf{w}^*, \mathbf{w}_1^*)$ that correspond to the post-collisional velocities $(\mathbf{c}, \mathbf{c}_1, \mathbf{w}, \mathbf{w}_1)$. The unit vector which joins the centers of the spheres at collision will be denoted by $\mathbf{k}^*$ and the relationships between post- and pre-collisional velocities have the same form of (5.118) through (5.121). Furthermore, according to Figure 2.2, one infers that $\mathbf{k}^* = -\mathbf{k}$ and it is easy to prove the relationships

$$\mathbf{g}\cdot\mathbf{k} = -\mathbf{g}'\cdot\mathbf{k} = \mathbf{g}'\cdot\mathbf{k}' = -\mathbf{g}^*\cdot\mathbf{k} = \mathbf{g}^*\cdot\mathbf{k}^*. \tag{5.122}$$

Moreover, it is easy to show that the twelfth order Jacobian of the velocity transformations is equal to one, which implies that

$$d\mathbf{c}_1 d\mathbf{w}_1 d\mathbf{c} d\mathbf{w} = d\mathbf{c}_1' d\mathbf{w}_1' d\mathbf{c}' d\mathbf{w}' = d\mathbf{c}_1^* d\mathbf{w}_1^* d\mathbf{c}^* d\mathbf{w}^*. \tag{5.123}$$

Exercises

5.19 Obtain the post-collisional velocities in terms of the pre-collisional velocities, which are given by (5.118) through (5.121).

5.20 Prove the relationships (5.122) and (5.123).

5.4.2 Transport Coefficients

As was previously anticipated in the Exercise 5.15, the internal energy state of a molecule that corresponds to its rotational energy is $e_\omega = Iw^2/2$, so that the Maxwellian distribution function and the specific rotational energy of the polyatomic gas are given by

$$f^{(0)} = n\left(\frac{\sqrt{mI}}{2\pi kT}\right)^3 e^{-(mC^2+Iw^2)/2kT}, \qquad \varepsilon^I = \frac{3}{2}\frac{k}{m}T. \tag{5.124}$$

Furthermore, for this case, Grad's distribution function (5.52) becomes

$$\begin{aligned} f = f^{(0)}\Bigg\{1 &+ \frac{p_{\langle ij\rangle}}{2\varrho}\left(\frac{m}{kT}\right)^2 C_iC_j + \frac{\varpi}{p}\left[\frac{mC^2}{2kT} - \frac{Iw^2}{2kT}\right] \\ &+ \frac{2}{5}\frac{q_i^T}{\varrho}\left(\frac{m}{kT}\right)^2\left(\frac{mC^2}{2kT} - \frac{5}{2}\right)C_i + \frac{2}{3}\frac{q_i^I}{\varrho}\left(\frac{m}{kT}\right)^2\left(\frac{Iw^2}{2kT} - \frac{3}{2}\right)C_i\Bigg\}. \end{aligned} \tag{5.125}$$

Above, the fields of mass density, momentum density, dynamic pressure, temperature, pressure deviator and heat flux vectors are obtained from equations (5.89) through (5.91) by considering $e_\omega = Iw^2/2$, e.g.,

$$\varrho = \int mf d\mathbf{c}\, d\mathbf{w}, \quad \varrho v_i = \int mc_i f d\mathbf{c}\, d\mathbf{w}, \quad \varpi = \frac{1}{3}\int\left(\frac{mC^2}{2} - \frac{Iw^2}{2}\right) f d\mathbf{c}\, d\mathbf{w}, \tag{5.126}$$

$$T = \frac{1}{3nk}\int\left(\frac{mC^2}{2} + \frac{Iw^2}{2}\right) f d\mathbf{c}\, d\mathbf{w}, \quad p_{\langle ij\rangle} = \int mC_{\langle i}C_{j\rangle} f d\mathbf{c}\, d\mathbf{w}, \tag{5.127}$$

$$q_i^T = \int \frac{mC^2}{2} C_i f d\mathbf{c}\, d\mathbf{w}, \qquad q_i^I = \int \frac{Iw^2}{2} C_i f d\mathbf{c}\, d\mathbf{w}. \tag{5.128}$$

In this case, (5.58) reduces to

$$f^{(0)}\left\{\left(\frac{mC^2}{6kT}-\frac{Iw^2}{6kT}\right)\frac{\partial v_k}{\partial x_k}+\frac{1}{T}\frac{\partial T}{\partial x_k}\left(\frac{mC^2}{2kT}+\frac{Iw^2}{2kT}-4\right)C_k\right.$$
$$\left.+\frac{m}{kT}C_kC_l\frac{\partial v_{\langle k}}{\partial x_{l\rangle}}\right\}=\frac{p_{\langle kl\rangle}}{2\varrho}\left(\frac{m}{kT}\right)^2\mathcal{I}^*[C_{\langle k}C_{l\rangle}]+\frac{\varpi}{p}\mathcal{I}^*\left[\frac{mC^2}{2kT}-\frac{Iw^2}{2kT}\right]$$
$$+\frac{2}{5}\frac{q_j^T}{\varrho}\left(\frac{m}{kT}\right)^2\mathcal{I}^*\left[\left(\frac{mC^2}{2kT}-\frac{5}{5}\right)C_j\right]+\frac{2}{3}\frac{q_j^I}{\varrho}\left(\frac{m}{kT}\right)^2\mathcal{I}^*\left[\left(\frac{Iw^2}{2kT}-\frac{3}{2}\right)C_j\right]. \tag{5.129}$$

In the above equation, the integral $\mathcal{I}^*[\phi]$ reads

$$\mathcal{I}^*[\phi]=\int f^{(0)}f_1^{(0)}\left(\phi_1^*+\phi^*-\phi_1-\phi\right)\mathsf{d}^2(\mathbf{g}\cdot\mathbf{k})d\mathbf{k}\,d\mathbf{c}_1d\mathbf{w}_1, \tag{5.130}$$

since by the geometry of a binary encounter (see Figure 5.3), one has

$$b=\mathsf{d}\sin\theta,\quad b\,db=\mathsf{d}^2\sin\theta\cos\theta\,d\theta,\quad \mathbf{g}\cdot\mathbf{k}=g\cos\theta,\quad d\mathbf{k}\equiv\sin\theta\,d\theta\,d\varepsilon. \tag{5.131}$$

The determination of the transport coefficients of a polyatomic gas of rough spherical molecules is a hard task. Here, it is shown how to obtain the coefficient of shear viscosity, and the determination of the other transport coefficients is left as an exercise for the reader.

By following the same methodology used in Section 5.2.6, the multiplication of (5.129) by $mC_{\langle i}C_{j\rangle}/nkT$ and the integration of the resulting equation over all values of $\mathbf{c}$ and $\mathbf{w}$, leads to

$$p_{\langle ij\rangle}=-2\mu\frac{\partial v_{\langle i}}{\partial x_{j\rangle}},\quad\text{where}\quad \mu=-10\frac{\varrho^2k^3T^3}{m^4}\left[\int C_{\langle k}C_{l\rangle}\mathcal{I}\left[C_{\langle k}C_{l\rangle}\right]d\mathbf{c}\,d\mathbf{w}\right]^{-1}, \tag{5.132}$$

due to (5.106) and (4.75).

For the integration of the expression for the coefficient of shear viscosity, first, one should note that

$$\int C_{\langle k}C_{l\rangle}\mathcal{I}\left[C_{\langle k}C_{k\rangle}\right]d\mathbf{c}d\mathbf{w}=\int C_{\langle k}C_{l\rangle}\mathcal{I}\left[C_kC_k\right]d\mathbf{c}d\mathbf{w}, \tag{5.133}$$

and that one may change the integral variables $(\mathbf{C},\mathbf{C}_1,\mathbf{w},\mathbf{w}_1)$ by introducing the new variables $(\mathbf{g},\mathbf{G},\mathbf{z},\mathbf{Z})$ defined by

$$\mathbf{g}=\mathbf{C}_1-\mathbf{C},\quad \mathbf{G}=\frac{1}{2}\left(\mathbf{C}_1+\mathbf{C}\right),\quad \mathbf{z}=\mathbf{w}_1-\mathbf{w},\quad \mathbf{Z}=\frac{1}{2}\left(\mathbf{w}_1+\mathbf{w}\right). \tag{5.134}$$

From the above relationships, it is easy to prove that

$$d\mathbf{c}_1\,d\mathbf{w}_1\,d\mathbf{c}\,d\mathbf{w}=d\mathbf{C}_1\,d\mathbf{w}_1\,d\mathbf{C}\,d\mathbf{w}=d\mathbf{g}\,d\mathbf{G}\,d\mathbf{z}\,d\mathbf{Z}. \tag{5.135}$$

In terms of the new variables, one can get the following expression for the product of the Maxwellian distribution functions

$$f_1^{(0)} f^{(0)} = n^2 \left(\frac{\sqrt{mI}}{2\pi kT}\right)^6 \exp\left[-\frac{m}{2kT}\left(2G^2+\frac{g^2}{2}\right) - \frac{I}{2kT}\left(2Z^2+\frac{z^2}{2}\right)\right], \tag{5.136}$$

as well as the product of the velocities

$$C_{\langle k}C_{l\rangle} = \left(G_{\langle k}G_{l\rangle} - \underline{g_{\langle k}G_{l\rangle}} + \frac{1}{4}g_{\langle k}g_{l\rangle}\right). \tag{5.137}$$

For the difference of the products of the velocities, one has to use (5.118) and (5.119), yielding

$$\begin{aligned} C_k^{1'}C_l^{1'} + C_k'C_l' - C_k^1C_l^1 - C_kC_l &= \frac{2(\mathbf{g}\cdot\mathbf{k})^2}{(\kappa+1)^2}k_kk_l - \frac{2\kappa}{(\kappa+1)^2}g_kg_l \\ &+\frac{\kappa-1}{(\kappa+1)^2}(\mathbf{g}\cdot\mathbf{k})(k_kg_l+g_kk_l) + \frac{2\kappa^2\mathsf{d}^2}{(\kappa+1)^2}\varepsilon_{kpq}k_pZ_q\varepsilon_{lrs}k_rZ_s \\ &\underline{-\frac{\kappa(\kappa-1)\mathsf{d}}{(\kappa+1)^2}(g_k\varepsilon_{lrs}+g_l\varepsilon_{krs})k_rZ_s} - \underline{\frac{2\kappa\mathsf{d}(\mathbf{g}\cdot\mathbf{k})}{(\kappa+1)^2}(k_k\varepsilon_{lrs}+k_l\varepsilon_{krs})k_rZ_s}. \end{aligned} \tag{5.138}$$

Note that the integrals corresponding to the underlined terms in equations (5.137) and (5.138) vanish since they are odd in **G** and **Z**, respectively.

Now, by taking into account (5.137) and (5.138), the integration of (5.133) over all values of **k** can be performed by using (5.152) of the Appendix. Indeed, after some rearrangements it follows

$$\begin{aligned} \int C_{\langle k}C_{l\rangle}\mathcal{I}\left[C_kC_k\right]d\mathbf{c}d\mathbf{w} &= 2\pi\int\left(G_{\langle k}G_{l\rangle}+\frac{1}{4}g_{\langle k}g_{l\rangle}\right)\left\{-\frac{(2\kappa+1)}{4(\kappa+1)^2}g_kg_l\right. \\ &\left.+\frac{\kappa^2\mathsf{d}^2}{4(\kappa+1)^2}\varepsilon_{kpq}\varepsilon_{lrs}Z_qZ_s\frac{1}{g^2}(g^2\delta_{pr}+g_pg_r)\right\}f^{(0)}f_1^{(0)}g\mathsf{d}^2d\mathbf{g}\,d\mathbf{G}\,d\mathbf{z}\,d\mathbf{Z}. \end{aligned} \tag{5.139}$$

Finally, one may integrate the above equation with respect to the variables **g**, **G**, **z** and **Z** and obtain

$$\int C_{\langle k}C_{l\rangle}\mathcal{I}\left[C_kC_k\right]d\mathbf{c}d\mathbf{w} = -\frac{16}{3}\sqrt{\pi}\left(\frac{kT}{m}\right)^{\frac{5}{2}}n^2\mathsf{d}^2\frac{(13\kappa+6)}{(\kappa+1)^2}. \tag{5.140}$$

Hence, the final expression for the coefficient of shear viscosity follows from the insertion of (5.140) into $(5.132)_2$, yielding

$$\mu = \frac{15}{8\mathsf{d}^2}\sqrt{\frac{mkT}{\pi}}\frac{(\kappa+1)^2}{(13\kappa+6)}. \tag{5.141}$$

Similarly, one may obtain the coefficients of bulk viscosity η and thermal conductivity associated with the translational energy λ^T and with the rotational energy of the molecule λ^I. They read

$$\eta = \frac{1}{32\mathsf{d}^2}\sqrt{\frac{mkT}{\pi}}\frac{(\kappa+1)^2}{\kappa}, \tag{5.142}$$

$$\lambda^T = \frac{225}{16\mathsf{d}^2}\frac{k}{m}\sqrt{\frac{mkT}{\pi}}\frac{(2\kappa+1)(\kappa+1)^3}{(102\kappa^3+101\kappa^2+75\kappa+12)}, \tag{5.143}$$

$$\lambda^I = \frac{9}{4\mathsf{d}^2}\frac{k}{m}\sqrt{\frac{mkT}{\pi}}\frac{(19\kappa+3)(\kappa+1)^2}{(102\kappa^3+101\kappa^2+75\kappa+12)}. \tag{5.144}$$

The thermal conductivity of the polyatomic gas of rough spherical follows by adding the translational and the rotational thermal conductivities, i.e.,

$$\lambda = \lambda^T + \lambda^I = \frac{9}{16\mathsf{d}^2}\frac{k}{m}\sqrt{\frac{mkT}{\pi}}\frac{(50\kappa^2+151\kappa+37)(\kappa+1)^2}{(102\kappa^3+101\kappa^2+75\kappa+12)}. \tag{5.145}$$

For rough spherical molecules, Eucken's number is given by

$$f_E = \frac{\lambda}{\mu c_v} = \frac{(13\kappa+6)(50\kappa^2+151\kappa+37)}{10(102\kappa^3+101\kappa^2+75\kappa+12)}, \tag{5.146}$$

since $c_v = 3k/m$. Furthermore, one can also build the ratio of the bulk and shear viscosities and the ratio of the rotational and translational thermal conductivities, namely,

$$\frac{\eta}{\mu} = \frac{13\kappa+6}{60\kappa}, \qquad \frac{\lambda^I}{\lambda^T} = \frac{4(19\kappa+3)}{25(2\kappa^2+3\kappa+1)}. \tag{5.147}$$

In order to have some estimation of these ratios, consider a molecule where the mass is uniformly distributed so that $\kappa = 2/5$ and which could represent the molecules of a methane gas. In this case, Eucken's number has the value $f_E \approx 1.83$ which is approximately equal to its experimental value $f_E = 1.81$ at a temperature 300 K. The ratio of the bulk and shear viscosities is $\eta/\mu \approx 0.47$, indicating that the bulk viscosity is about 50% of the shear viscosity. The ratio of the thermal conductivities is $\lambda^I/\lambda^T \approx 0.67$, showing that the transported rotational energy is about 70% of the transported translational energy.

It is important to examine the case where the whole mass of the spherical molecules is concentrated on its center, i.e., when $\kappa = 0$. In this case, one obtains from (5.141) to (5.144) the limiting values:

$$\mu = \frac{5}{16\mathsf{d}^2}\sqrt{\frac{mkT}{\pi}}, \qquad \eta \to \infty, \tag{5.148}$$

$$\lambda^T = \frac{75}{64\mathsf{d}^2}\frac{k}{m}\sqrt{\frac{mkT}{\pi}}, \qquad \lambda^I = \frac{9}{16\mathsf{d}^2}\frac{k}{m}\sqrt{\frac{mkT}{\pi}}. \tag{5.149}$$

From the above equations, one recognizes that the coefficients of shear viscosity and thermal conductivity associated with the translational energy are the same as those of a monatomic gas. However, in this case, the thermal conductivity associated with the rotational energy of the molecules does not vanish, indicating that there exists a contribution to the total thermal conductivity due to the rotational energy of the molecules. Furthermore, as mentioned previously, the dynamic pressure is responsible for the relaxation processes that correspond to the transfer of the translational and internal energies of the molecules. In the limiting case, when $\kappa \to 0$, the exchange from the translational energy to the energy of the internal variable of the molecules proceeds very slowly and no information about the dynamic pressure can be obtained from the integral equation (see the remarks at the end of Section 5.2.7).

Exercises

5.21 Insert Grad's distribution function (5.125) into the definitions of the dynamic pressure $(5.126)_3$, pressure deviator $(5.127)_2$, translational heat flux vector $(5.128)_1$ and heat flux vector of the internal variable $(5.128)_2$, integrate the resulting equations and show that one becomes identities.

5.22 Obtain through integration (5.139) and (5.140).

5.23 Obtain the transport coefficients (5.142) - (5.144).

5.5 Appendix

For the determination of the transport coefficients for the rough sphere model one has to use the integrals

$$\int (\mathbf{g}\cdot\mathbf{k})^n d\mathbf{k} = \frac{2\pi}{n+1} g^n, \tag{5.150}$$

$$\int k_i (\mathbf{g}\cdot\mathbf{k})^n d\mathbf{k} = \frac{2\pi}{n+2} g^{n-1} g_i, \tag{5.151}$$

$$\int k_i k_j (\mathbf{g}\cdot\mathbf{k})^n d\mathbf{k} = \frac{2\pi}{(n+1)(n+3)} g^{n-2}(g^2\delta_{ij} + n g_i g_j), \tag{5.152}$$

$$\begin{aligned}\int k_i k_j k_k (\mathbf{g}\cdot\mathbf{k})^n d\mathbf{k} = {} & \frac{2\pi}{(n+2)(n+4)} g^{n-3}[g^2(g_i\delta_{jk} + g_j\delta_{ik} + g_k\delta_{ij}) \\ & +(n-1) g_i g_j g_k],\end{aligned} \tag{5.153}$$

$$\int k_i k_j k_k k_l (\mathbf{g}\cdot\mathbf{k})^n d\mathbf{k} = \frac{2\pi}{(n+1)(n+3)(n+5)} g^{n-4}[g^4(\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})$$

$$+ng^2(g_ig_j\delta_{kl}+g_ig_k\delta_{jl}+g_ig_l\delta_{jk}+g_kg_j\delta_{il}+g_lg_j\delta_{ik}+g_kg_l\delta_{ij})+n(n-2)g_ig_jg_kg_l]. \tag{5.154}$$

In the following, it will be shown how to obtain (5.152). For that end, one recalls that the element of solid angle is written as $d\mathbf{k} = \sin\theta\, d\theta\, d\varepsilon$, where $0 \leqslant \theta \leqslant \pi/2$ and $0 \leqslant \varepsilon \leqslant 2\pi$ are polar angles of $\mathbf{k}$, so that without loss of generality one may write

$$(\mathbf{k}) = (\sin\theta\cos\varepsilon, \sin\theta\sin\varepsilon, \cos\theta), \qquad (\mathbf{g}) = g(0,0,1). \tag{5.155}$$

Hence, the left-hand side of (5.152) becomes

$$\int_0^{2\pi}\int_0^{\frac{\pi}{2}} \begin{pmatrix} \sin^2\theta\cos^2\varepsilon & \sin^2\theta\cos\varepsilon\,\sin\varepsilon & \sin\theta\cos\theta\cos\varepsilon \\ \sin^2\theta\cos\varepsilon\,\sin\varepsilon & \sin^2\theta\,\sin^2\varepsilon & \sin\theta\cos\theta\,\sin\varepsilon \\ \sin\theta\cos\theta\cos\varepsilon & \sin\theta\cos\theta\,\sin\varepsilon & \cos^2\theta \end{pmatrix}$$

$$\times g^n\cos^n\theta\,\sin\theta\, d\theta\, d\varepsilon = \frac{2\pi g^n}{(n+1)(n+3)} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & (n+1) \end{pmatrix}. \tag{5.156}$$

Now, from the above equation, it is easy to infer the right-hand side of (5.152).

Chapter 6

Dense Gases

6.1 The Thermal Equation of State

6.1.1 The Van der Waals Equation

The equation proposed by van der Waals is the oldest equation of state which takes into account the volume occupied by the molecules of the gas as well as the attractive forces between its molecules. Here, the van der Waals equation of state will be determined from the virial theorem proposed by Clausius.

Consider a system of N molecules all having the same mass m. The equation of motion of each molecule is given by

$$m\ddot{\mathbf{x}}^\alpha = \mathbf{F}^\alpha, \qquad\qquad (\alpha = 1, 2, \dots, N), \tag{6.1}$$

where $\ddot{\mathbf{x}}^\alpha$ is the acceleration of the molecule and $\mathbf{F}^\alpha$ denotes the force which is acting upon it. The scalar multiplication of (6.1) by $\mathbf{x}^\alpha$ leads to

$$\frac{d}{dt}(m\mathbf{x}^\alpha \cdot \dot{\mathbf{x}}^\alpha) = m(\dot{\mathbf{x}}^\alpha)^2 + \mathbf{F}^\alpha \cdot \mathbf{x}^\alpha. \tag{6.2}$$

By summing (6.2) over all particles and taking its time average—denoted by an over bar—it follows

$$\begin{aligned}\frac{1}{\tau}\int_0^\tau \frac{d}{dt}\left(\sum_{\alpha=1}^N m\mathbf{x}^\alpha \cdot \dot{\mathbf{x}}^\alpha\right) dt &= \frac{1}{\tau}\left[\sum_{\alpha=1}^N m\mathbf{x}^\alpha \cdot \dot{\mathbf{x}}^\alpha\bigg|_{t=\tau} - \sum_{\alpha=1}^N m\mathbf{x}^\alpha \cdot \dot{\mathbf{x}}^\alpha\bigg|_{t=0}\right]\\ &= \sum_{\alpha=1}^N \overline{m(\dot{\mathbf{x}}^\alpha)^2} + \sum_{\alpha=1}^N \overline{\mathbf{F}^\alpha \cdot \mathbf{x}^\alpha}.\end{aligned} \tag{6.3}$$

If the motion of the molecules is periodic, there exists a recurrence of the coordinates and velocities over a period of time, and in the case that this period is just equal to τ, the left-hand side of (6.3) vanishes. If the motion of the molecules is not periodic but the coordinates and velocities of all molecules remain finite such that there exists an upper limit for the quantity $\sum_{\alpha=1}^{N} m\mathbf{x}^\alpha \cdot \dot{\mathbf{x}}^\alpha$, the left-hand side of the above equation also vanishes by considering a large value of the time τ. By taking into account these conditions it follows from (6.3) the virial theorem of Clausius:

$$\underbrace{\frac{1}{2}\sum_{\alpha=1}^{N}\overline{m(\dot{\mathbf{x}}^\alpha)^2}}_{\text{vis viva}} = \underbrace{-\frac{1}{2}\sum_{\alpha=1}^{N}\overline{\mathbf{F}^\alpha \cdot \mathbf{x}^\alpha}}_{\text{virial}}. \tag{6.4}$$

Clausius called the right-hand side of the above equation as "virial"—which is derived from the Latin word "vis" which means force or energy—and stated the virial theorem as: *The mean "vis viva" of the system is equal to its "virial".* At that time "vis viva" was the denomination of the kinetic energy, the living force of the system.

If the N molecules which make-up a monatomic gas are enclosed in a recipient of volume V at a temperature T, the principle of energy equipartition states that the mean translational kinetic energy of each molecule—the "vis viva"—is given by

$$\frac{1}{2}\overline{m(\dot{\mathbf{x}}^\alpha)^2} = \frac{3}{2}kT. \tag{6.5}$$

The forces that act on the molecules of a gas are of two types: (a) the forces exerted by the recipient walls on the adjacent molecules $\mathbf{F}^\alpha_{\text{ext}}$ (b) the attraction and repulsion forces between the molecules $\mathbf{F}^\alpha_{\text{int}}$. Hence, (6.4) can be written—thanks to (6.5)—as

$$-3NkT = \sum_{\alpha=1}^{N}\overline{\mathbf{F}^\alpha_{\text{ext}} \cdot \mathbf{x}^\alpha} + \sum_{\alpha=1}^{N}\overline{\mathbf{F}^\alpha_{\text{int}} \cdot \mathbf{x}^\alpha}. \tag{6.6}$$

The forces exerted by the recipient walls on the adjacent molecules represent a pressure p. If dS denotes a surface element of the wall with a unit normal $\mathbf{n}$ directed to its interior, $p\,dS$ will represent such a force and

$$\sum_{\alpha=1}^{N}\overline{\mathbf{F}^\alpha_{\text{ext}} \cdot \mathbf{x}^\alpha} = -\oint p(\mathbf{n}\cdot\mathbf{x})dS = -p\int_V \operatorname{div}\mathbf{x}\,dV = -3pV. \tag{6.7}$$

In the above equation the sum was transformed into an integral, the pressure was considered constant and Gauss' divergence theorem was used (note that $\operatorname{div}\mathbf{x} = 3$).

Now by combining (6.6) and (6.7) it follows that

$$pV = NkT + \frac{1}{3}\sum_{\alpha=1}^{N}\overline{\mathbf{F}^\alpha_{\text{int}} \cdot \mathbf{x}^\alpha}. \tag{6.8}$$

For ideal gases the second term on the right-hand side of the above equation is zero, since the forces between the molecules are not taken into account and (6.8) reduces to the equation of state of an ideal gas $pV = NkT$.

The force which acts on the molecule α due to the other molecules reads

$$\mathbf{F}^{\alpha}_{\text{int}} = -\sum_{\beta=1}^{N} K(|\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}|)\frac{\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}}{|\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}|}. \tag{6.9}$$

This force is directed along the versor that characterizes the relative distance between the molecules $(\mathbf{x}^{\beta} - \mathbf{x}^{\alpha})/(|\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}|)$ with the term $K(|\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}|)$ being only a function of the modulus of the relative distance.

From the scalar multiplication of (6.9) by $\mathbf{x}^{\alpha}$ and the sum of the resulting equation over all values of α, it follows after some rearrangements, that

$$\begin{aligned}
\sum_{\alpha=1}^{N} \mathbf{F}^{\alpha}_{\text{int}} \cdot \mathbf{x}^{\alpha} &= -\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} K(|\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}|)\frac{\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}}{|\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}|} \cdot \mathbf{x}^{\alpha} \\
&= -\frac{1}{2}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} K(|\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}|)\frac{\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}}{|\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}|} \cdot \mathbf{x}^{\alpha} \\
&- \frac{1}{2}\sum_{\beta=1}^{N}\sum_{\alpha=1}^{N} K(|\mathbf{x}^{\alpha} - \mathbf{x}^{\beta}|)\frac{\mathbf{x}^{\alpha} - \mathbf{x}^{\beta}}{|\mathbf{x}^{\alpha} - \mathbf{x}^{\beta}|} \cdot \mathbf{x}^{\beta} \\
&= \frac{1}{2}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} K(|\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}|)|\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}|.
\end{aligned} \tag{6.10}$$

In the above equation, the exchange of the dummy indexes $\alpha \leftrightarrow \beta$ was performed.

Now the time average of (6.10) leads to

$$\sum_{\alpha=1}^{N} \overline{\mathbf{F}^{\alpha}_{\text{int}} \cdot \mathbf{x}^{\alpha}} = \frac{1}{2}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} \overline{K(|\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}|)|\mathbf{x}^{\beta} - \mathbf{x}^{\alpha}|}. \tag{6.11}$$

The next step is to transform the sums in (6.11) into integrals. For this end let $n(r)$ be the particle number density at a distance $r = |\mathbf{r}|$ of a molecule. Hence, one of the sums in (6.11) can be transformed into an integral over the volume V, i.e.,

$$\sum_{\alpha=1}^{N} \longrightarrow \int_V n(r)dV. \tag{6.12}$$

The other sum over all molecules gives the number of molecules of the gas N, so that (6.11) can be expressed as

$$\sum_{\alpha=1}^{N}\overline{\mathbf{F}_{\text{int}}^{\alpha}\cdot\mathbf{x}^{\alpha}}=\frac{N}{2}\int_V K(r)r\,n(r)dV=4\pi\frac{N}{2}\int_0^\infty K(r)r^3n(r)dr. \tag{6.13}$$

In the last equality above the volume element was written in spherical coordinates $dV=r^2\sin\theta d\theta d\varphi$ and the integration of the resulting equation over the angles $0\leqslant\theta\leqslant\pi$ and $0\leqslant\varphi\leqslant 2\pi$ was performed.

Now it is considered that the force $K(r)$ is given in terms of a potential energy $\varPhi(r)$ and that the particle number density $n(r)$ is determined from a Maxwell–Boltzmann distribution, i.e.,

$$K(r)=-\frac{d\varPhi(r)}{dr},\qquad\qquad n(r)=\frac{N}{V}\exp\left(-\frac{\varPhi(r)}{kT}\right). \tag{6.14}$$

Under these assumptions (6.13) can be written as

$$\sum_{\alpha=1}^{N}\overline{\mathbf{F}_{\text{int}}^{\alpha}\cdot\mathbf{x}^{\alpha}}=-2\pi N\int_0^\infty\frac{d\varPhi(r)}{dr}\frac{N}{V}e^{-\frac{\varPhi(r)}{kT}}r^3dr$$

$$=2\pi\frac{N^2kT}{V}\int_0^\infty\frac{d}{dr}\left(e^{-\frac{\varPhi(r)}{kT}}-1\right)r^3dr=6\pi\frac{N^2kT}{V}\int_0^\infty\left(1-e^{-\frac{\varPhi(r)}{kT}}\right)r^2dr. \tag{6.15}$$

The last equality above was obtained from an integration by parts and by taking into account that $\lim_{r\to0}\varPhi(r)\to\infty$ and $\lim_{r\to\infty}\varPhi(r)\to0$.

By considering now that $\varPhi(r)$ is given by the Lennard–Jones (6-12) potential (1.56), one can split the last integral in (6.15) into two contributions one within the range of $(0,\sigma)$ and another within the range of (σ,∞) and perform the approximations

$$\begin{cases}1-e^{-\frac{\varPhi(r)}{kT}}\approx 1 & \text{for } r<\sigma,\\ 1-e^{-\frac{\varPhi(r)}{kT}}\approx\frac{\varPhi(r)}{kT}=-\frac{4\varepsilon}{kT}\frac{\sigma^6}{r^6} & \text{for } r>\sigma.\end{cases} \tag{6.16}$$

The above approximations are consequences that the potential function: (i) tends to infinity very rapidly when $r<\sigma$ and (ii) could be represented only by its attractive part when $r>\sigma$.

From the substitution of (6.16) into (6.15) and subsequent integration of the resulting equation leads to

$$\sum_{\alpha=1}^{N}\overline{\mathbf{F}_{\text{int}}^{\alpha}\cdot\mathbf{x}^{\alpha}}=6\pi\frac{N^2kT}{V}\left[\int_0^\sigma r^2dr-\frac{4\varepsilon\sigma^6}{kT}\int_\sigma^\infty\frac{1}{r^4}dr\right]$$

$$=6\pi\frac{N^2kT}{V}\left[\frac{\sigma^3}{3}-\frac{4\varepsilon\sigma^3}{3kT}\right]. \tag{6.17}$$

The pressure (6.8) is now rewritten as

$$pV = NkT + \frac{2\pi}{3}\sigma^3 \frac{N^2kT}{V}\left[1 - \frac{4\varepsilon}{kT}\right], \tag{6.18}$$

thanks to (6.17).

Another expression for the pressure follows by the introduction of the specific volume v and the constants b^* e a^* defined by

$$v = \frac{V}{mN}, \qquad b^* = \frac{2\pi}{3}\frac{\sigma^3}{m}, \qquad a^* = \frac{8\pi}{3}\frac{\sigma^3\varepsilon}{m^2}. \tag{6.19}$$

Indeed, by dividing (6.18) by the total mass of the gas mN, the equation for the pressure reduces to

$$pv = \frac{k}{m}T\left(1 + \frac{b^*}{v}\right) - \frac{a^*}{v}. \tag{6.20}$$

The constant b^* is known as covolume since it is related to the volume occupied by the molecules, while the constant a^* is connected with the attractive part of the function.

If the term b^*/v is considered as a small quantity one may approximate $(1 + b^*/v) \approx (1 - b^*/v)^{-1}$, so that (6.20) becomes

$$pv = \frac{kT/m}{\left(1 - \frac{b^*}{v}\right)} - \frac{a^*}{v} \qquad \text{or} \qquad p = \frac{kT/m}{v - b^*} - \frac{a^*}{v^2}, \tag{6.21}$$

which is the usual expression of the van der Waals equation of state.

Exercise

6.1 Verify (6.10), (6.15) and (6.17).

6.1.2 The Virial Equation of State

Equation (6.20) suggests an expansion of the thermal equation of state in power series of the mass density ($\varrho = 1/v$) as

$$p = \varrho\frac{k}{m}T\left[1 + B(T)\varrho + C(T)\varrho^2 + D(T)\varrho^3 + \dots\right]. \tag{6.22}$$

The above equation is known as the virial equation of state and the coefficients $B(T)$, $C(T)$, $D(T)$, etc., which depend only on the temperature, are denominated second, third, fourth and so on, virial coefficients. All virial coefficients can be determined from the potential partition function using the techniques of equilibrium statistical mechanics which is out of the scope of this book.

For gases of hard spheres the virial coefficients do not depend on the temperature and one may express the thermal equation of state as

$$p = \varrho\frac{k}{m}T(1+\chi^* b^* \varrho), \qquad \text{where} \qquad b^* = \frac{2\pi}{3}\frac{\mathsf{d}^3}{m}, \tag{6.23}$$

is the covolume defined in terms of the diameter d of the spherical molecule.

The expression for χ^*, which corresponds to a thermal equation of state up to the seventh virial coefficient, reads[1]

$$\chi^* = 1+\frac{5}{8}b^*\varrho+0.2869(b^*\varrho)^2+0.1103(b^*\varrho)^3+0.0386(b^*\varrho)^4+0.0138(b^*\varrho)^5+\dots. \tag{6.24}$$

Another known expression in the literature for χ^* is given by[2]

$$\chi^* = \frac{1-b^*\varrho/8}{(1-b^*\varrho/4)^3}. \tag{6.25}$$

For a dense gas of hard spherical molecules the specific internal energy does not depend on the mass density but only on the temperature. To prove this affirmation consider the integrability condition of the Gibbs equation (2.149), namely,

$$\frac{\partial^2 s}{\partial\varrho\partial T} = \frac{\partial^2 s}{\partial T\partial\varrho}, \qquad \text{so that} \qquad \frac{\partial\varepsilon}{\partial\varrho} = \frac{1}{\varrho^2}\left(p - T\frac{\partial p}{\partial T}\right). \tag{6.26}$$

Since from (6.23) one has $\partial p/\partial T = p/T$, it follows from $(6.26)_2$ that

$$\frac{\partial\varepsilon}{\partial\varrho} = 0, \qquad \text{i.e.,} \qquad \varepsilon = \varepsilon(T). \tag{6.27}$$

Exercise

6.2 Show that the expansion of (6.25) in power series of $b^*\varrho$ is a good approximation of the one given by (6.24).

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[1] F. H. Ree and W. G. Hoover, "Seventh virial coefficients for hard spheres and hard disks", *J. Chem. Phys.* **46**, 4181-4197 (1967).

[2] N. F. Carnahan and K. E. Starling, "Equation of state for nonattracting rigid spheres", *J. Chem. Phys.* **51**, 635-636 (1969).

6.2 Enskog's Dense Gas

6.2.1 The Enskog's Equation

In order to describe the transport phenomena of moderately dense gases of hard spherical molecules, Enskog[3] introduced the following modifications into the collision term of the Boltzmann equation:

(a) The volume occupied by the molecules of a dense gas is comparable to the volume filled up by the gas. Hence, the molecules should not be treated as punctiform objects and the two distribution functions in the collision term should be evaluated at different points, since the molecular centers at collision are separated by a distance $\mp \mathsf{d}\mathbf{k}$. The minus or plus sign refers to encounters that take $(\mathbf{c}, \mathbf{c}_1)$ or $(\mathbf{c}', \mathbf{c}_1')$ as initial velocities, respectively.

(b) For a dense gas there exists an increase in the collision probability; hence, the product of the two distribution functions should be multiplied by a factor χ which depends on the density of the gas at the contact point of the colliding spheres, i.e., the factor χ is a function of $\mathbf{x} \mp \mathsf{d}\mathbf{k}/2$ and time t. Here, the sign $\mp$ has the same meaning of the previous item.

By taking into account the above modifications the Boltzmann equation (2.20) is rewritten as

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} + F_i \frac{\partial f}{\partial c_i} = \int \left[\chi\left(\mathbf{x} + \frac{\mathsf{d}}{2}\mathbf{k}, t\right) f(\mathbf{x}, \mathbf{c}', t) f(\mathbf{x} + \mathsf{d}\mathbf{k}, \mathbf{c}_1', t) \right.$$
$$\left. - \chi\left(\mathbf{x} - \frac{\mathsf{d}}{2}\mathbf{k}, t\right) f(\mathbf{x}, \mathbf{c}, t) f(\mathbf{x} - \mathsf{d}\mathbf{k}, \mathbf{c}_1, t) \right] \mathsf{d}^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{c}_1, \qquad (6.28)$$

since for hard spheres $g\, b\, db\, d\varepsilon = \mathsf{d}^2 g \cos\theta \sin\theta d\theta d\varepsilon = \mathsf{d}^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k}$.

If the distribution functions and the factor χ are considered smooth functions one may approximate the functions on the right-hand side of (6.28) through a Taylor series near the point $\mathbf{x}$. By considering terms up to second gradients one obtains

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} + F_i \frac{\partial f}{\partial c_i} = \mathcal{Q}_K(f, f) + \mathcal{Q}_{P_1}(f, f) + \mathcal{Q}_{P_2}(f, f), \qquad (6.29)$$

where the expanded collision terms read

$$\mathcal{Q}_K(f, f) = \chi \int (f' f_1' - f f_1)\, \mathsf{d}^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{c}_1, \qquad (6.30)$$

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[3] D. Enskog, "Kinetische Theorie der Wärmeleitung, Reibung und Selbstdiffusion in gewissen verdichteten Gasen und Flssigkeiten", *Kungl. Svenska vetenskapsakademiens handlingar* **63**, 44p. (1922).

$$\begin{aligned}\mathcal{Q}_{P_1}(f,f) &= \chi \mathsf{d}\int\left[f'\frac{\partial f_1'}{\partial x_i}+f\frac{\partial f_1}{\partial x_i}\right]k_i\,\mathsf{d}^2(\mathbf{g}\cdot\mathbf{k})d\mathbf{k}d\mathbf{c}_1\\ &+\frac{\mathsf{d}}{2}\frac{\partial\chi}{\partial x_i}\int k_i(f'f_1'+ff_1)\,\mathsf{d}^2(\mathbf{g}\cdot\mathbf{k})d\mathbf{k}d\mathbf{c}_1,\end{aligned}\tag{6.31}$$

$$\begin{aligned}\mathcal{Q}_{P_2}(f,f) &= \frac{\mathsf{d}^2}{2}\frac{\partial\chi}{\partial x_i}\int\left[f'\frac{\partial f_1'}{\partial x_j}-f\frac{\partial f_1}{\partial x_j}\right]k_ik_j\,\mathsf{d}^2(\mathbf{g}\cdot\mathbf{k})d\mathbf{k}d\mathbf{c}_1\\ &+\frac{\mathsf{d}^2}{8}\frac{\partial^2\chi}{\partial x_i\partial x_j}\int k_ik_j(f'f_1'-ff_1)\,\mathsf{d}^2(\mathbf{g}\cdot\mathbf{k})d\mathbf{k}d\mathbf{c}_1\\ &+\frac{\mathsf{d}^2}{2}\chi\int\left[f'\frac{\partial^2 f_1'}{\partial x_i\partial x_j}-f\frac{\partial^2 f_1}{\partial x_i\partial x_j}\right]k_ik_j\,\mathsf{d}^2(\mathbf{g}\cdot\mathbf{k})d\mathbf{k}d\mathbf{c}_1.\end{aligned}\tag{6.32}$$

In the above equations all functions f, f_1, f_1', f' and χ are evaluated at the point $\mathbf{x}$. The collision term $\mathcal{Q}_K(f,f)$ with $\chi=1$ is the usual collision term of the Boltzmann equation for rarefied gases. The collision term $\mathcal{Q}_{P_1}(f,f)$ includes only first-order gradients, while $\mathcal{Q}_{P_2}(f,f)$ takes into account second-order gradients and products of first-order gradients.

Exercise

6.3 Obtain the collision terms (6.30)–(6.32).

6.2.2 The Transfer Equation

As usual the transfer equation is obtained through multiplication of (6.29) by an arbitrary function $\psi\equiv\psi(\mathbf{x},\mathbf{c},t)$ and the integration of the resulting equation over all values of $\mathbf{c}$, yielding

$$\frac{\partial\Psi}{\partial t}+\frac{\partial}{\partial x_i}\left(\Psi v_i+\Phi_i^K+\Phi_i^{P_1}+\Phi_i^{P_2}\right)=P_K+P_{P_1}+P_{P_2}+S.\tag{6.33}$$

In the above equation Ψ is the density of an arbitrary additive quantity, Φ_i^K is a kinetic flux density associated with the flow of the molecules, while $\Phi_i^{P_1}$ and $\Phi_i^{P_2}$ are potential flux densities due to the collisional transfer of the molecules. Furthermore, P_K, P_{P_1} and P_{P_2} are production terms that correspond also to kinetic and potential contributions and S is the density supply related to the external forces. The expressions for these quantities are given by

$$\Psi=\int\psi f\,d\mathbf{c},\qquad \Phi_i^K=\int\psi C_i f\,d\mathbf{c},\tag{6.34}$$

$$\Phi_i^{P_1}=\frac{\mathsf{d}}{2}\int\chi(\psi'-\psi)ff_1k_i\,\mathsf{d}^2(\mathbf{g}\cdot\mathbf{k})d\mathbf{k}\,d\mathbf{c}_1d\mathbf{c},\tag{6.35}$$

$$
\begin{aligned}
\varPhi_i^{P_2} &= -\underline{\frac{\mathsf{d}^2}{8}\frac{\partial}{\partial x_j}\int \chi(\psi'-\psi) f f_1 k_i k_j \, \mathsf{d}^2(\mathbf{g}\cdot\mathbf{k}) d\mathbf{k}\, d\mathbf{c}_1 d\mathbf{c}} \\
&+\frac{\mathsf{d}^2}{4}\int \chi\left[(\psi'-\psi)\frac{\partial}{\partial x_j}\left(\ln\frac{f}{f_1}\right)+\underline{\frac{\partial(\psi'-\psi)}{\partial x_j}}\right] f f_1 k_i k_j \, \mathsf{d}^2(\mathbf{g}\cdot\mathbf{k}) d\mathbf{k}\, d\mathbf{c}_1 d\mathbf{c},
\end{aligned}
\tag{6.36}
$$

$$
P_K = \int\left[\frac{\partial\psi}{\partial t}+c_i\frac{\partial\psi}{\partial x_i}\right] f\, d\mathbf{c} + \underline{\int \chi(\psi'-\psi) f f_1 \, \mathsf{d}^2(\mathbf{g}\cdot\mathbf{k}) d\mathbf{k}\, d\mathbf{c}_1 d\mathbf{c}}, \tag{6.37}
$$

$$
P_{P_1} = \frac{\mathsf{d}}{2}\int \chi\left[\underline{(\psi'-\psi)\frac{\partial}{\partial x_i}\left(\ln\frac{f}{f_1}\right)}+\frac{\partial(\psi'-\psi)}{\partial x_i}\right] f f_1 k_i \, \mathsf{d}^2(\mathbf{g}\cdot\mathbf{k}) d\mathbf{k}\, d\mathbf{c}_1 d\mathbf{c}, \tag{6.38}
$$

$$
\begin{aligned}
P_{P_2} = \frac{\mathsf{d}^2}{4}\int \chi\Bigg\{ &\frac{\partial(\psi'-\psi)}{\partial x_i}\frac{\partial}{\partial x_j}\left(\ln\frac{f}{f_1}\right)+\underline{\frac{1}{2}\frac{\partial^2(\psi'-\psi)}{\partial x_i\partial x_j}}-\underline{(\psi'-\psi)\frac{\partial \ln f}{\partial x_i}\frac{\partial \ln f_1}{\partial x_j}} \\
&+\underline{\frac{1}{2}(\psi'-\psi)\left[\frac{1}{f}\frac{\partial^2 f}{\partial x_i\partial x_j}+\frac{1}{f_1}\frac{\partial^2 f_1}{\partial x_i\partial x_j}\right]}\Bigg\} f f_1 k_i k_j \, \mathsf{d}^2(\mathbf{g}\cdot\mathbf{k}) d\mathbf{k}\, d\mathbf{c}_1 d\mathbf{c},
\end{aligned}
\tag{6.39}
$$

$$
S = \int F_i \frac{\partial\psi}{\partial c_i} f d\mathbf{c}. \tag{6.40}
$$

In order to obtain the above equations all gradients of the factor χ were transformed into gradients of integrals and the latter were defined as gradients of fluxes as indicated by (6.35) and (6.36). The introduction of ψ' proceeds in the same manner as that explained in Section 2.3. Moreover, the expression $(\psi'-\psi)$ within the above underlined terms can be replaced also by $(\psi_1'+\psi'-\psi_1-\psi)/2$.

Exercise

6.4 Obtain the flux densities (6.34)–(6.36) and the production terms (6.37)–(6.39).

6.2.3 Macroscopic Description

A macroscopic state of a monatomic dense gas can be characterized by the fields of mass density ϱ, momentum density ϱv_i and internal energy density $\varrho\varepsilon$ defined by (2.86), (2.87) and $(2.89)_2$, respectively. Note that the energy density is defined in terms of a translational kinetic energy, since according to (6.27) the specific internal energy does not depend on the mass density.

As usual, the balance equations for these fields are obtained by choosing successively $\psi = m$, mc_i and $mC^2/2$ in (6.33). After some rearrangements it follows

$$\mathcal{D}\varrho + \varrho\frac{\partial v_i}{\partial x_i} = 0, \tag{6.41}$$

$$\varrho\mathcal{D}v_i + \frac{\partial}{\partial x_i}\left(p_{ij}^K + p_{ij}^{P_1} + p_{ij}^{P_2}\right) = \varrho F_i, \tag{6.42}$$

$$\varrho\mathcal{D}\varepsilon + \frac{\partial}{\partial x_i}\left(q_i^K + q_i^{P_1} + q_i^{P_2}\right) + \left(p_{ji}^K + p_{ji}^{P_1} + p_{ji}^{P_2}\right)\frac{\partial v_j}{\partial x_i} = 0. \tag{6.43}$$

In the above equations p_{ij}^K represents the pressure tensor associated with the flow of the molecules, while the pressure tensors $p_{ij}^{P_1}$ and $p_{ij}^{P_2}$ are connected with the collisional transfer of the molecules. The same interpretation holds for the heat flux vectors q_i^K, $q_i^{P_1}$ and $q_i^{P_2}$. These quantities are defined by

$$p_{ij}^K = \int mC_iC_j f\, d\mathbf{c}, \qquad p_{ij}^{P_1} = \frac{\mathsf{d}}{2}\int \chi m(c_i' - c_i) f f_1 k_j\, \mathsf{d}^2(\mathbf{g}\cdot\mathbf{k})\, d\mathbf{k}d\mathbf{c_1}d\mathbf{c}, \tag{6.44}$$

$$p_{ij}^{P_2} = \frac{\mathsf{d}^2}{4}\int \chi m(c_i' - c_i)\frac{\partial}{\partial x_k}\left(\ln\frac{f}{f_1}\right) f f_1 k_k k_j\, \mathsf{d}^2(\mathbf{g}\cdot\mathbf{k})\, d\mathbf{k}d\mathbf{c_1}d\mathbf{c}, \tag{6.45}$$

$$q_i^K = \int \frac{m}{2}C^2 C_i f\, d\mathbf{c}, \qquad q_i^{P_1} = \frac{\mathsf{d}}{2}\int \chi\frac{m}{2}(C'^2 - C^2) f f_1 k_i\, \mathsf{d}^2(\mathbf{g}\cdot\mathbf{k})\, d\mathbf{k}d\mathbf{c_1}d\mathbf{c}, \tag{6.46}$$

$$q_i^{P_2} = \frac{\mathsf{d}^2}{4}\int \chi\frac{m}{2}(C'^2 - C^2)\frac{\partial}{\partial x_j}\left(\ln\frac{f}{f_1}\right) f f_1 k_j k_i\, \mathsf{d}^2(\mathbf{g}\cdot\mathbf{k})\, d\mathbf{k}d\mathbf{c_1}d\mathbf{c}. \tag{6.47}$$

The total pressure tensor and the total heat flux vector are given by the respective sums of the kinetic and potential contributions, i.e.,

$$p_{ij} = p_{ij}^K + p_{ij}^{P_1} + p_{ij}^{P_2}, \qquad q_i = q_i^K + q_i^{P_1} + q_i^{P_2}. \tag{6.48}$$

Exercise

6.5 Obtain the balance equations (6.41)–(6.43).

6.2.4 Determination of the Potential Contributions

The potential contributions $p_{ij}^{P_1}$ and $q_i^{P_1}$ can be expressed in terms of the corresponding kinetic ones p_{ij}^K and q_i^K. To prove this assertion, consider first the pressure tensor whose definition is given by $(6.44)_2$. By using the relationships $\mathbf{c}' = \mathbf{c} + \mathbf{k}(\mathbf{k}\cdot\mathbf{g})$ (see (1.87)) and (5.152) one obtains

$$p_{ij}^{P_1} = \frac{\mathsf{d}}{2}\int \chi m f f_1 \mathsf{d}^2 k_i k_j (\mathbf{g}\cdot\mathbf{k})^2 d\mathbf{k}\, d\mathbf{c}_1 d\mathbf{c}$$

$$= \frac{\mathsf{d}^3}{2}\chi m \int \frac{2\pi}{15}(g^2\delta_{ij} + 2g_i g_j) f f_1 d\mathbf{c}_1 d\mathbf{c}. \tag{6.49}$$

If in the above equation one goes back to the variables $\mathbf{c}$ and $\mathbf{c}_1$ by using the relationship $\mathbf{g} = \mathbf{c}_1 - \mathbf{c}$, the integration of the resulting equation with respect to the variables $\mathbf{c}$ and $\mathbf{c}_1$ becomes

$$p_{ij}^{P_1} = \chi b^* \varrho \left[\varrho \frac{k}{m} T\delta_{ij} + \frac{2}{5} p_{\langle ij\rangle}^{K}\right]. \tag{6.50}$$

Note that for the determination of (6.50) no assumption on the distribution functions f and f_1 was taken into account. In this equation b^* is the covolume whose expression is given by $(6.23)_2$.

Following the same scheme used for the calculation of $p_{ij}^{P_1}$, the potential contribution to the heat flux vector $(6.46)_2$ reads

$$q_i^{P_1} = \frac{3}{5}\chi b^* \varrho q_i^K. \tag{6.51}$$

For the determination of the potential contribution $p_{ij}^{P_2}$–given by (6.45)—one makes use again of (1.87) and the resulting equation is integrated over all values of $\mathbf{k}$. Hence, by employing (5.153) it follows

$$p_{ij}^{P_2} = \frac{\mathsf{d}^2}{4}\int \chi m \frac{\partial}{\partial x_k}\left(\ln\frac{f}{f_1}\right) f f_1 \mathsf{d}^2 \frac{\pi}{12} g^{-1}\Big[g_i g_j g_k$$

$$+ g^2(g_i\delta_{jk} + g_j\delta_{ik} + g_k\delta_{ij})\Big] d\mathbf{g} d\mathbf{G}. \tag{6.52}$$

In the above equation the velocity variables $(\mathbf{C}, \mathbf{C}_1)$ were replaced by the relative velocity $\mathbf{g} = \mathbf{c}_1 - \mathbf{c}$ and the center of mass velocity $\mathbf{G} = (\mathbf{C}_1 + \mathbf{C})/2$ and the relationship $d\mathbf{c}\, d\mathbf{c}_1 = d\mathbf{g}\, d\mathbf{G}$ was used. Unfortunately, one cannot determine the potential contribution $p_{ij}^{P_2}$ without the knowledge of the distribution function. In order to obtain constitutive quantities that depend only on linearized first-order gradients, the distribution function in equation (6.52) should be a Maxwellian distribution function, so that

$$\frac{\partial}{\partial x_k}\left(\ln\frac{f^{(0)}}{f_1^{(0)}}\right) = -\frac{m}{kT^2} g_r G_r \frac{\partial T}{\partial x_k} - \frac{m}{kT} g_r \frac{\partial v_r}{\partial x_k}. \tag{6.53}$$

The insertion of (6.53) into (6.52) and the integration of the resulting equation yields

$$p_{ij}^{P_2} = -\frac{\chi {b^*}^2 \varrho^2}{\pi \mathsf{d}^2}\sqrt{\frac{mkT}{\pi}}\left[\frac{\partial v_r}{\partial x_r}\delta_{ij} + \frac{6}{5}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}\right]. \tag{6.54}$$

Hence, the potential contribution to the pressure tensor $p_{ij}^{P_2}$ is a function of the deviator of the velocity gradient and of the divergence of velocity.

By applying the same methodology to the potential contribution to the heat flux vector $q_i^{P_2}$, it follows from (6.47) that

$$q_i^{P_2} = -\frac{3}{2}\frac{\chi {b^*}^2 \varrho^2}{\pi \mathsf{d}^2}\frac{k}{m}\sqrt{\frac{mkT}{\pi}}\frac{\partial T}{\partial x_i}, \tag{6.55}$$

which shows that the potential contribution to the heat flux vector is proportional to the gradient of temperature.

Exercise

6.6 Obtain the expressions for the potential contributions to the heat flux vector (6.51) and (6.55).

6.2.5 Equilibrium Constitutive Equations

The equilibrium state is characterized by a Maxwellian distribution function so that the kinetic contributions to the pressure tensor $(6.44)_1$ and to the heat flux vector $(6.46)_1$ become

$$p_{ij}^K\big|_E = \varrho\frac{k}{m}T\delta_{ij}, \qquad q_i^K\big|_E = 0. \tag{6.56}$$

Furthermore, in equilibrium the temperature gradient, the divergence of the velocity and the deviator of the velocity gradient must vanish, i.e.,

$$\left.\frac{\partial T}{\partial x_i}\right|_E = 0, \qquad \left.\frac{\partial v_r}{\partial x_r}\right|_E = 0, \qquad \left.\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}\right|_E = 0. \tag{6.57}$$

Hence, from (6.54) and (6.55) one obtains that in equilibrium $p_{ij}^{P_2}\big|_E = 0$ and $q_i^{P_2}\big|_E = 0$.

Now by combining (6.48), (6.50), (6.51) and (6.56) it follows the equilibrium constitutive equations for the pressure tensor and for the heat flux vector for a dense gas of hard spherical particles, namely,

$$p_{ij}\big|_E = \varrho\frac{k}{m}T\left(1+\chi b^*\varrho\right)\delta_{ij}, \qquad q_i\big|_E = 0. \tag{6.58}$$

From the constitutive equation for the pressure tensor $(6.58)_1$ one can identify that the hydrostatic pressure of a dense gas of hard spherical particles reads

$$p = \varrho\frac{k}{m}T\left(1+\chi b^*\varrho\right). \tag{6.59}$$

Until this point the factor χ in Enskog's equation was left unspecified. By comparing $(6.23)_1$ and (6.59) one may identify $\chi \equiv \chi^*$.

6.2.6 Determination of the Kinetic Contributions

In order to determine the kinetic contributions for the pressure tensor $p^K_{\langle ij\rangle}$ and the heat flux vector q_i^K, the Chapman–Enskog–Grad combined method will be used (see Section 4.3). Since the main objective is to obtain linearized constitutive equations with first-order gradients one neglects the collision term (6.32) and introduces: (**i**) the Maxwellian distribution function into the left-hand side of equation (6.29), (**ii**) Grad's distribution function (4.25) into the collision term (6.30) and (**iii**) the Maxwellian distribution function into the collision term (6.31). Hence, it follows

$$
\begin{aligned}
f^{(0)}\Bigg\{&\frac{\mathcal{D}\varrho}{\varrho}+\frac{\mathcal{D}T}{T}\left(\frac{mC^2}{2kT}-\frac{3}{2}\right)+\frac{m}{kT}C_i\mathcal{D}v_i+C_i\Bigg[\frac{1}{\varrho}\frac{\partial\varrho}{\partial x_i}+\frac{m}{kT}C_j\frac{\partial v_j}{\partial x_i}\\
&+\frac{1}{T}\frac{\partial T}{\partial x_i}\left(\frac{mC^2}{2kT}-\frac{3}{2}\right)\Bigg]-\frac{m}{kT}F_iC_i\Bigg\}=\frac{p^K_{\langle kl\rangle}}{2\varrho}\left(\frac{m}{kT}\right)^2\mathcal{I}_\chi[C_kC_l]\\
&+\frac{2}{5}\frac{q_i^K}{\varrho}\left(\frac{m}{kT}\right)^2\mathcal{I}_\chi\left[\left(\frac{mC^2}{2kT}-\frac{5}{2}\right)C_k\right]+\mathcal{Q}^{(0)}_{P_1}.
\end{aligned}
\tag{6.60}
$$

Above, $\mathcal{I}_\chi$ is the collision integral

$$
\mathcal{I}_\chi[\phi]=\chi\int f^{(0)}f_1^{(0)}\left(\phi_1'+\phi'-\phi_1-\phi\right)\mathsf{d}^2(\mathbf{g}\cdot\mathbf{k})d\mathbf{k}d\mathbf{c}_1,
\tag{6.61}
$$

and the term $\mathcal{Q}^{(0)}_{P_1}$ is given by

$$
\begin{aligned}
\mathcal{Q}^{(0)}_{P_1}=\chi\mathsf{d}\int f^{(0)}f_1^{(0)}\Bigg\{&\frac{2}{\varrho}\frac{\partial\varrho}{\partial x_i}+\frac{1}{T}\frac{\partial T}{\partial x_i}\left[\frac{m(C_1'^2+C_1^2)}{2kT}-3\right]+\frac{\partial\ln\chi}{\partial x_i}\\
&+\frac{m}{kT}(C_j^{1\prime}+C_j^1)\frac{\partial v_j}{\partial x_i}\Bigg\}k_i\mathsf{d}^2(\mathbf{g}\cdot\mathbf{k})\,d\mathbf{k}\,d\mathbf{c}_1.
\end{aligned}
\tag{6.62}
$$

By performing the integrations with respect to the variables $\mathbf{k}$ and $\mathbf{c}_1$ one obtains, after some rearrangements, that the term $\mathcal{Q}^{(0)}_{P_1}$ reduces to

$$
\begin{aligned}
\mathcal{Q}^{(0)}_{P_1}=-\chi b^*\varrho f^{(0)}\Bigg\{&\left(\frac{2}{\varrho}\frac{\partial\varrho}{\partial x_i}+\frac{\partial\ln\chi}{\partial x_i}\right)C_i-\frac{1}{10T}\frac{\partial T}{\partial x_i}C_i\left(1-\frac{3mC^2}{kT}\right)\\
&-\frac{\partial v_i}{\partial x_j}\left[\left(1-\frac{mC^2}{3kT}\right)\delta_{ij}-\frac{2m}{5kT}C_{\langle i}C_{j\rangle}\right]\Bigg\}.
\end{aligned}
\tag{6.63}
$$

From (6.60) it is easy to obtain the balance equations for mass density, momentum density and specific internal energy through the multiplication of (6.60) successively by m, mc_i and $mC^2/2$ and by integrating the resulting equations. They read

$$\mathcal{D}\varrho+\varrho\frac{\partial v_i}{\partial x_i}=0, \tag{6.64}$$

$$\varrho\mathcal{D}v_i+\frac{\partial}{\partial x_i}\left[\varrho\frac{k}{m}T\left(1+\chi b^*\varrho\right)\right]=\varrho F_i, \tag{6.65}$$

$$\frac{3}{2}\varrho\frac{k}{m}\mathcal{D}T+\varrho\frac{k}{m}T\left(1+\chi b^*\varrho\right)\frac{\partial v_i}{\partial x_i}=0. \tag{6.66}$$

Note that the above balance equations correspond to (6.41)–(6.43) for the case of an Eulerian fluid where $p_{ij}=p\,\delta_{ij}$ and $q_i=0$.

The elimination of the material time derivatives of the mass density, velocity and temperature from (6.60) combined with (6.63), through the use of the balance equations (6.64)–(6.66), leads to

$$f^{(0)}\left\{\frac{1}{T}\frac{\partial T}{\partial x_k}C_k\left(\frac{mC^2}{2kT}-\frac{5}{2}\right)\underline{\left(1+\frac{3}{5}\chi b^*\varrho\right)}+\frac{m}{kT}C_kC_l\frac{\partial v_{\langle k}}{\partial x_{l\rangle}}\underline{\left(1+\frac{2}{5}\chi b^*\varrho\right)}\right\}$$

$$=\frac{p^K_{\langle kl\rangle}}{2\varrho}\left(\frac{m}{kT}\right)^2 I_\chi[C_kC_l]+\frac{2q^K_k}{5\varrho}\left(\frac{m}{kT}\right)^2 I_\chi\left[\left(\frac{mC^2}{2kT}-\frac{5}{2}\right)C_k\right]. \tag{6.67}$$

Now it is easy to obtain the constitutive equations of the kinetic contributions for the pressure deviator and heat flux vector, since (6.67) differs from the one for a rarefied gas, namely (4.69), by the inclusion of the underlined terms and of the factor χ. Hence, the desired constitutive equations read

$$p^K_{\langle ij\rangle}=-\frac{5}{8}\frac{1}{\chi\mathsf{d}^2}\sqrt{\frac{mkT}{\pi}}\left(1+\frac{2}{5}\chi b^*\varrho\right)\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \tag{6.68}$$

$$q^K_i=-\frac{75}{64}\frac{1}{\chi\mathsf{d}^2}\frac{k}{m}\sqrt{\frac{mkT}{\pi}}\left(1+\frac{3}{5}\chi b^*\varrho\right)\frac{\partial T}{\partial x_i}. \tag{6.69}$$

Exercises

6.7 Integrate (6.62) and obtain (6.63).

6.8 Show that the equation for the determination of the kinetic contributions for the pressure deviator and heat flux vector reduces to (6.67).

6.2.7 The Laws of Navier–Stokes and Fourier

According to (6.48) the final expressions for the pressure tensor p_{ij} and for the heat flux vector q_i are obtained by collecting the kinetic contributions (6.68), (6.69) and the potential contributions (6.50), (6.51), (6.54) and (6.55), yielding

$$p_{ij} = \left(p - \eta\frac{\partial v_r}{\partial x_r}\right)\delta_{ij} - 2\mu\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \qquad q_i = -\lambda\frac{\partial T}{\partial x_i}. \tag{6.70}$$

The above equations represent the laws of Navier–Stokes and Fourier, respectively, where the coefficients of bulk viscosity η, shear viscositity μ and thermal conductivity λ are given by

$$\eta = \frac{1}{\pi\mathsf{d}^2}\sqrt{\frac{mkT}{\pi}}\chi {b^*}^2\varrho^2, \tag{6.71}$$

$$\mu = \frac{5}{16}\frac{1}{\chi\mathsf{d}^2}\sqrt{\frac{mkT}{\pi}}\left[1 + \frac{4}{5}\chi b^*\varrho + \frac{4}{25}\left(1 + \frac{12}{\pi}\right)\chi^2{b^*}^2\varrho^2\right], \tag{6.72}$$

$$\lambda = \frac{75}{64}\frac{1}{\chi\mathsf{d}^2}\frac{k}{m}\sqrt{\frac{mkT}{\pi}}\left[1 + \frac{6}{5}\chi b^*\varrho + \frac{9}{25}\left(1 + \frac{32}{9\pi}\right)\chi^2{b^*}^2\varrho^2\right]. \tag{6.73}$$

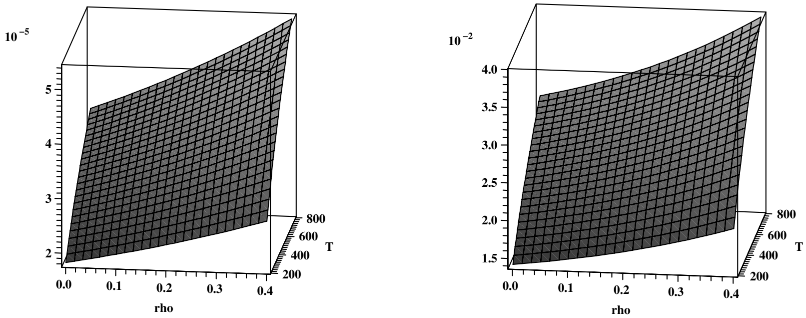

Fig. 6.1 Transport coefficients versus T and $\rho = b^*\varrho$ for argon gas. Left frame: shear viscosity μ; right frame: thermal conductivity λ.

In Figures 6.1 and 6.2 the transport coefficients of argon gas as functions of the temperature T and of the factor $\rho = b^*\varrho$ are plotted. One infers from these figures that by increasing the value of $b^*\varrho$ the gas becomes denser and the transport coefficients increase. However, one should note that Enskog's theory describes a moderately dense gas so that the value of the dimensionless factor

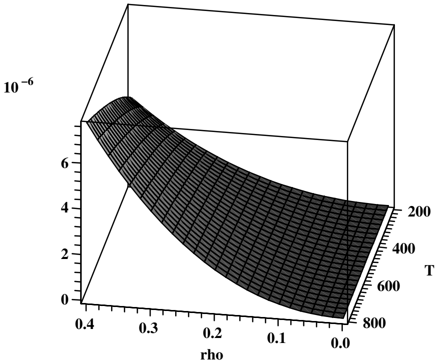

Fig. 6.2 Bulk viscosity η versus T and $\rho = b^*\varrho$ for argon gas.

$b^*\varrho$ should be considered small. Note that the value $b^*\varrho = 0$ corresponds to a rarefied gas and in this case the bulk viscosity vanishes.

In order to compare the magnitude of the bulk viscosity one can build the ratio of the bulk and shear viscosities, namely,

$$\frac{\eta}{\mu} = \frac{16}{5\pi}\frac{\chi^2 b^{*2}\varrho^2}{\left[1+\frac{4}{5}\chi b^*\varrho + \frac{4}{25}\left(1+\frac{12}{\pi}\right)\chi^2 {b^*}^2\varrho^2\right]}. \tag{6.74}$$

From the above equation one verifies that the coefficient of bulk viscosity becomes comparable to the shear viscosity by increasing the factor $b^*\varrho$. Indeed, for $b^*\varrho \approx 0.4$ the bulk viscosity is approximately 14% of the shear viscosity.

Exercise

6.9 Draw the curves of Figures 6.1 and 6.2 for argon gas.

6.3 The Modified Enskog Equation

On the basis of the distribution function $f_n(\mathbf{x}_1, \dots, \dot{\mathbf{x}}_n, t)$ defined in Section 2.2.3 one may introduce the spatial distribution function, namely,

$$n_n(\mathbf{x}_1, \dots, \mathbf{x}_n, t) = \int f_n(\mathbf{x}_1, \dots, \dot{\mathbf{x}}_n, t)\, d\dot{\mathbf{x}}_1 \dots d\dot{\mathbf{x}}_n. \tag{6.75}$$

The spatial distribution function $n_1(\mathbf{x}_1, t) \equiv n(\mathbf{x}, t)$ is the particle number density and $n_2(\mathbf{x}_1, \mathbf{x}_2, t)$ is the so-called pair distribution function.

If $r_{\alpha\beta} = |\mathbf{x}_\alpha - \mathbf{x}_\beta|$ denotes the relative distance of two molecules α and β, it is expected that the following relationship holds for the pair distribution function:

$$\lim_{r_{12}\to\infty} n_2(\mathbf{x}_1, \mathbf{x}_2, t) = n^2, \tag{6.76}$$

when the two molecules are far apart each other. Hence, one may introduce another function which measures the deviation of $n_2(\mathbf{x}_1, \mathbf{x}_2, t)$ from the value n^2 when the two molecules are far apart. The deviation function, known as the pair correlation function, is defined by

$$g_2(\mathbf{x}_1, \mathbf{x}_2, t) = \frac{n_2(\mathbf{x}_1, \mathbf{x}_2, t)}{n^2} - 1. \tag{6.77}$$

In Section 2.2.3 the Boltzmann equation for a rarefied gas was derived from the BBGKY hierarchy by assuming that—due to the molecular chaos assumption—the distribution function f_2 was written as a product of two f_1 distribution functions. For dense gases, the pair correlation function is introduced in the representation for the distribution function f_2, i.e.,

$$f_2(\mathbf{x}_1, \mathbf{x}_2, \dot{\mathbf{x}}_1, \dot{\mathbf{x}}_2, t) = g_2(\mathbf{x}_1, \mathbf{x}_2, t) f_1(\mathbf{x}_1, \dot{\mathbf{x}}_1, t) f_2(\mathbf{x}_2, \dot{\mathbf{x}}_2, t). \tag{6.78}$$

One recognizes that the pair correlation function plays the role of the factor χ introduced by Enskog into the Boltzmann equation. According to the item **(b)** of Section 6.2.1, the pair correlation function should be dependent on the density of the gas at the contact point of the colliding spheres so that one may write $g_2(\mathbf{x}_1, \mathbf{x}_2 | n(t))$. Hence, instead of (6.28) one should have the modified Enskog equation[4]

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} + F_i \frac{\partial f}{\partial c_i} = \int \Big[g_2(\mathbf{x}, \mathbf{x} + \mathsf{d}\mathbf{k} | n(t))\, f(\mathbf{x}, \mathbf{c}', t)\, f(\mathbf{x} + \mathsf{d}\mathbf{k}, \mathbf{c}_1', t) \\ - g_2(\mathbf{x}, \mathbf{x} - \mathsf{d}\mathbf{k} | n(t))\, f(\mathbf{x}, \mathbf{c}, t)\, f(\mathbf{x} - \mathsf{d}\mathbf{k}, \mathbf{c}_1, t) \Big] \mathsf{d}^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{c}_1. \tag{6.79}$$

The Enskog equation (6.28) and the modified Enskog equation (6.79) are referred in the literature as standard Enskog theory (SET) and revised Enskog equation (RET), respectively.

One is referred to books on statistical mechanics[5] for the determination of the pair correlation function since it is out of the scope of this book. Its expression is given by

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[4] This equation was proposed by H. van Beijeren and M. H. Ernst, "The modified Enskog equation", *Physica* **68** 437-456 (1973).

[5] See e.g., D.A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976).

$$
\begin{aligned}
g_2(\mathbf{x}_1,\mathbf{x}_2|n(t)) = \exp\left(-\frac{\varPhi(|\mathbf{x}_1-\mathbf{x}_2|)}{kT}\right)\Bigg\{1 &+ \int n(t,\mathbf{x}_3)\lambda_{13}\lambda_{23}d\mathbf{x}_3 \\
&+ \frac{1}{2}\int n(t,\mathbf{x}_3)n(t,\mathbf{x}_4)\Big[2\lambda_{13}\lambda_{24}\lambda_{34} + 4\lambda_{13}\lambda_{23}\lambda_{24}\lambda_{34} \\
&+ \lambda_{13}\lambda_{14}\lambda_{23}\lambda_{24} + \lambda_{13}\lambda_{14}\lambda_{23}\lambda_{24}\lambda_{34}\Big]d\mathbf{x}_3 d\mathbf{x}_4 + \dots\Bigg\}. \qquad (6.80)
\end{aligned}
$$

In the above equation $\varPhi(|\mathbf{x}_\alpha - \mathbf{x}_\beta|)$ is the potential of molecular interaction and $\lambda_{\alpha\beta} = \exp\left(-\varPhi(|\mathbf{x}_\alpha - \mathbf{x}_\beta|)/kT\right) - 1$ represents the Mayer function. For the hard-sphere potential the Mayer function has the following expression:

$$
\lambda_{\alpha\beta} = \varTheta\left(|\mathbf{x}_\alpha - \mathbf{x}_\beta|) - \mathsf{d}\right) - 1, \quad \text{where} \quad \varTheta(r) = \begin{cases} 1 & \text{for} \quad r > 0, \\ 0 & \text{for} \quad r < 0, \end{cases} \qquad (6.81)
$$

is the unit step function.

Consider in (6.80) $\mathbf{x}_1 \equiv \mathbf{x}$, $\mathbf{x}_2 \equiv \mathbf{x} \pm \mathsf{d}\mathbf{k}$ and all particle number densities $n(t,\mathbf{x}_3), n(t,\mathbf{x}_4), \dots$ as functions of $n(t,\mathbf{x}\pm\mathsf{d}\mathbf{k}/2)$. In this case, one may obtain that the expansion of the pair correlation function (6.80) in Taylor series around the point $\mathbf{x}$ leads to an expression where the terms of order $(\nabla n)^0$ and $(\nabla n)^1$ in the SET and RET theories do not differ from each other. Hence, for a single gas the SET and RET theories lead to the same expressions for the transport coefficients at the level of Navier–Stokes–Fourier constitutive equations. However, the terms of order $(\nabla n)^\alpha$ for $\alpha > 2$ in the SET and RET theories are dissimilar, and so are the transport coefficients of the Burnett and other higher order constitutive equations. The SET theory is not adequate to describe mixtures of moderately dense gases and in this case the RET theory should be used (for more details one is referred to the work of van Beijeren and Ernst).

It is important to compute the second term of the pair correlation function (6.80) for a hard-sphere potential, since it leads to the determination of the third virial coefficient. Here, it is employed the methodology of Katsura[6] which makes use of Fourier transforms.

The Fourier transform of the function $\lambda(\mathbf{r})$ and its inverse transformation[7] in a three-dimensional space are defined by the relationships

$$
\varLambda(\mathbf{q}) = \frac{1}{(2\pi)^{3/2}}\int \lambda(\mathbf{r})\, e^{\imath\,\mathbf{q}\cdot\mathbf{r}}d\mathbf{r}, \qquad \lambda(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}}\int \varLambda(\mathbf{q})\, e^{-\imath\,\mathbf{q}\cdot\mathbf{r}}d\mathbf{q}. \qquad (6.82)
$$

In order to evaluate the Fourier transform of the Mayer function $\lambda(|\mathbf{r}|)$ which is given by

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[6] S. Katsura, "Fourth virial coefficient for the square well potential", *Phys. Rev.* **115**, 1417 - 1426 (1959). See also the book by McQuarrie.

[7] See e.g. G. B. Arfken and H. J. Weber, "Mathematical methods for physicists" 4th edition (Academic Press, San Diego, 1995).

$$\lambda(|\mathbf{r}|) = \begin{cases} -1 & \text{for} \quad r < \mathsf{d}, \\ \;\;0 & \text{for} \quad r > \mathsf{d}, \end{cases} \tag{6.83}$$

one can orient, without loss of generality, the vector $\mathbf{r}$ in the direction of the x_3-axis and write $d\mathbf{r}$ in spherical coordinates $d\mathbf{r} = r^2 \sin\theta d\phi d\theta dr$. In this case, $(6.82)_1$ is written as

$$\begin{aligned} \Lambda(|\mathbf{q}|) &= \frac{1}{(2\pi)^{3/2}} \int_0^\infty \int_0^\pi \int_0^{2\pi} \lambda(|\mathbf{r}|) e^{\imath\, qr\cos\theta} r^2 \sin\theta d\phi d\theta dr \\ &= \sqrt{\frac{2}{\pi}} \int_0^\infty \frac{r\sin(qr)}{q} \lambda(|\mathbf{r}|) dr, \end{aligned} \tag{6.84}$$

where the last equality was obtained through the integration over the angles θ and ϕ. Now the integration over the variable r by taking into account (6.83) leads to

$$\Lambda(|\mathbf{q}|) = \sqrt{\frac{2}{\pi}} \frac{qd\cos(qd) - \sin(qd)}{q^3}. \tag{6.85}$$

For the determination of the second term of the pair correlation function (6.80) one proceeds as follows. First, the vectors $\mathbf{r}_2 = \mathbf{x}_2 - \mathbf{x}$ and $\mathbf{r}_3 = \mathbf{x}_3 - \mathbf{x}$ are introduced and only the first term of the development of $n(t, \mathbf{x} \pm \mathsf{d}\mathbf{k}/2)$ in Taylor series around $\mathbf{x}$ is considered. Hence, it follows

$$\int n(t, \mathbf{x}_3) \lambda_{13} \lambda_{23} d\mathbf{x}_3 = n(\mathbf{x}, t) \int \lambda(|\mathbf{r}_3|) \lambda(|\mathbf{r}_3 - \mathbf{r}_2|) d\mathbf{r}_3. \tag{6.86}$$

Now one may write $\lambda(|\mathbf{r}_3 - \mathbf{r}_2|)$ in terms of a Fourier transform as

$$\lambda(|\mathbf{r}_3 - \mathbf{r}_2|) = \frac{1}{(2\pi)^{3/2}} \int \Lambda(|\mathbf{q}|)\, e^{\imath\, \mathbf{q}\cdot\mathbf{r}_3}\, e^{-\imath\, \mathbf{q}\cdot\mathbf{r}_2} d\mathbf{q}. \tag{6.87}$$

The insertion of (6.87) into (6.86) leads to

$$\begin{aligned} \int n(t, \mathbf{x}_3) \lambda_{13} \lambda_{23} d\mathbf{x}_3 &= \frac{n(\mathbf{x}, t)}{(2\pi)^{3/2}} \int \lambda(|\mathbf{r}_3|) \Lambda(|\mathbf{q}|)\, e^{\imath\, \mathbf{q}\cdot\mathbf{r}_3}\, e^{-\imath\, \mathbf{q}\cdot\mathbf{r}_2} d\mathbf{q}\, d\mathbf{r}_3 \\ &= n(\mathbf{x}, t) \int (\Lambda(|\mathbf{q}|))^2\, e^{-\imath\, \mathbf{q}\cdot\mathbf{r}_2} d\mathbf{q}, \end{aligned} \tag{6.88}$$

due to the definition of the Fourier transform $(6.82)_1$. Now one may perform the integration of the above equation over the spherical angles resulting

$$\int n(t, \mathbf{x}_3) \lambda_{13} \lambda_{23} d\mathbf{x}_3 = 4\pi n(\mathbf{x}, t) \int_0^\infty (\Lambda(|\mathbf{q}|))^2 \frac{q\sin(qr_2)}{r_2} dq. \tag{6.89}$$

At collision $r_2 = \mathsf{d}$ and one may insert (6.85) into (6.89) and perform the integration over q, which leads to

$$\int n(t,\mathbf{x}_3)\lambda_{13}\lambda_{23}d\mathbf{x}_3\bigg|_{r_2=\mathsf{d}} = \frac{5\pi}{12}\mathsf{d}^3 n(\mathbf{x},t) = \frac{5}{8}\,b^*\,\varrho(\mathbf{x},t). \tag{6.90}$$

In the last equality, the covolume b^* was introduced, defined by $(6.23)_2$.

Now one recognizes that the result given by (6.90) is the second term of the factor χ^* which is given by the expression (6.24).

Exercise

6.10 Obtain the expressions given in (6.85), (6.89) and (6.90).

Chapter 7
Granular Gases

7.1 Dynamics of a Binary Collision

As it was discussed in the previous chapters, the mechanical energy of a gas is conserved when its molecules undergo elastic collisions and, in this case, the gas relaxes toward an equilibrium state characterized by a Maxwellian distribution function. The inelastic collisions of the gas molecules transform the translational kinetic energy into heat, and the mechanical energy lost implies a temperature decay of the gas. Gases whose molecules undergo inelastic collisions are known in the literature as granular gases.

The kinetic theory of granular gases is based on the following premises: (**a**) only binary collisions are taken into account; (**b**) the rarefied gas is consisted of hard spherical molecules; (**c**) the energy lost from inelastic collisions is small and (**d**) external body forces are absent.

Consider the encounter of two identical molecules of mass m, diameter d, pre-collisional velocities $(\mathbf{c}, \mathbf{c}_1)$ and post-collisional velocities $(\mathbf{c}', \mathbf{c}_1')$. For inelastic collisions, the momentum conservation law $m\mathbf{c} + m\mathbf{c}_1 = m\mathbf{c}' + m\mathbf{c}_1'$ holds. However, the inelastic encounters are characterized by the relationship $(\mathbf{g}' \cdot \mathbf{k}) = -\alpha(\mathbf{g} \cdot \mathbf{k})$, which relates the pre- and post-collisional relative velocities at collision. The parameter $0 \leqslant \alpha \leqslant 1$ is the normal restitution coefficient and $\mathbf{k}$ the unit vector directed along the line which joins the molecules centers and pointing from center of the molecule labeled by the index 1 to the center of the molecule without label (see Figure 5.3). In inelastic collisions, the component of the velocity perpendicular to the collision vector $\mathbf{k}$ does not change so that $\mathbf{k} \times \mathbf{g}' = \mathbf{k} \times \mathbf{g}$.

From the momentum conservation law (1.75), one may obtain the post-collisional velocities in terms of the pre-collisional ones, yielding

$$\mathbf{c}' = \mathbf{c} + \frac{1+\alpha}{2}(\mathbf{g} \cdot \mathbf{k})\mathbf{k}, \qquad \mathbf{c}_1' = \mathbf{c}_1 - \frac{1+\alpha}{2}(\mathbf{g} \cdot \mathbf{k})\mathbf{k}. \tag{7.1}$$

Furthermore, the relationships which connect the relative velocities and their modulus read

$$\mathbf{g}' = \mathbf{g} - (1+\alpha)(\mathbf{g}\cdot\mathbf{k})\mathbf{k}, \qquad g'^2 = g^2 - (1-\alpha^2)(\mathbf{g}\cdot\mathbf{k})^2. \tag{7.2}$$

From $(7.2)_2$, one can obtain the variation of the kinetic energy in terms of the pre- and post-collisional velocities, namely,

$$\frac{m}{2}c'^2 + \frac{m}{2}c_1'^2 - \frac{m}{2}c^2 - \frac{m}{2}c_1^2 = \frac{m}{4}(\alpha^2 - 1)(\mathbf{g}\cdot\mathbf{k})^2. \tag{7.3}$$

When $\alpha = 1$, which is the case of elastic collisions, it follows the conservation of the kinetic energy

$$\frac{m}{2}c'^2 + \frac{m}{2}c_1'^2 = \frac{m}{2}c^2 + \frac{m}{2}c_1^2, \qquad \text{or} \qquad g = g'. \tag{7.4}$$

The analysis of this chapter is restricted to the case where the normal restitution coefficient is a constant.

Exercise

7.1 Obtain (7.1)–(7.3).

7.2 The Boltzmann Equation

As in the classical model for a polyatomic gas (see Section 5.3.2), there exists a restitution collision with pre-collisional velocities $(\mathbf{c}^*, \mathbf{c}_1^*)$ that corresponds to the post-collisional velocities $(\mathbf{c}, \mathbf{c}_1)$. The equations that relate the velocities are obtained from (7.1) and read

$$\mathbf{c} = \mathbf{c}^* + \frac{1+\alpha}{2}(\mathbf{g}^*\cdot\mathbf{k}^*)\mathbf{k}^*, \qquad \mathbf{c}_1 = \mathbf{c}_1^* - \frac{1+\alpha}{2}(\mathbf{g}^*\cdot\mathbf{k}^*)\mathbf{k}^*. \tag{7.5}$$

By using the relationships $\mathbf{k}^* = -\mathbf{k}$ and $(\mathbf{g}\cdot\mathbf{k}) = -\alpha(\mathbf{g}^*\cdot\mathbf{k})$, the above equations can be written as

$$\mathbf{c}^* = \mathbf{c} + \frac{1+\alpha}{2\alpha}(\mathbf{g}\cdot\mathbf{k})\mathbf{k}, \qquad \mathbf{c}_1^* = \mathbf{c}_1 - \frac{1+\alpha}{2\alpha}(\mathbf{g}\cdot\mathbf{k})\mathbf{k}. \tag{7.6}$$

In order to determine the Boltzmann equation, one has to know the transformation of the volume elements. The modulus of the Jacobian of the transformation $d\mathbf{c}_1^*\, d\mathbf{c}^* = |J| d\mathbf{c}_1\, d\mathbf{c}$ is given by $|J| = 1/\alpha$ and one may obtain the relationship

$$(\mathbf{g}^*\cdot\mathbf{k}^*)\, d\mathbf{c}^*\, d\mathbf{c}_1^* = \frac{1}{\alpha^2}(\mathbf{g}\cdot\mathbf{k})\, d\mathbf{c}\, d\mathbf{c}_1. \tag{7.7}$$

As in the case of the dense gas, the factor χ associated with the pair correlation function (see Section 6.3) is also introduced into the Boltzmann equation (2.20) for granular gases, yielding

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} = \chi \int \left(\frac{1}{\alpha^2} f_1^* f^* - f_1 f \right) \mathsf{d}^2 \, (\mathbf{g} \cdot \mathbf{k}) \, d\mathbf{k} \, d\mathbf{c}_1 \equiv \mathcal{Q}_I(f, f), \tag{7.8}$$

where the relationship (7.7) was used in order to transform the starred into non-starred volume elements. Furthermore, the collision term was written in terms of the bilinear form

$$\mathcal{Q}_I(F, G) = \frac{\chi}{2} \int \left(\frac{1}{\alpha^2} F_1' G' + \frac{1}{\alpha^2} F' G_1' - F_1 G - F G_1 \right) \mathsf{d}^2 \, (\mathbf{g} \cdot \mathbf{k}) \, d\mathbf{k} \, d\mathbf{c}_1. \tag{7.9}$$

Exercise

7.2 Show that the modulus of the Jacobian of the transformation $d\mathbf{c}_1^* \, d\mathbf{c}^* = |J| d\mathbf{c}_1 \, d\mathbf{c}$ is given by $|J| = 1/\alpha$.

7.3 Macroscopic Description of a Granular Gas

By following the same methodology of Section 5.3.2, it is easy to get a transfer equation for an arbitrary function $\psi(\mathbf{x}, \mathbf{c}, t) \equiv \psi$. Indeed, the multiplication of the Boltzmann equation (7.8) by ψ and the integration of the resulting equation leads to the transfer equation

$$\frac{\partial}{\partial t} \int \psi f \, d\mathbf{c} + \frac{\partial}{\partial x_i} \int \psi c_i f \, d\mathbf{c} - \int \left[\frac{\partial \psi}{\partial t} + c_i \frac{\partial \psi}{\partial x_i} \right] f \, d\mathbf{c}$$
$$= \frac{\chi}{2} \int \left(\psi_1' + \psi' - \psi_1 - \psi \right) f_1 f \, \mathsf{d}^2 \, (\mathbf{g} \cdot \mathbf{k}) \, d\mathbf{k} \, d\mathbf{c}_1 \, d\mathbf{c}, \tag{7.10}$$

where on the right-hand side of the above equation, the symmetry properties of the collision term were used (see Section 5.3.2).

The balance equations for the mass density ϱ, for the momentum density ϱv_i and for the specific internal energy $\varepsilon = 3kT/2m$ are obtained from the transfer equation (7.10) by choosing successively $\psi = m$, $\psi = mc_i$ and $\psi = mC^2/2$. Hence, it follows

$$\mathcal{D}\varrho + \varrho \frac{\partial v_i}{\partial x_i} = 0, \qquad \mathcal{D}v_i + \frac{\partial p_{ij}}{\partial x_j} = 0, \tag{7.11}$$

$$\mathcal{D}T + \frac{2}{3nk} \left(\frac{\partial q_i}{\partial x_i} + p_{ij} \frac{\partial v_i}{\partial x_j} \right) + T\zeta = 0. \tag{7.12}$$

The balance equation for the temperature (7.12) has the additional term $T\zeta$, which represents the energy loss due to inelastic collisions. The coefficient ζ is known as cooling rate of the granular gas and it is given by

$$\zeta = \frac{\chi \mathsf{d}^2 m(1-\alpha^2)}{12nkT} \int f_1 f (\mathbf{g}\cdot\mathbf{k})^3 d\mathbf{k}\, d\mathbf{c}_1\, d\mathbf{c}. \tag{7.13}$$

Note that the cooling rate vanishes for elastic collisions where $\alpha = 1$.

Exercise

7.3 Calculate the cooling rate (7.13) for a Maxwellian distribution function. Hint: use the table of integrals given in the Appendix 5.5.

7.4 The Chapman–Enskog Method

The determination of the constitutive equations for the pressure tensor and for the heat flux vector of a monatomic rarefied gas was described in Section 3.3. The methodology to obtain the constitutive equations for granular gases is similar, but one has to take into account that there exists no equilibrium state characterized by a Maxwellian distribution function.

7.4.1 Integral Equations

The first step is to expand the distribution function in series of the parameter ϵ which is of order of the Knudsen number (see Section 3.3.2)

$$f = f^{(0)} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \ldots = \sum_{r=0}^{\infty} \epsilon^r f^{(r)}, \tag{7.14}$$

as well as the material time derivative

$$\mathcal{D} = \mathcal{D}_0 + \epsilon\mathcal{D}_1 + \epsilon^2\mathcal{D}_2 + \ldots = \sum_{r=1}^{\infty} \epsilon^r \mathcal{D}_r. \tag{7.15}$$

The series expansions for the pressure deviator $p_{\langle ij\rangle}$ and for the heat flux vector q_i are the same as those for a monatomic rarefied gas, namely

$$p_{\langle ij\rangle} = \int C_{\langle i}C_{j\rangle} \sum_{r=1}^{\infty} \epsilon^r f^{(r)} d\mathbf{c} = \sum_{r=1}^{\infty} \epsilon^r p_{\langle ij\rangle}^{(r)}, \tag{7.16}$$

$$q_i = \int \frac{m}{2} C^2 C_i \sum_{r=1}^{\infty} \epsilon^r f^{(r)} d\mathbf{c} = \sum_{r=1}^{\infty} \epsilon^r q_i^{(r)}. \tag{7.17}$$

The first difference with respect to a monatomic gas of elastic spherical molecules refers to the decomposition of the balance equations, since they are written as

$$\mathcal{D}_0 n = 0, \qquad \mathcal{D}_1 n = -n \frac{\partial v_i}{\partial x_i}, \tag{7.18}$$

$$\mathcal{D}_0 v_i = 0, \qquad \mathcal{D}_1 v_i = -\frac{1}{\varrho} \frac{\partial p}{\partial x_i}. \tag{7.19}$$

$$\mathcal{D}_0 T = -T\zeta^{(0)}, \qquad \mathcal{D}_1 T = -T\zeta^{(1)} - \frac{2T}{3} \frac{\partial v_i}{\partial x_i}. \tag{7.20}$$

In (7.20), the first and the second approximation to the cooling rate are given by

$$\zeta^{(0)} = \frac{\chi \mathsf{d}^2 m (1-\alpha^2)}{12nkT} \int f_1^{(0)} f^{(0)} (\mathbf{g} \cdot \mathbf{k})^3 d\mathbf{k}\, d\mathbf{c}_1\, d\mathbf{c}, \tag{7.21}$$

$$\zeta^{(1)} = \frac{\chi \mathsf{d}^2 m (1-\alpha^2)}{12nkT} \int \left(f_1^{(1)} f^{(0)} + f_1^{(0)} f^{(1)} \right) (\mathbf{g} \cdot \mathbf{k})^3 d\mathbf{k}\, d\mathbf{c}_1\, d\mathbf{c}. \tag{7.22}$$

In terms of the parameter ϵ, the Boltzmann equation (7.8) is written as

$$\mathcal{D} f + \epsilon\, C_i \frac{\partial f}{\partial x_i} = \mathcal{Q}_I(f, f), \tag{7.23}$$

indicating that the material time derivative and the collision term are of same order, while the spatial gradients are of higher order.

The integral equations for the determination of the distribution function are obtained by inserting the expansions (7.14) and (7.15) into the Boltzmann equation (7.23) and equating the equal powers of ϵ, yielding

$$\mathcal{D}_0 f^{(0)} = \mathcal{Q}_I(f^{(0)}, f^{(0)}), \tag{7.24}$$

$$\mathcal{D}_1 f^{(0)} + \mathcal{D}_0 f^{(1)} + C_i \frac{\partial f^{(0)}}{\partial x_i} = 2\mathcal{Q}_I(f^{(1)}, f^{(0)}). \tag{7.25}$$

The above equations represent the two first integral equations for the determination of $f^{(0)}$ and $f^{(1)}$.

Exercise

7.4 Obtain the integral equations (7.24) and (7.25).

7.4.2 First Approximation $f^{(0)}$

In order to determine the first approximation of the distribution function, one relies on the integral equation (7.24) and uses the following relationship for the elimination of the material time derivatives:

$$\mathcal{D}_0 f^{(0)} = \mathcal{D}_0 n \frac{\partial f^{(0)}}{\partial n} + \mathcal{D}_0 v_i \frac{\partial f^{(0)}}{\partial v_i} + \mathcal{D}_0 T \frac{\partial f^{(0)}}{\partial T} = -T\zeta^{(0)} \frac{\partial f^{(0)}}{\partial T}. \tag{7.26}$$

Above, the balance equations $(7.18)_1$, $(7.19)_1$ and $(7.20)_1$ were used.

Hence, the integral equation (7.24) can be written, thanks to (7.26), as

$$-T\zeta^{(0)} \frac{\partial f^{(0)}}{\partial T} = \mathcal{Q}_I(f^{(0)}, f^{(0)}). \tag{7.27}$$

The solution of the integral equation (7.27) for the distribution function $f^{(0)}$ is not a Maxwellian, but one may write $f^{(0)}$ as a Maxwellian plus an expansion in Sonine polynomials of the peculiar velocity, namely,

$$f^{(0)} = n\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} e^{-\beta C^2}\left[1 + \sum_{n=1}^{\infty} a_n S_{\frac{1}{2}}^{(n)}(\beta C^2)\right], \qquad \text{where} \qquad \beta = \frac{m}{2kT}. \tag{7.28}$$

The scalar coefficients a_n do not depend on the peculiar velocity $\mathbf{C}$ and it is supposed that this series expansion converges for large values of the peculiar velocity.

As it will be shown in the sequel, the first non-vanishing term of the series expansion (7.28) comes from the coefficient a_2, hence one may approximate the representation of the distribution function (7.28) as

$$f^{(0)} = n\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} e^{-\beta C^2}\left[1 + a_1\left(\frac{3}{2} - \beta C^2\right) + a_2\left(\frac{15}{8} - \frac{5\beta C^2}{2} + \frac{\beta^2 C^4}{2}\right)\right], \tag{7.29}$$

where a_1 and a_2 are two coefficients that should be determined from the integral equation (7.27).

For the determination of the first approximation to the cooling rate (7.21), one proceeds as follows. First, the product of the distribution functions is written as

$$f^{(0)} f_1^{(0)} = n^2\left(\frac{\beta}{\pi}\right)^3 e^{-\beta\left(2G^2 + \frac{g^2}{2}\right)}\left\{1 + a_1\left[3 - \beta\left(2G^2 + \frac{g^2}{2}\right)\right]\right.$$

$$\left. + a_2\left[\frac{15}{4} - \frac{5\beta}{2}\left(2G^2 + \frac{g^2}{2}\right) + \frac{\beta^2}{2}\left(2G^4 + G^2 g^2 + \frac{g^4}{8} + 2(\mathbf{G}\cdot\mathbf{g})^2\right)\right]\right\}, \tag{7.30}$$

by neglecting all product of the coefficients a_1 and a_2 and by changing the velocity variables $(\mathbf{C}, \mathbf{C}_1)$ by the relative and the center of mass velocities $(\mathbf{g}, \mathbf{G})$.

Now, the insertion of the product of the distribution functions (7.30) into the first approximation to the cooling rate (7.21) and the integration of the resulting equation, yields

$$\zeta^{(0)} = \frac{2\sqrt{2\pi} n \chi \mathsf{d}^2 (1-\alpha^2)}{3\beta^{1/2}} \left(1 - \frac{3}{2} a_1 + \frac{3}{16} a_2\right). \tag{7.31}$$

Hence, to determine completely the cooling rate, one has to know the coefficients a_1 and a_2.

The search for the coefficients a_1 and a_2 proceeds as follows. First, one multiplies the integral equation (7.27) by an arbitrary function of the peculiar velocity $\psi(C^2)$ and integrates the resulting equation over all values of $\mathbf{c}$:

$$\int \psi(C^2) \zeta^{(0)} \beta \frac{df^{(0)}}{d\beta} d\mathbf{c} = \frac{\chi}{2} \int \big[\psi(C_1'^2) + \psi(C'^2) \\ - \psi(C_1^2) - \psi(C^2)\big] f_1^{(0)} f^{(0)} \, \mathsf{d}^2 \, (\mathbf{g}\cdot\mathbf{k}) \, d\mathbf{k} \, d\mathbf{c}_1 \, d\mathbf{c}. \tag{7.32}$$

Next, by choosing $\psi(C^2) = 1$, the integration of (7.32) leads to an identity.

If in (7.32) one chooses $\psi(C^2) = C^2$ and uses the relationship

$$C_1'^2 + C'^2 - C_1^2 - C^2 = \frac{\alpha^2 - 1}{2} (\mathbf{g}\cdot\mathbf{k})^2, \tag{7.33}$$

it follows after the integration that $\zeta^{(0)}(1 - a_1) = \zeta^{(0)}$, which implies that $a_1 = 0$.

Finally, by choosing $\psi(C^2) = C^4$ into (7.32) and by using the relationship

$$C_1'^4 + C'^4 - C_1^4 - C^4 = 2(\alpha+1)^2 (\mathbf{g}\cdot\mathbf{k})^2 (\mathbf{G}\cdot\mathbf{k})^2 + \frac{(\alpha^2-1)^2}{8} (\mathbf{g}\cdot\mathbf{k})^4 \\ + (\alpha^2 - 1)(\mathbf{g}\cdot\mathbf{k})^2 G^2 + \frac{(\alpha^2-1)}{4} (\mathbf{g}\cdot\mathbf{k})^2 g^2 - 4(\alpha+1)(\mathbf{g}\cdot\mathbf{k})(\mathbf{G}\cdot\mathbf{k})(\mathbf{G}\cdot\mathbf{g}), \tag{7.34}$$

one obtains through the integration of the resulting equation that the coefficient a_2 has the form

$$a_2 = \frac{16(1-\alpha)(1-2\alpha^2)}{81 - 17\alpha + 30\alpha^2(1-\alpha)}. \tag{7.35}$$

Once the coefficient a_2 is known the distribution function (7.29) becomes

$$f^{(0)} = n \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} e^{-\beta C^2} \left[1 + \frac{16(1-\alpha)(1-2\alpha^2)}{81 - 17\alpha + 30\alpha^2(1-\alpha)} \left(\frac{15}{8} - \frac{5\beta C^2}{2} + \frac{\beta^2 C^4}{2}\right)\right]. \tag{7.36}$$

Furthermore, the expression for the cooling rate (7.31) in the first approximation reads

$$\zeta^{(0)} = \frac{4}{3} n\chi \mathsf{d}^2 (1-\alpha^2)\sqrt{\frac{\pi k T}{m}}\left[1 + \frac{3(1-\alpha)(1-2\alpha^2)}{81 - 17\alpha + 30\alpha^2(1-\alpha)}\right]. \tag{7.37}$$

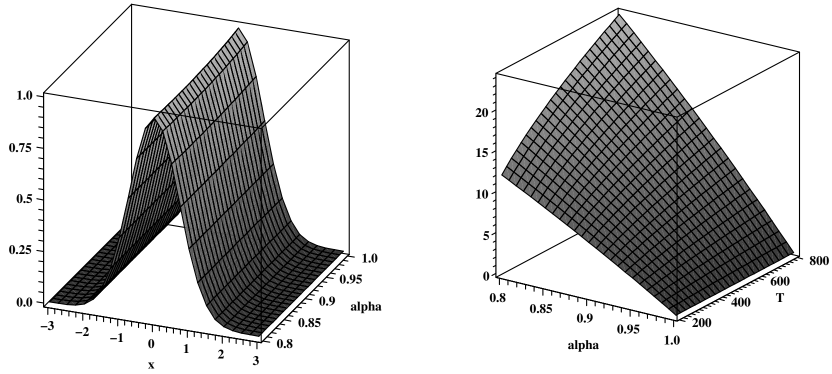

Fig. 7.1 Left frame: distribution function $\pi^{3/2} f^{(0)}/n\beta^{3/2}$ versus $x = \beta C^2$ and α. Right frame: cooling rate $\zeta^{(0)}/n\chi\mathsf{d}^2$ versus T and α.

In the left frame of Figure 7.1, the distribution function $\pi^{3/2} f^{(0)}/n\beta^{3/2}$ is represented as a function of $x = \beta C^2$ and α. One infers from the figure that the peak of the curve decreases by decreasing the normal restitution coefficient. In the right frame of figure 7.1, the cooling rate $\zeta^{(0)}/n\chi\mathsf{d}^2$ versus the temperature and the normal restitution coefficient are plotted. It shows that the cooling rate increases by decreasing the normal restitution coefficient and by increasing the temperature. Note that the cooling rate is zero when $\alpha = 1$, i.e., for elastic collisions of the molecules. For both figures, it was supposed that $\chi = 1$ and $0.8 \leqslant \alpha \leqslant 1$.

Consider a spatially homogeneous problem where the fields depend only on time, i.e., $\varrho(t)$, $v_i(t)$ and $T(t)$. In this case, the evolution equation for the temperature field (7.12) reads

$$\frac{dT_d(t_d)}{dt_d} + \frac{\chi(1-\alpha^2)}{3}\left[1 + \frac{3(1-\alpha)(1-2\alpha^2)}{81 - 17\alpha + 30\alpha^2(1-\alpha)}\right] T_d^{\frac{3}{2}} = 0. \tag{7.38}$$

Above, the dimensionless quantities $T_d(t_d) = T(t)/T(0)$ and $t_d = t/\tau$ were introduced, where τ is the mean free time $(1.29)_1$.

The solution of the differential equation (7.38) is given by

$$T_d(t) = \frac{1}{\left\{1 + \frac{\chi(1-\alpha^2)}{6}\left[1 + \frac{3(1-\alpha)(1-2\alpha^2)}{81-17\alpha+30\alpha^2(1-\alpha)}\right] t_d\right\}^2}. \tag{7.39}$$

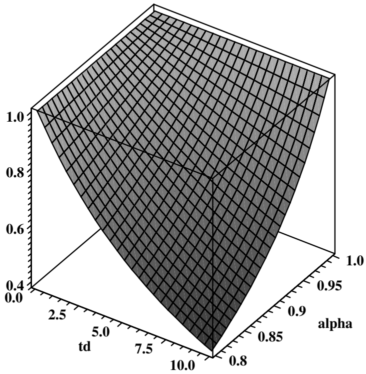

Fig. 7.2 Temperature decay: $T_d = T/T(0)$ versus $t_d = t/\tau$ and α.

The temperature decay of a granular gas is known in the literature as Haff's law. In Figure 7.2, the dimensionless temperature field T_d is plotted as a function of the dimensionless time t_d and of the normal restitution coefficient α for $\chi = 1$. As was expected, one may infer from the figure that the decrease of the normal restitution coefficient implies a more accentuated temperature decay. Furthermore, for elastic collisions of the molecules, the temperature remains constant.

Exercises

7.5 Obtain (7.31) for the cooling rate.

7.6 Show that the coefficient a_2 is given by (7.35).

7.4.3 Second Approximation $f^{(1)}$

In order to determine the second approximation to the distribution function $f^{(1)}$, let first evaluate the following derivatives which appear in the integral equation (7.25), namely,

$$\mathcal{D}_1 f^{(0)} + C_i \frac{\partial f^{(0)}}{\partial x_i} = \left[\frac{\partial f^{(0)}}{\partial n}\mathcal{D}_1 n + \frac{\partial f^{(0)}}{\partial C_i}\mathcal{D}_1 C_i + \frac{\partial f^{(0)}}{\partial T}\mathcal{D}_1 T\right]$$
$$+ C_i \left[\frac{\partial f^{(0)}}{\partial n}\frac{\partial n}{\partial x_i} + \frac{\partial f^{(0)}}{\partial C_j}\frac{\partial C_j}{\partial x_i} + \frac{\partial f^{(0)}}{\partial T}\frac{\partial T}{\partial x_i}\right]. \tag{7.40}$$

The insertion of the first approximation (7.36) into (7.40) and the elimination of the material time derivatives $\mathcal{D}_1$—through the use of the balance equations $(7.18)_2$, $(7.19)_2$ and $(7.20)_2$—leads to

$$\mathcal{D}_1 f^{(0)} + C_i \frac{\partial f^{(0)}}{\partial x_i} = -T\zeta^{(1)}\frac{\partial f^{(0)}}{\partial T} + f_M\Bigg\{2\beta\left[1 + a_2\left(\frac{35}{8} - \frac{7\beta C^2}{2}\right.\right.$$
$$\left.\left. + \frac{\beta^2 C^4}{2}\right)\right] C_i C_j \frac{\partial v_{\langle i}}{\partial x_{j\rangle}} + a_2\left(\beta C^2 - \frac{5}{2}\right) C_i \frac{\partial \ln n}{\partial x_i} + \left[\beta C^2 - \frac{5}{2}\right.$$
$$\left. - a_2\left(\frac{115}{16} - \frac{93\beta C^2}{8} + \frac{19\beta^2 C^4}{4} - \frac{\beta^3 C^6}{2}\right)\right] C_i \frac{\partial \ln T}{\partial x_i}\Bigg\}. \tag{7.41}$$

In the above equation, the coefficient a_2 is given by (7.35) and f_M denotes the Maxwellian distribution function

$$f_M = n\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} e^{-\beta C^2}. \tag{7.42}$$

Now, one can write the integral equation (7.25) as

$$2\mathcal{Q}_I(f^{(1)}, f^{(0)}) - \mathcal{D}_0 f^{(1)} + T\zeta^{(1)}\frac{\partial f^{(0)}}{\partial T} = f_M\{\dots\}, \tag{7.43}$$

thanks to (7.41). Above, $\{\dots\}$ is an abbreviated form of the expression within the braces in (7.41), which is function of

$$\{\dots\} = \mathcal{F}\left(\beta, a_2, \mathbf{C}, \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \frac{\partial T}{\partial x_i}, \frac{\partial n}{\partial x_i}\right). \tag{7.44}$$

One notes that the right-hand side of the integral equation (7.43) is a function of the thermodynamic forces: deviator of the velocity gradient $\partial v_{\langle i}/\partial x_{j\rangle}$, gradient of the particle number density $\partial n/\partial x_i$ and gradient of temperature $\partial T/\partial x_i$. Since the objective of this section is to determine linearized constitutive equations and there exists no scalar thermodynamic force, one has to consider that $\zeta^{(1)}$ must be zero in this approximation, i.e., $\zeta^{(1)} \equiv 0$. Furthermore, by analyzing the integral equation (7.43), one infers that the second approximation $f^{(1)}$ can be written as

$$f^{(1)} = f_M \left[\varGamma_1 C_i \frac{\partial \ln T}{\partial x_i} + \varGamma_2 C_i C_j \frac{\partial v_{\langle i}}{\partial x_{j\rangle}} + \varGamma_3 C_i \frac{\partial \ln n}{\partial x_i} \right]. \tag{7.45}$$

Above, the scalar coefficients $\varGamma_1$, $\varGamma_2$ and $\varGamma_3$ depend on n, T, C^2 and will be determined from the integral equation (7.43).

Here, the search for a solution of the integral equation (7.43) where the scalar coefficients $\varGamma_1$, $\varGamma_2$ and $\varGamma_3$ are given in terms of the first approximation in the Sonine polynomials will be carried on. Hence, one may write

$$\varGamma_1 = \gamma_1 \left(\frac{5}{2} - \beta C^2 \right) = \gamma_1 S^{(1)}_{\frac{3}{2}}(C^2), \qquad \varGamma_2 = \gamma_2 = \gamma_2 S^{(0)}_{\frac{5}{2}}(C^2), \tag{7.46}$$

$$\varGamma_3 = \gamma_3 \left(\frac{5}{2} - \beta C^2 \right) = \gamma_3 S^{(1)}_{\frac{3}{2}}(C^2), \tag{7.47}$$

where γ_1, γ_2 and γ_3 are scalar coefficients that depend only on n and T.

In order to evaluate $\mathcal{D}_0 f^{(1)}$, one has to know the following derivatives

$$\mathcal{D}_0 f_M = \zeta^{(0)} \left(\frac{3}{2} - \beta C^2 \right) f_M, \tag{7.48}$$

$$\mathcal{D}_0(\varGamma_1 C_i) = -\zeta^{(0)} C_i \frac{\partial \varGamma_1}{\partial \beta} \beta, \tag{7.49}$$

$$\mathcal{D}_0(\varGamma_2 C_i) = \zeta^{(0)} C_i \frac{\partial \varGamma_2}{\partial \beta} \beta, \qquad \mathcal{D}_0(\varGamma_3 C_i C_j) = \zeta^{(0)} C_i C_j \frac{\partial \varGamma_3}{\partial \beta} \beta, \tag{7.50}$$

$$\begin{aligned} \mathcal{D}_0 \left(\frac{\partial \ln T}{\partial x_i} \right) &= \frac{\partial}{\partial x_i} \left[\mathcal{D}_0 (\ln T) \right] - \underline{\frac{\partial v_j}{\partial x_i} \frac{\partial \ln T}{\partial x_j}} = - \frac{\partial \zeta^{(0)}}{\partial x_i} - \underline{\frac{\partial v_j}{\partial x_i} \frac{\partial \ln T}{\partial x_j}} \\ &= -\zeta^{(0)} \left[\frac{\partial \ln n}{\partial x_i} + \frac{1}{2} \frac{\partial \ln T}{\partial x_i} \right] - \underline{\frac{\partial v_j}{\partial x_i} \frac{\partial \ln T}{\partial x_j}}. \end{aligned} \tag{7.51}$$

Above, the balance equations $(7.18)_1$, $(7.19)_1$ and $(7.20)_1$ were used and the relationship that $\zeta^{(0)}$ is proportional to $n\sqrt{T}$ (see (7.37)). Here, a linearized theory is developed so that one may neglect the underlined term in (7.51). Furthermore, the dimensional analysis of the coefficients suggests that $\gamma_1 \propto 1/\sqrt{T}$, $\gamma_2 \propto 1/\sqrt{T^3}$ and $\gamma_3 \propto 1/\sqrt{T}$. Hence, by collecting all results, one has

$$\begin{aligned} \mathcal{D}_0 f^{(1)} = f_M \zeta^{(0)} \Bigg\{ & \left[\gamma_3 \left(5 - \frac{11}{2} \beta C^2 + \beta^2 C^4 \right) - \gamma_1 \left(\frac{5}{2} - \beta C^2 \right) \right] C_i \frac{\partial \ln n}{\partial x_i} \\ & + \gamma_1 \left(\frac{15}{4} - 5 \beta C^2 + \beta^2 C^4 \right) C_i \frac{\partial \ln T}{\partial x_i} + \gamma_2 \left(3 - \beta C^2 \right) C_i C_j \frac{\partial v_{\langle i}}{\partial x_{j\rangle}} \Bigg\}. \end{aligned} \tag{7.52}$$

Now, by multiplying the integral equation (7.43) by an arbitrary function of the peculiar velocity $\psi(\mathbf{C})$ and by integrating the resulting equation over all values of $\mathbf{c}$, one obtains an equation which can be represented as $\mathcal{I}_1 - \mathcal{I}_2 = \mathcal{I}_3$, where

$$\mathcal{I}_1 = \int \psi(\mathbf{C}) f_M \zeta^{(0)} \Bigg\{ \gamma_1 \left(\frac{15}{4} - 5\beta C^2 + \beta^2 C^4 \right) \frac{C_i}{T} \frac{\partial T}{\partial x_i} + \gamma_2 (3 - \beta C^2) C_i C_j \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}$$

$$+ \left[\gamma_3 \left(5 - \frac{11}{2} \beta C^2 + \beta^2 C^4 \right) - \gamma_1 \left(\frac{5}{2} - \beta C^2 \right) \right] C_i \frac{\partial \ln n}{\partial x_i} \Bigg\} d\mathbf{c}, \qquad (7.53)$$

$$\mathcal{I}_2 = \frac{\chi}{2} \int \left(f_1^{(1)} f^{(0)} + f_1^{(0)} f^{(1)} \right) \left[\psi(\mathbf{C}_1') + \psi(\mathbf{C}') \right.$$
$$\left. - \psi(\mathbf{C}_1) - \psi(\mathbf{C}) \right] \mathsf{d}^2 \, (\mathbf{g} \cdot \mathbf{k}) \, d\mathbf{k} \, d\mathbf{c}_1 \, d\mathbf{c}, \qquad (7.54)$$

$$\mathcal{I}_3 = - \int \psi(\mathbf{C}) f_M \Bigg\{ 2\beta \left[1 + a_2 \left(\frac{35}{8} - \frac{7\beta C^2}{2} + \frac{\beta^2 C^4}{2} \right) \right] C_i C_j \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}$$
$$+ \left[\beta C^2 - \frac{5}{2} - a_2 \left(\frac{115}{16} - \frac{93\beta C^2}{8} + \frac{19\beta^2 C^4}{4} - \frac{\beta^3 C^6}{2} \right) \right] C_i \frac{\partial \ln T}{\partial x_i}$$
$$+ a_2 \left(\beta C^2 - \frac{5}{2} \right) C_i \frac{\partial \ln n}{\partial x_i} \Bigg\} d\mathbf{c}. \qquad (7.55)$$

For simplicity, from now on, the terms of order $\mathcal{O}(a_2)$ will not be considered. However, the approximation used here will furnish the leading contributions to the transport coefficients.

Now, by choosing $\psi(\mathbf{C}) = C_k C_l$ into the integrals $\mathcal{I}_1, \mathcal{I}_2$ and $\mathcal{I}_3$ and by integrating the resulting equations, one obtains that the factors of the velocity gradient deviator $\partial v_{\langle i}/\partial x_{j\rangle}$ are given by

$$\begin{cases} \mathcal{I}_1 = -\frac{4}{3} n^2 \chi \mathsf{d}^2 (1 - \alpha^2) \sqrt{\pi \left(\frac{kT}{m}\right)^5} \gamma_2, \\ \mathcal{I}_2 = \frac{8}{5} n^2 \chi \mathsf{d}^2 (1 + \alpha)(\alpha - 3) \sqrt{\pi \left(\frac{kT}{m}\right)^5} \gamma_2, \\ \mathcal{I}_3 = -2n \frac{kT}{m}. \end{cases} \qquad (7.56)$$

By solving the equation $\mathcal{I}_1 - \mathcal{I}_2 = \mathcal{I}_3$ for γ_2, yields

$$\gamma_2 = \frac{-15}{2\chi \mathsf{d}^2 n (13 - \alpha)(\alpha + 1)} \sqrt{\frac{1}{\pi} \left(\frac{m}{kT} \right)^3}. \qquad (7.57)$$

By following the same procedure, i.e., by choosing $\psi(\mathbf{C}) = C^2 C_j$ in the integrals $\mathcal{I}_1, \mathcal{I}_2$ and $\mathcal{I}_3$ and by performing the integrals, it follows that the factors of the temperature gradient $\partial \ln T/\partial x_j$ are given by

$$\begin{cases} \mathcal{I}_1 = \frac{40}{3} n^2 \chi \mathsf{d}^2 (1 - \alpha^2) \sqrt{\pi \left(\frac{kT}{m}\right)^5} \gamma_1, \\ \mathcal{I}_2 = -\frac{1}{3} n^2 \chi \mathsf{d}^2 (1 + \alpha)(33\alpha - 49) \sqrt{\pi \left(\frac{kT}{m}\right)^5} \gamma_1, \\ \mathcal{I}_3 = -5n \left(\frac{kT}{m}\right)^2, \end{cases} \qquad (7.58)$$

whose solution for γ_1 reads

$$\gamma_1 = \frac{15}{\chi \mathsf{d}^2 n(9+7\alpha)(\alpha+1)}\sqrt{\frac{m}{\pi kT}}. \tag{7.59}$$

Moreover, the factors of the particle number density gradient $\partial \ln n/\partial x_j$ become

$$\begin{cases} \mathcal{I}_1 = \frac{10}{3} n^2 \chi \mathsf{d}^2 (1-\alpha^2)\sqrt{\pi \left(\frac{kT}{m}\right)^5}(3\gamma_3 + 2\gamma_1), \\ \mathcal{I}_2 = -\frac{1}{3} n^2 \chi \mathsf{d}^2 (1+\alpha)(33\alpha - 49)\sqrt{\pi \left(\frac{kT}{m}\right)^5}\gamma_3, \\ \mathcal{I}_3 = \mathcal{O}(a_2). \end{cases} \tag{7.60}$$

In this case, the coefficient γ_3 is given by

$$\gamma_3 = \frac{300(1-\alpha)}{\chi \mathsf{d}^2 n(9+7\alpha)(\alpha+1)(19-3\alpha)}\sqrt{\frac{m}{\pi kT}}. \tag{7.61}$$

Hence the second approximation to the distribution function (7.45) is determined and the distribution function up to the second approximation reads

$$\begin{aligned} f = n\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} e^{-\beta C^2}\Bigg\{1 &+ \gamma_1\left(\frac{5}{2} - \beta C^2\right) C_i \frac{\partial \ln T}{\partial x_i} + \gamma_2 C_i C_j \frac{\partial v_{\langle i}}{\partial x_{j\rangle}} \\ &+ \gamma_3\left(\frac{5}{2} - \beta C^2\right) C_i \frac{\partial \ln n}{\partial x_i} + a_2\left(\frac{15}{8} - \frac{5\beta C^2}{2} + \frac{\beta^2 C^4}{2}\right)\Bigg\}, \end{aligned} \tag{7.62}$$

where the coefficients a_2, γ_1, γ_2 and γ_3 are given by (7.35), (7.59), (7.57) and (7.61), respectively.

Exercises

7.7 Obtain (7.52) for the material time derivative $\mathcal{D}_0 f^{(1)}$.

7.8 Determine the integrals $\mathcal{I}_1, \mathcal{I}_2$ and $\mathcal{I}_3$ given in (7.56), (7.58) and (7.60).

7.4.4 Constitutive Equations for the Pressure Tensor and the Heat Flux Vector

The constitutive equations for the pressure tensor and heat flux vector are obtained through the substitution of the distribution function (7.62) into their definitions and by integrating the resulting equations, yielding

$$p_{ij} = \int m C_i C_j f d\mathbf{c} = p\,\delta_{ij} - 2\mu \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \tag{7.63}$$

$$q_i = \int \frac{m}{2} C^2 C_i f d\mathbf{c} = -\lambda \frac{\partial T}{\partial x_i} - \vartheta T \frac{\partial \ln n}{\partial x_i}. \tag{7.64}$$

The coefficients of shear viscosity μ, thermal conductivity λ and the one associated with the gradient of particle number density ϑ are given by

$$\mu = \frac{15}{2\chi \mathsf{d}^2(13-\alpha)(\alpha+1)} \sqrt{\frac{mkT}{\pi}}, \tag{7.65}$$

$$\lambda = \frac{75}{2\chi \mathsf{d}^2(9+7\alpha)(\alpha+1)} \frac{k}{m} \sqrt{\frac{mkT}{\pi}}, \tag{7.66}$$

$$\vartheta = \frac{750(1-\alpha)}{\chi \mathsf{d}^2(9+7\alpha)(\alpha+1)(19-3\alpha)} \frac{k}{m} \sqrt{\frac{mkT}{\pi}}. \tag{7.67}$$

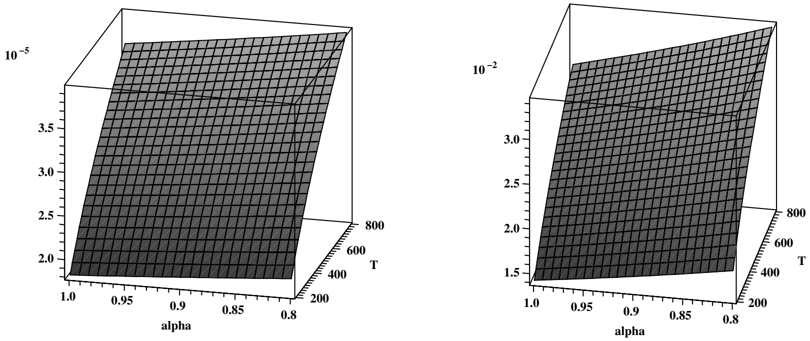

Fig. 7.3 Transport coefficients versus T and α for argon gas when $\chi = 1$. Left frame: shear viscosity μ; right frame: thermal conductivity λ.

The coefficients of shear viscosity μ and thermal conductivity λ are plotted in Figure 7.2 as functions of the temperature 200 K$\leqslant T \leqslant$800 K and of the normal coefficient of restitution $0.8 \leqslant \alpha \leqslant 1$ for argon gas when $\chi = 1$. The behavior of the two coefficients with respect to the temperature is the same as that of a monatomic gas of hard spherical particles, since both coefficients are proportional to $\sqrt{T}$. With respect to the normal restitution coefficient, one infers that both coefficients of shear viscosity and thermal conductivity increase by decreasing the values of α.

In Figure 7.3, the coefficient associated with the particle number density ϑ is represented as function of T and α. One concludes that this coefficient increases according to the square root of the temperature, vanishes when the gas molecules suffer elastic collisions ($\alpha = 1$) and increases by decreasing the value of the normal restitution coefficient.

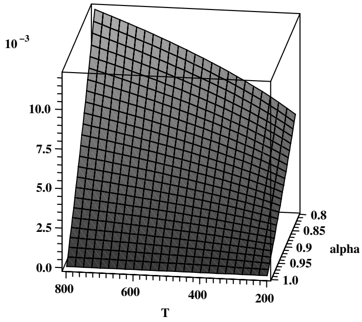

Fig. 7.4 Coefficient ϑ versus T and α for argon gas when $\chi = 1$.

Exercise

7.9 Obtain the expressions for the transport coefficients (7.65)–(7.67).

7.5 Granular Gases of Rough Spherical Molecules

In Section 5.4, it was stated that (5.113) and (5.114) relate the post-collisional $(\mathbf{c}, \mathbf{c}_1, \mathbf{w}, \mathbf{w}_1)$ to the pre-collisional $(\mathbf{c}', \mathbf{c}_1', \mathbf{w}', \mathbf{w}_1')$ velocities of rough spherical molecules at collision. Moreover, the relationships of the pre-collisional $\mathbf{u}$ and post-collisional $\mathbf{u}'$ relative velocities of the points of the spheres which are in contact during a binary encounter are given by $(5.115)_1$ and $(5.115)_2$. For simplicity, these equations are reproduced here:

$$m\mathbf{c}' = m\mathbf{c} - \mathbf{J}, \qquad I\mathbf{w}' = I\mathbf{w} + \frac{\mathsf{d}}{2}\mathbf{k} \times \mathbf{J}, \tag{7.68}$$

$$m\mathbf{c}_1' = m\mathbf{c}_1 + \mathbf{J}, \qquad I\mathbf{w}_1' = I\mathbf{w}_1 + \frac{\mathsf{d}}{2}\mathbf{k} \times \mathbf{J}, \tag{7.69}$$

$$\mathbf{u} = \mathbf{g} - \frac{\mathsf{d}}{2}\mathbf{k} \times (\mathbf{w} + \mathbf{w}_1), \qquad \mathbf{u}' = \mathbf{g}' - \frac{\mathsf{d}}{2}\mathbf{k} \times (\mathbf{w}' + \mathbf{w}_1'), \tag{7.70}$$

where $\mathbf{J}$ denotes the impulse exerted by the molecule without the label on the labeled molecule.

The inelastic collisions of rough spherical molecules are characterized by the relationships

$$(\mathbf{k} \cdot \mathbf{u}') = -\alpha(\mathbf{k} \cdot \mathbf{u}), \qquad (\mathbf{k} \times \mathbf{u}') = -\epsilon(\mathbf{k} \times \mathbf{u}). \tag{7.71}$$

where $0 \leqslant \alpha \leqslant 1$ and $-1 \leqslant \epsilon \leqslant 1$ are the normal and tangential restitution coefficients, respectively. For an elastic collision of perfectly smooth spheres, $\alpha = 1$ and $\epsilon = -1$, whereas for an elastic encounter of perfectly rough spherical molecules, $\alpha = 1$ and $\epsilon = 1$.

From (7.68) through (7.71), one may obtain the relationships

$$\mathbf{u}' = (\epsilon - \alpha)\,(\mathbf{u}\cdot\mathbf{k})\,\mathbf{k} - \epsilon\mathbf{u}, \qquad \mathbf{u}' = \mathbf{u} + \frac{2}{m}\left[\mathbf{J} - \frac{1}{\kappa}\mathbf{k}\times(\mathbf{k}\times\mathbf{J})\right]. \tag{7.72}$$

Furthermore, from the above equations, it follows that the impulse may be expressed as

$$\mathbf{J} = m\widetilde{\epsilon}\,[(\mathbf{u}\cdot\mathbf{k})\,\mathbf{k} - \mathbf{u}] - m\widetilde{\alpha}(\mathbf{u}\cdot\mathbf{k})\mathbf{k}, \tag{7.73}$$

where the following abbreviations were introduced:

$$\widetilde{\epsilon} = \frac{(1+\epsilon)\kappa}{2(\kappa+1)}, \qquad \widetilde{\alpha} = \frac{(1+\alpha)}{2}. \tag{7.74}$$

Once the impulse **J** is determined, the pre-collisional velocities can be written in terms of the post-collisional velocities. Indeed, (7.68)–(7.70) and (7.73) furnish the following relationships:

$$\mathbf{c}' = \mathbf{c} + \widetilde{\epsilon}\left[\mathbf{g} - \frac{\mathsf{d}}{2}\mathbf{k}\times(\mathbf{w}+\mathbf{w}_1)\right] + [\widetilde{\alpha} - \widetilde{\epsilon}]\,(\mathbf{g}\cdot\mathbf{k})\mathbf{k}, \tag{7.75}$$

$$\mathbf{c}_1' = \mathbf{c}_1 - \widetilde{\epsilon}\left[\mathbf{g} - \frac{\mathsf{d}}{2}\mathbf{k}\times(\mathbf{w}+\mathbf{w}_1)\right] - [\widetilde{\alpha} - \widetilde{\epsilon}]\,(\mathbf{g}\cdot\mathbf{k})\mathbf{k}, \tag{7.76}$$

$$\mathbf{w}' = \mathbf{w} - \frac{2\widetilde{\epsilon}}{\kappa\,\mathsf{d}}\mathbf{k}\times\left[\mathbf{g} - \frac{\mathsf{d}}{2}\mathbf{k}\times(\mathbf{w}+\mathbf{w}_1)\right], \tag{7.77}$$

$$\mathbf{w}_1' = \mathbf{w}_1 - \frac{2\widetilde{\epsilon}}{\kappa\,\mathsf{d}}\mathbf{k}\times\left[\mathbf{g} - \frac{\mathsf{d}}{2}\mathbf{k}\times(\mathbf{w}+\mathbf{w}_1)\right]. \tag{7.78}$$

From (7.75)–(7.78), it is easy to obtain the variation of the translational and rotational energies before and after a collision. For that end, one may build the relationship

$$\frac{m}{2}c'^2 + \frac{I}{2}w'^2 + \frac{m}{2}c_1'^2 + \frac{I}{2}w_1'^2 - \frac{m}{2}c^2 - \frac{I}{2}w^2 - \frac{m}{2}c_1^2 - \frac{I}{2}w_1^2 = m\left\{\frac{\alpha^2-1}{4}(\mathbf{g}\cdot\mathbf{k})^2\right.$$

$$\left. + \frac{\epsilon^2-1}{4}\frac{\kappa}{\kappa+1}\left[\mathbf{g} - (\mathbf{g}\cdot\mathbf{k})\mathbf{k} - \frac{\mathsf{d}}{2}\mathbf{k}\times(\mathbf{w}+\mathbf{w}_1)\right]^2\right\}. \tag{7.79}$$

The right-hand side of the above equation vanishes for elastic collisions of perfectly smooth spheres ($\alpha = 1, \epsilon = -1$) and for elastic collisions of perfectly rough spherical molecules ($\alpha = 1, \epsilon = 1$). In these cases, the total energy—translational plus rotational energies—is conserved at collision.

A direct encounter is characterized by the pre-collisional velocities $(\mathbf{c}, \mathbf{c}_1, \mathbf{w}, \mathbf{w}_1)$, by the post-collisional velocities $(\mathbf{c}', \mathbf{c}_1', \mathbf{w}', \mathbf{w}_1')$ and by the collision vector $\mathbf{k}$. For a restitution encounter, the pre- and post-collisional velocities are denoted by $(\mathbf{c}^*, \mathbf{c}_1^*, \mathbf{w}^*, \mathbf{w}_1^*)$ and $(\mathbf{c}, \mathbf{c}_1, \mathbf{w}, \mathbf{w}_1)$, respectively, and the collision vector by $\mathbf{k}^* = -\mathbf{k}$. It is easy to verify also that the relationship $\mathbf{g}\cdot\mathbf{k}^* = -\alpha(\mathbf{g}^*\cdot\mathbf{k}^*) = -(\mathbf{g}\cdot\mathbf{k})$ holds.

Furthermore, the modulus of the Jacobian of the volume transformations

$$d\mathbf{c}^*\, d\mathbf{w}^*\, d\mathbf{c}_1^*\, d\mathbf{w}_1^* = |J| d\mathbf{c}\, d\mathbf{w}\, d\mathbf{c}_1\, d\mathbf{w}_1 \qquad \text{is} \qquad |J| = \frac{1}{\alpha\epsilon^2}, \tag{7.80}$$

so that the relationship of the volume elements reads

$$(\mathbf{g}^*\cdot\mathbf{k}^*) d\mathbf{c}^*\, d\mathbf{w}^*\, d\mathbf{c}_1^*\, d\mathbf{w}_1^* = \frac{1}{\alpha^2\epsilon^2}(\mathbf{g}\cdot\mathbf{k}) d\mathbf{c}\, d\mathbf{w}\, d\mathbf{c}_1\, d\mathbf{w}_1. \tag{7.81}$$

From (7.81), one may infer that the Boltzmann equation for granular gases of rough spherical molecules without external forces and torques is given by

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} = \chi \int \left(\frac{1}{\alpha^2\epsilon^2} f_1^* f^* - f_1 f \right) \mathsf{d}^2\, (\mathbf{g}\cdot\mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_1 d\mathbf{w}_1. \tag{7.82}$$

As in the case of rough spherical molecules, the distribution function f depends on $(\mathbf{c}, \mathbf{w}, t)$.

The balance equation for the temperature is obtained from the multiplication of the Boltzmann equation by $mC^2/2 + Iw^2/2$ and the integration of the resulting equation over all values of $\mathbf{c}$ and $\mathbf{w}$. After some rearrangements, one has

$$\frac{\partial T}{\partial t} + v_i \frac{\partial T}{\partial x_i} + \frac{1}{3nk}\left[\frac{\partial (q_i^T + q_i^I)}{\partial x_i} + p_{ij} \frac{\partial v_i}{\partial x_j} \right] + T\zeta = 0. \tag{7.83}$$

Above, the temperature, the pressure tensor and the heat flux vectors are given by (5.127) and (5.128). Furthermore, the cooling rate ζ reads

$$\zeta = \frac{\chi \mathsf{d}^2 m}{6nkT} \int \Bigg\{ \frac{1-\epsilon^2}{4} \frac{\kappa}{\kappa+1} \left[\mathbf{g} - (\mathbf{g}\cdot\mathbf{k})\mathbf{k} - \frac{\mathsf{d}}{2}\mathbf{k}\times(\mathbf{w}+\mathbf{w}_1) \right]^2 + \frac{1-\alpha^2}{4}(\mathbf{g}\cdot\mathbf{k})^2 \Bigg\} f_1 f\, (\mathbf{g}\cdot\mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_1\, d\mathbf{w}_1\, d\mathbf{c}\, d\mathbf{w}. \tag{7.84}$$

Note that the cooling rate vanishes for elastic collisions of perfectly smooth spheres ($\alpha = 1, \epsilon = -1$) and for elastic collisions of perfectly rough spherical molecules ($\alpha = 1, \epsilon = 1$).

The first approximation to the cooling rate can be obtained by the insertion of the Maxwellian distribution function $(5.124)_1$ into its definition (7.84) and the integration of the resulting equation. Hence, it follows

$$\zeta^{(0)}=\frac{2}{3}n\chi\mathsf{d}^2(2-\alpha^2-\epsilon^2)\sqrt{\frac{\pi kT}{m}}. \tag{7.85}$$

It is noteworthy that the cooling rate depends on both the normal and the tangential restitution coefficients.

Exercises

7.10 Obtain the expressions (7.75)–(7.78).

7.11 Show that the modulus of the Jacobian is given by $(7.80)_2$.

7.12 Obtain the expression for the cooling rate (7.85).

Chapter 8
Mixtures of Monatomic Gases

8.1 Boltzmann and Transfer Equations

The state of a mixture of n monatomic gases in the μ-phase space is characterized by a set of distribution functions $f_\alpha \equiv f(\mathbf{x}, \mathbf{c}_\alpha, t)$ with $\alpha = 1, 2, \dots, n$, such that $f(\mathbf{x}, \mathbf{c}_\alpha, t) d\mathbf{x} d\mathbf{c}_\alpha$ gives at time t the number of molecules of constituent α in the volume element whose position vectors are within the range $\mathbf{x}$ and $\mathbf{x}+d\mathbf{x}$, while the velocity vectors are within the range $\mathbf{c}_\alpha$ and $\mathbf{c}_\alpha + d\mathbf{c}_\alpha$. The distribution function $f(\mathbf{x}, \mathbf{c}_\alpha, t)$ of the constituent α satisfies the following Boltzmann equation:

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} + F_i \frac{\partial f_\alpha}{\partial c_i^\alpha} = \sum_{\beta=1}^{n} \int \left(f_\alpha' f_\beta' - f_\alpha f_\beta \right) g_{\beta\alpha} b \, db \, d\varepsilon \, d\mathbf{c}_\beta. \tag{8.1}$$

The above equation is a natural extension of the Boltzmann equation (2.20) because the collision term in the right-hand side of (8.1) takes into account the encounters of the various molecules of the mixture. The term F_i represents the specific external force which acts on the molecule of the constituent α. Here, it is supposed that the specific external force is only of gravitational nature, so that it is the same for all constituents. As usual, in (8.1), the abbreviations $f_\alpha' \equiv f(\mathbf{x}, \mathbf{c}_\alpha', t)$, $f_\beta' \equiv f(\mathbf{x}, \mathbf{c}_\beta', t)$, and $f_\beta \equiv f(\mathbf{x}, \mathbf{c}_\beta, t)$ were introduced. Furthermore, the post-collisional velocities $(\mathbf{c}_\alpha', \mathbf{c}_\beta')$ are given in terms of the pre-collisional velocities $(\mathbf{c}_\alpha, \mathbf{c}_\beta)$ by the relationships (1.94).

The transfer equation for the constituent α is obtained through the multiplication of the Boltzmann equation (8.1) by an arbitrary function $\psi_\alpha \equiv \psi(\mathbf{x}, \mathbf{c}_\alpha, t)$ and the integration of the resulting equation over all values of $\mathbf{c}_\alpha$. By following the same methodology of Section 2.3, yields

$$\frac{\partial}{\partial t} \int \psi_\alpha f_\alpha d\mathbf{c}_\alpha + \frac{\partial}{\partial x_i} \int \psi_\alpha c_i^\alpha f_\alpha d\mathbf{c}_\alpha - \int \left[\frac{\partial \psi_\alpha}{\partial t} + c_i^\alpha \frac{\partial \psi_\alpha}{\partial x_i} + F_i \frac{\partial \psi_\alpha}{\partial c_i^\alpha} \right] d\mathbf{c}_\alpha$$
$$= \sum_{\beta=1}^{n} \int (\psi_\alpha' - \psi_\alpha) f_\alpha f_\beta g_{\beta\alpha} b \, db \, d\varepsilon \, d\mathbf{c}_\beta d\mathbf{c}_\alpha. \tag{8.2}$$

Note that the right-hand side of the above equation was obtained by changing the velocities $(\mathbf{c}_\alpha, \mathbf{c}_\beta)$ by $(\mathbf{c}'_\alpha, \mathbf{c}'_\beta)$ and using the relationships $g'_{\beta\alpha} = g_{\beta\alpha}$, $b' = b$, $d\varepsilon' = d\varepsilon$, $d\mathbf{c}'_\beta d\mathbf{c}'_\alpha = d\mathbf{c}_\beta d\mathbf{c}_\alpha$.

The sum of (8.2) over all constituents $\alpha = 1, \ldots, n$ leads to the transfer equation for the mixture, namely,

$$\frac{\partial}{\partial t}\sum_{\alpha=1}^{n}\int \psi_\alpha f_\alpha d\mathbf{c}_\alpha + \frac{\partial}{\partial x_i}\sum_{\alpha=1}^{n}\int \psi_\alpha c_i^\alpha f_\alpha d\mathbf{c}_\alpha - \sum_{\alpha=1}^{n}\int\left[\frac{\partial\psi_\alpha}{\partial t} + c_i^\alpha\frac{\partial\psi_\alpha}{\partial x_i}\right.$$

$$\left. + F_i\frac{\partial\psi_\alpha}{\partial c_i^\alpha}\right] d\mathbf{c}_\alpha = \frac{1}{4}\sum_{\alpha,\beta=1}^{n}\int(\psi_\alpha + \psi_\beta - \psi'_\alpha - \psi'_\beta)(f'_\alpha f'_\beta - f_\alpha f_\beta) g_{\beta\alpha} b\, db\, d\varepsilon\, d\mathbf{c}_\beta\, d\mathbf{c}_\alpha, \tag{8.3}$$

where the sum on the right-hand side of the above equation is over all values of α and β.

Exercise

8.1 Obtain the right-hand side of the transfer equation for the mixture (8.3) by following the same arguments of Section 2.3.

8.2 Macroscopic Description

From the microscopic quantities associated with the molecules of the constituent α, namely, mass m_α, momentum $m_\alpha c_i^\alpha$ and translational energy $m_\alpha c_\alpha^2/2$, one defines the macroscopic fields

$$\varrho_\alpha(\mathbf{x}, t) = \int m_\alpha f_\alpha(\mathbf{x}, \mathbf{c}_\alpha, t) d\mathbf{c}_\alpha \quad - \quad \text{mass density,} \tag{8.4}$$

$$\varrho_\alpha v_i^\alpha(\mathbf{x}, t) = \int m_\alpha c_i^\alpha f_\alpha(\mathbf{x}, \mathbf{c}_\alpha, t) d\mathbf{c}_\alpha \quad - \quad \text{momentum density,} \tag{8.5}$$

$$\varrho_\alpha u_\alpha(\mathbf{x}, t) = \frac{1}{2}\int m_\alpha c_\alpha^2 f_\alpha(\mathbf{x}, \mathbf{c}_\alpha, t) d\mathbf{c}_\alpha \quad - \quad \text{energy density.} \tag{8.6}$$

By introducing the peculiar velocity $C_i^\alpha = c_i^\alpha - v_i^\alpha$ of the constituent α, one may decompose the energy density as

$$\varrho_\alpha u_\alpha = \frac{1}{2}\varrho_\alpha v_\alpha^2 + \varrho_\alpha\varepsilon_\alpha, \qquad \text{where} \qquad \varrho_\alpha\varepsilon_\alpha = \frac{1}{2}\int m_\alpha C_\alpha^2 f_\alpha d\mathbf{c}_\alpha \tag{8.7}$$

is the internal energy density of constituent α.

The balance equations for the fields (8.4)–(8.6) are obtained from the transfer equation (8.2) by choosing ψ_α equal to

(a) *Balance of mass density* ($\psi_\alpha = m_\alpha$):

$$\frac{\partial \varrho_\alpha}{\partial t} + \frac{\partial \varrho_\alpha v_i^\alpha}{\partial x_i} = 0, \tag{8.8}$$

(b) *Balance of momentum density* ($\psi_\alpha = m_\alpha c_i^\alpha$):

$$\frac{\partial \varrho_\alpha v_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j}(\varrho_\alpha v_i^\alpha v_j^\alpha + p_{ij}^\alpha) = \varrho_\alpha F_i + \pi_i^\alpha, \tag{8.9}$$

(c) *Balance of energy density* ($\psi_\alpha = m_\alpha c_\alpha^2/2$):

$$\frac{\partial}{\partial t}\left[\varrho_\alpha\left(\varepsilon_\alpha + \frac{1}{2}v_\alpha^2\right)\right] + \frac{\partial}{\partial x_i}\left[\varrho_\alpha\left(\varepsilon_\alpha + \frac{1}{2}v_\alpha^2\right)v_i^\alpha + q_i^\alpha + p_{ji}^\alpha v_j^\alpha\right]$$
$$= \varrho_\alpha F_i v_i^\alpha + \zeta_\alpha. \tag{8.10}$$

The production term of the mass density of the constituent α is zero, since the collision term of the Boltzmann equation (8.1) does not take into account chemical reactions (see Chapter 9 for the inclusion of chemical reactions). The production term of the momentum density π_i^α and the production term of the energy density ζ_α represent the momentum and energy exchanges among the constituents, respectively. Their expressions are given by

$$\pi_i^\alpha = \sum_{\beta=1}^{n}\int m_\alpha(c_i'^\alpha - c_i^\alpha) f_\alpha f_\beta g_{\beta\alpha} b\, db\, d\varepsilon\, d\mathbf{c}_\beta\, d\mathbf{c}_\alpha, \tag{8.11}$$

$$\zeta_\alpha = \sum_{\beta=1}^{n}\frac{1}{2}\int m_\alpha(c_\alpha'^2 - c_\alpha^2) f_\alpha f_\beta g_{\beta\alpha} b\, db\, d\varepsilon\, d\mathbf{c}_\beta\, d\mathbf{c}_\alpha. \tag{8.12}$$

Moreover, in (8.9) and (8.10), the pressure tensor p_{ij}^α and the heat flux vetor q_i^α of the constitutive α were introduced, which are defined by

$$p_{ij}^\alpha = \int m_\alpha C_i^\alpha C_j^\alpha f_\alpha d\mathbf{c}_\alpha, \qquad q_i^\alpha = \frac{1}{2}\int m_\alpha C_\alpha^2 C_i^\alpha f_\alpha d\mathbf{c}_\alpha. \tag{8.13}$$

The sum of the balance equations (8.8), (8.9) and (8.10) over all values of $\alpha = 1, \dots, n$ leads to the corresponding balance equations for the mixture. These equations should have the same structure as the balance equations (2.97), (2.98) and (2.99) for a single component, namely,

$$\frac{\partial \varrho}{\partial t} + \frac{\partial \varrho v_i}{\partial x_i} = 0, \tag{8.14}$$

$$\frac{\partial \varrho v_i}{\partial t} + \frac{\partial}{\partial x_j}(\varrho v_i v_j + p_{ij}) = \varrho F_i, \tag{8.15}$$

$$\frac{\partial}{\partial t}\left[\varrho\Big(\varepsilon+\frac{1}{2}v^2\Big)\right]+\frac{\partial}{\partial x_i}\left[\varrho\Big(\varepsilon+\frac{1}{2}v^2\Big)v_i+q_i+p_{ij}v_j\right]=\varrho F_i v_i. \quad (8.16)$$

From the comparison of the sums of (8.9) and (8.10) with the corresponding ones (8.15) and (8.16), it follows that the momentum and energy production terms must vanish, i.e.,

$$\sum_{\alpha=1}^{n}\pi_i^\alpha=0, \qquad \sum_{\alpha=1}^{n}\zeta_\alpha=0. \quad (8.17)$$

The above conditions can be obtained from the right-hand side of the transfer equation for the mixture (8.3), since at collision, the conservation laws hold: $m_\alpha\mathbf{c}_\alpha+m_\beta\mathbf{c}_\beta=m_\alpha\mathbf{c}'_\alpha+m_\beta\mathbf{c}'_\beta$ and $m_\alpha c_\alpha^2/2+m_\beta c_\beta^2/2=m_\alpha c_\alpha'^2/2+m_\beta c_\beta'^2/2$. Furthermore, the comparison of (8.14) with the sum of (8.8) leads to the identification of the mass density and momentum density of the mixture:

$$\varrho=\sum_{\alpha=1}^{n}\varrho_\alpha=\sum_{\alpha=1}^{n}\int m_\alpha f_\alpha d\mathbf{c}_\alpha, \quad \varrho v_i=\sum_{\alpha=1}^{n}\varrho_\alpha v_i^\alpha=\sum_{\alpha=1}^{n}\int m_\alpha c_i^\alpha f_\alpha d\mathbf{c}_\alpha. \quad (8.18)$$

In order to obtain the expressions for the internal energy density, pressure tensor and heat flux vector of the mixture, one has to introduce the diffusion velocity u_i^α of the constituent α, defined by

$$u_i^\alpha=v_i^\alpha-v_i, \qquad \text{so that} \qquad \sum_{\alpha=1}^{n}\varrho_\alpha u_i^\alpha=0. \quad (8.19)$$

The constraint $(8.19)_2$ indicates that there exist only $(n-1)$ linearly independent diffusion velocities.

Once the diffusion velocity is introduced into the sums of the balance equations (8.9) and (8.10), one can obtain the following expressions for the pressure tensor, internal energy density and heat flux vector of the mixture:

$$p_{ij}=\sum_{\alpha=1}^{n}\left(p_{ij}^\alpha+\varrho_\alpha u_i^\alpha u_j^\alpha\right), \quad (8.20)$$

$$\varrho\varepsilon=\sum_{\alpha=1}^{n}\varrho_\alpha\left(\varepsilon_\alpha+\frac{1}{2}u_\alpha^2\right), \quad (8.21)$$

$$q_i=\sum_{\alpha=1}^{n}\left[q_i^\alpha+\varrho_\alpha\left(\varepsilon_\alpha+\frac{1}{2}u_\alpha^2\right)u_i^\alpha+p_{ji}^\alpha u_j^\alpha\right]. \quad (8.22)$$

One infers from the above equations that: **(a)** the pressure tensor of the mixture is a sum of the pressure tensors of the constituents p_{ij}^α and of the momentum fluxes in diffusive motion $\varrho_\alpha u_i^\alpha u_j^\alpha$; **(b)** the internal energy density of the mixture is a sum of the internal energy densities of the constituents $\varrho_\alpha\varepsilon_\alpha$

and of the kinetic energy of the diffusive motion $\varrho_\alpha u_\alpha^2/2$ and **(c)** the heat flux vector of the mixture is a sum of the heat flux vectors of the constituents q_i^α, of the internal and kinetic energies in the diffusive motion $\varrho_\alpha\left(\varepsilon_\alpha + u_\alpha^2/2\right)u_i^\alpha$ and of the power of the pressure tensors in diffusive motion $p_{ji}^\alpha u_i^\alpha$.

Often, in the theory of mixtures, the diffusion flux of the constituent α is introduced, which is defined by $J_i^\alpha = \varrho_\alpha u_i^\alpha$. Due to the constraint $(8.19)_2$, there exist only $(n-1)$ linearly independent diffusion fluxes. Furthermore, in terms of the distribution function f_α, the diffusion flux of constituent α can be represented as

$$J_i^\alpha = \varrho_\alpha\left(v_i^\alpha - v_i\right) = \int m_\alpha\left(c_i^\alpha - v_i\right)f_\alpha d\mathbf{c}_\alpha = \int m_\alpha \xi_i^\alpha f_\alpha d\mathbf{c}_\alpha, \tag{8.23}$$

where $\xi_i^\alpha = v_i^\alpha - v_i$ is a peculiar velocity of constituent α with respect to the velocity of the mixture.

Another useful balance equation is the one for the internal energy density of the mixture. It can be obtained from the balance equations (8.15) and (8.16) by following the same methodology described in Section 2.5.2, yielding

$$\frac{\partial \varrho\varepsilon}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho\varepsilon v_i + q_i\right) + p_{ij}\frac{\partial v_i}{\partial x_j} = 0. \tag{8.24}$$

The balance equation for the entropy density of the mixture is obtained by choosing $\psi_\alpha = -k\ln \mathtt{b}_\alpha f_\alpha$, where $\mathtt{b}_\alpha$ is a constant, into the transfer equation of the mixture (8.3), yielding

$$\frac{\partial \varrho s}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho s v_i + \varphi_i\right) = \varsigma. \tag{8.25}$$

The entropy density ϱs, the entropy flux φ_i and the entropy production density ς of the mixture are given by

$$\varrho s = \sum_{\alpha=1}^{n}\varrho_\alpha s_\alpha, \qquad \varrho_\alpha s_\alpha = -k\int(f_\alpha \ln \mathtt{b}_\alpha f_\alpha)d\mathbf{c}_\alpha, \tag{8.26}$$

$$\varphi_i = \sum_{\alpha=1}^{n}(\varphi_i^\alpha + \varrho_\alpha s_\alpha u_i^\alpha), \qquad \varphi_i^\alpha = -k\int(f_\alpha \ln \mathtt{b}_\alpha f_\alpha)C_i^\alpha d\mathbf{c}_\alpha, \tag{8.27}$$

$$\varsigma = \frac{k}{4}\sum_{\alpha,\beta=1}^{n}\int \ln\frac{f_\alpha' f_\beta'}{f_\alpha f_\beta}\left(\frac{f_\alpha' f_\beta'}{f_\alpha f_\beta} - 1\right)f_\alpha f_\beta g_{\beta\alpha} b\, db\, d\varepsilon\, d\mathbf{c}_\beta d\mathbf{c}_\alpha, \tag{8.28}$$

where $\varrho_\alpha s_\alpha$ and φ_i^α denote the entropy density and the entropy flux of the constituent α, respectively.

One may infer from (8.26)–(8.28) that: **(a)** the entropy density of the mixture is a sum of the entropy densities of the constituents $\varrho_\alpha s_\alpha$; **(b)** the entropy flux of the mixture is a sum of the entropy fluxes of the constituents

φ_i^α and of the entropy densities of the diffusive motion $\varrho_\alpha s_\alpha u_i^\alpha$ and **(c)** the entropy production density of the mixture is a positive semi-definite quantity $\varsigma \geqslant 0$, thanks to the inequality $(x-1)\ln x \geqslant 0$, which is valid for all $x > 0$.

Exercise

8.2 Obtain the expressions for the pressure tensor (8.20), internal energy density (8.21) and heat flux vector (8.22) of the mixture.

8.3 Thermodynamics of Fluid Mixtures

Within the framework of the thermodynamic theory of irreversible processes, a fluid mixture of n constituents is described by $(n+4)$ scalar fields:

$$\begin{cases} \varrho_\alpha \text{ - mass densities, } (\alpha = 1, 2, \dots, n) \\ v_i \text{ - hydrodynamic velocity of the mixture,} \\ T \text{ - temperature of the mixture.} \end{cases} \tag{8.29}$$

By introducing the mass concentration c_α of the constituent α

$$\mathsf{c}_\alpha = \frac{\varrho_\alpha}{\varrho}, \qquad \text{such that} \qquad \sum_{\alpha=1}^{n} \mathsf{c}_\alpha = 1, \tag{8.30}$$

the set of macroscopic fields (8.29) is equivalent to

$$\begin{cases} \varrho \text{ - mixture's mass density,} \\ \mathsf{c}_\alpha \text{ - mass concentrations, } (\alpha = 1, 2, \dots, n-1) \\ v_i \text{ - hydrodynamic velocity of the mixture,} \\ T \text{ - temperature of the mixture.} \end{cases} \tag{8.31}$$

Note that, according to the constraint $(8.30)_2$, there exist only $(n-1)$ linearly independent mass concentrations.

The starting point of the thermodynamic theory of irreversible processes is the Gibbs equation (see (8.162) of the appendix)

$$ds = \frac{1}{T}\left[d\varepsilon - \frac{p}{\varrho^2}d\varrho - \sum_{\alpha=1}^{n} \mu_\alpha d\mathsf{c}_\alpha\right] = \frac{1}{T}\left[d\varepsilon - \frac{p}{\varrho^2}d\varrho - \sum_{\alpha=1}^{n-1} (\mu_\alpha - \mu_n)\, d\mathsf{c}_\alpha\right]. \tag{8.32}$$

In terms of the material time derivative $\mathcal{D} = \partial/\partial t + v_i \partial/\partial x_i$, the above equation can be written as

$$\mathcal{D}s = \frac{1}{T}\left[\mathcal{D}\varepsilon - \frac{p}{\varrho^2}\mathcal{D}\varrho - \sum_{\alpha=1}^{n-1}(\mu_\alpha - \mu_n)\mathcal{D}\mathsf{c}_\alpha\right]. \tag{8.33}$$

By following the methodology of the thermodynamic theory of irreversible processes, the material time derivatives of the fields c_α, ϱ and ε are eliminated from the Gibbs equation (8.33) through the use of the balance equations that follows from (8.8), (8.14) and (8.24), namely,

$$\varrho\mathcal{D}\mathsf{c}_\alpha + \frac{\partial J_i^\alpha}{\partial x_i} = 0, \qquad \mathcal{D}\varrho + \varrho\frac{\partial v_i}{\partial x_i} = 0, \qquad \varrho\mathcal{D}\varepsilon + \frac{\partial q_i}{\partial x_i} + p_{ij}\frac{\partial v_i}{\partial x_j} = 0. \tag{8.34}$$

Hence, after some rearrangements, the balance equation for the entropy density of the mixture reads

$$\varrho\mathcal{D}s + \frac{\partial \varphi_i}{\partial x_i} = \varsigma \geqslant 0, \tag{8.35}$$

where the entropy flux φ_i and the entropy production density ς of the mixture are given by

$$\varphi_i = \frac{q_i}{T} - \sum_{\alpha=1}^{n-1}\frac{\mu_\alpha - \mu_n}{T}J_i^\alpha \quad \text{and} \tag{8.36}$$

$$\varsigma = -q_i\frac{1}{T^2}\frac{\partial T}{\partial x_i} - \sum_{\alpha=1}^{n-1}\frac{\partial}{\partial x_i}\left(\frac{\mu_\alpha - \mu_n}{T}\right)J_i^\alpha - \frac{1}{T}\varpi\frac{\partial v_i}{\partial x_i} - \frac{1}{T}p_{\langle ij\rangle}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \tag{8.37}$$

respectively. Note that the entropy flux of the mixture is equal to the heat flux vector divided by the temperature—as in the case of a single gas (see $(3.7)_1$)—plus a term related with the diffusive motion of the constituents. Furthermore, the entropy production density is a positive semi-definite quantity. It is worth noticing that for mixtures of rarefied monatomic gases the dynamic pressure ϖ vanishes.

One may infer from the expression for the entropy production density (8.37) that it is a function of the thermodynamic forces and fluxes given in Table 8.1.

Table 8.1 Thermodynamic forces and fluxes

Thermodynamic forces (cause)	*Thermodynamic fluxes (effect)*
$\frac{\partial v_i}{\partial x_i}$, $\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}$, $\frac{\partial T}{\partial x_i}$, $\frac{\partial[(\mu_\alpha-\mu_n)/T]}{\partial x_i}$	ϖ, $p_{\langle ij\rangle}$, q_i, J_i^α

According to the methodology of the thermodynamic theory of irreversible processes, the thermodynamic fluxes are related with the thermodynamic forces by linear laws. Hence, one may write the following constitutive equations for the thermodynamic fluxes:

$$q_i = -\frac{\lambda'}{T}\frac{\partial T}{\partial x_i} - T\sum_{\alpha=1}^{n-1} D'_\alpha \frac{\partial}{\partial x_i}\left(\frac{\mu_\alpha - \mu_n}{T}\right), \tag{8.38}$$

$$J_i^\alpha = -\frac{D_\alpha}{T}\frac{\partial T}{\partial x_i} - T\sum_{\beta=1}^{n-1} D'_{\alpha\beta} \frac{\partial}{\partial x_i}\left(\frac{\mu_\beta - \mu_n}{T}\right), \tag{8.39}$$

$$\varpi = -\eta\frac{\partial v_i}{\partial x_i}, \qquad p_{\langle ij\rangle} = -2\mu\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}. \tag{8.40}$$

Equations (8.38), (8.39) and (8.40) represent the laws of Fourier, Fick and Navier–Stokes, respectively. The scalar coefficients in (8.38)–(8.40) are related to: **(a)** thermal conductivity λ' ; **(b)** diffusion $D'_{\alpha\beta}$ $(\alpha, \beta = 1, 2, \dots, n-1)$; **(c)** diffusion–thermal effects D'_α $(\alpha = 1, 2, \dots, n-1)$; **(d)** thermal–diffusion effects D_α $(\alpha = 1, 2, \dots, n-1)$; **(e)** bulk viscosity η and **(f)** shear viscosity μ.

The cross effects of thermal-diffusion and diffusion-thermal are also referred in the literature as Soret effect and Dufour effect, respectively.

The thermodynamic theory of irreversible processes postulates the following relationships for the coefficients

$$D'_{\alpha\beta} = D'_{\beta\alpha}, \qquad D_\alpha = D'_\alpha, \tag{8.41}$$

which are known in the literature as the Onsager reciprocity relations.[1] The first relation above indicates that the matrix of the diffusion coefficients is symmetric, while the second one reveals that the coefficients of cross effects are identical. In Section 8.9, it will be shown from a kinetic theory that the Onsager reciprocity relations hold for mixtures of monatomic gases.

Exercises

8.3 Obtain the expressions for the entropy flux (8.36) and entropy production density (8.37).

8.4 Insert the constitutive equations (8.38), (8.39) and (8.40) into the entropy production density (8.37) and show that $\eta \geqslant 0$, $\mu \geqslant 0$, $\lambda' \geqslant 0$ and $D_{\alpha\alpha} \geqslant 0$.

8.4 The Equilibrium Distribution Function

As in the case of a single gas (see Section 2.6.1), the state of equilibrium for mixtures of gases is defined as the process which renders the collision terms of the Boltzmann equation (8.1) to vanish. Hence, it follows

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[1] Lars Onsager (1903–1976) Norwegian-American physical chemist.

$$f_\alpha'^{(0)} f_\beta'^{(0)} = f_\alpha^{(0)} f_\beta^{(0)} \qquad \text{or} \qquad \ln f_\alpha'^{(0)} + \ln f_\beta'^{(0)} = \ln f_\alpha^{(0)} + \ln f_\beta^{(0)}. \quad (8.42)$$

It is easy to verify from the conservation laws of momentum (1.91) and energy (1.92) that the distribution function f_α must be represented as

$$\ln f_\alpha^{(0)} = A_\alpha + \mathbf{B}\cdot(m_\alpha \mathbf{c}_\alpha) + D\left(\frac{m_\alpha}{2}c_\alpha^2\right), \tag{8.43}$$

where A_α and D denote scalar functions, and $\mathbf{B}$ is a vectorial function, which does not depend on $\mathbf{c}_\alpha$. By introducing $a_\alpha^\star$, $\mathbf{u}$ and $b^\star$ such that $A_\alpha = \ln a_\alpha^\star - m_\alpha b^\star u^2$, $\mathbf{B} = 2b^\star \mathbf{u}$ and $D = -b^\star$, (8.43) can be rewritten as

$$f_\alpha^{(0)} = a_\alpha^\star e^{-m_\alpha b^\star (\mathbf{c}_\alpha - \mathbf{u})^2/2}, \qquad (\alpha = 1, 2, \dots, n). \tag{8.44}$$

The n equilibrium distribution functions $f_\alpha^{(0)}$ are determined from the $(n+4)$ basic fields of mass densities, hydrodynamic velocity and temperature of the mixture. To begin with, the substitution of the distribution function (8.44) into the definitions of the mass density (8.4) of constituent α and of the hydrodynamic velocity $(8.18)_2$ of the mixture and the integration of the resulting equations leads to the knowledge of the coefficients $a_\alpha^\star$ and $\mathbf{u}$, so that the distribution function becomes

$$f_\alpha^{(0)} = n_\alpha \left(\frac{m_\alpha b^\star}{2\pi}\right)^{\frac{3}{2}} e^{-m_\alpha b^\star \xi_\alpha^2/2}, \tag{8.45}$$

where $n_\alpha = \varrho_\alpha / m_\alpha$ is the particle number density of the constituent α.

The determination of the coefficient $b^\star$ is more involved. First, one evaluates the diffusion flux J_i^α at equilibrium by inserting the distribution function (8.45) into its definition (8.23) and integrating the resulting equation, yielding

$$J_i^\alpha|_E = \varrho_\alpha u_i^\alpha|_E = 0. \tag{8.46}$$

By using the above result, (8.21) reduces to

$$\varrho\varepsilon|_E = \sum_{\alpha=1}^{n} \varrho_\alpha \varepsilon_\alpha|_E. \tag{8.47}$$

Next, by using the same methodology, the substitution of the distribution function (8.45) into the expressions for the internal energy density $(8.7)_2$ and for the entropy density $(8.26)_2$ and the subsequent integration of the resulting equations leads to

$$\varrho_\alpha\varepsilon_\alpha|_E = \frac{3}{2}\frac{n_\alpha}{b^\star}, \qquad \varrho_\alpha s_\alpha|_E = k n_\alpha \left\{\frac{3}{2} - \ln n_\alpha - \ln\left[\mathsf{b}_\alpha \left(\frac{m_\alpha b^\star}{2\pi}\right)^{\frac{3}{2}}\right]\right\}. \tag{8.48}$$

By summing the above equations over all constituents, it follows the corresponding expressions for the internal energy density and entropy density of the mixture, namely,

$$\varrho\varepsilon|_E = \frac{3}{2}\frac{n}{b^\star}, \qquad \varrho s|_E = \frac{3}{2}kn - k\sum_{\alpha=1}^{n} n_\alpha\left\{\ln n_\alpha + \ln\left[\mathsf{b}_\alpha\left(\frac{m_\alpha b^\star}{2\pi}\right)^{\frac{3}{2}}\right]\right\}, \tag{8.49}$$

where $n = \sum_{\alpha=1}^{n} n_\alpha$ denotes the particle number density of the mixture.

Now, the determination of the coefficient $b^\star$ proceeds by differentiating the entropy density of the mixture $(8.49)_2$, which, after some rearrangements, becomes

$$ds|_E = kb^\star\left\{d\varepsilon|_E - \frac{n}{b^\star\varrho^2}d\varrho - \sum_{\alpha=1}^{n}\frac{1+\ln\left[\mathsf{b}_\alpha\left(\frac{m_\alpha b^\star}{2\pi}\right)^{\frac{3}{2}} n_\alpha\right]}{m_\alpha b^\star}d\mathsf{c}_\alpha\right\}, \tag{8.50}$$

by using the equation for the internal energy density $(8.49)_1$. From the comparison of the above equation with Gibbs'equation (8.32), one infers that $b^\star = 1/kT$, where T denotes the absolute temperature of the mixture. Furthermore, one identifies the hydrostatic pressure of the mixture and the chemical potential of the constituent α as

$$p = nkT, \qquad \mu_\alpha|_E = \frac{kT}{m_\alpha} + \frac{kT}{m_\alpha}\left\{\ln\frac{n_\alpha}{T^{\frac{3}{2}}} + \ln\left[\mathsf{b}_\alpha\left(\frac{m_\alpha}{2\pi k}\right)^{\frac{3}{2}}\right]\right\}. \tag{8.51}$$

The identification of $b^\star = 1/kT$ implies that the internal energy density $(8.48)_1$ and the entropy density $(8.48)_2$ of the constituent α become

$$\varepsilon_\alpha|_E = \frac{3}{2}\frac{k}{m_\alpha}T, \qquad s_\alpha|_E = \frac{k}{m_\alpha}\left\{\ln\frac{T^{\frac{3}{2}}}{n_\alpha} + \frac{3}{2} - \ln\left[\mathsf{b}_\alpha\left(\frac{m_\alpha}{2\pi k}\right)^{\frac{3}{2}}\right]\right\}. \tag{8.52}$$

Furthermore, the distribution function (8.45) reads

$$f_\alpha^{(0)} = n_\alpha\left(\frac{\beta_\alpha}{\pi}\right)^{\frac{3}{2}} e^{-\beta_\alpha\xi_\alpha^2}, \qquad \text{where} \qquad \beta_\alpha = \frac{m_\alpha}{2kT}. \tag{8.53}$$

One recognizes the above equation as the Maxwellian distribution function for the constituent α.

It is worth noticing that the chemical potential for a mixture of rarefied monatomic gases can be expressed—due to (8.51) and (8.52)—as

$$\mu_\alpha|_E = \varepsilon_\alpha|_E - Ts_\alpha|_E + \frac{p_\alpha}{\varrho_\alpha}, \qquad \text{where} \qquad p_\alpha = n_\alpha kT \tag{8.54}$$

is the hydrostatic pressure of the constituent α.

Exercises

8.5 Obtain the expressions for the distribution function (8.45).

8.6 Show that the differentiation of the entropy density of the mixture $(8.49)_2$ leads to the expression (8.50).

8.7 Show that for the constituent α: $p^\alpha_{\langle ij\rangle}|_E = 0$, $q^\alpha_i|_E = 0$ and $\varphi^\alpha_i|_E = 0$. Furthermore, show that for the mixture: $p_{\langle ij\rangle}|_E = 0$, $q_i|_E = 0$ and $\varphi_i|_E = 0$.

8.5 Equilibrium States

In the previous section, the Maxwellian distribution function (8.53) was obtained by using the argument that the right-hand side of the Boltzmann equation (8.1) —which refers to the collision between the molecules of the constituents—vanishes at equilibrium. Hence, by considering the Maxwellian distribution function, the left-hand side of the Boltzmann equation becomes

$$\frac{\partial f^{(0)}_\alpha}{\partial t} + c^\alpha_i \frac{\partial f^{(0)}_\alpha}{\partial x_i} + F_i \frac{\partial f^{(0)}_\alpha}{\partial c^\alpha_i} = 0, \tag{8.55}$$

which in terms of the derivatives of the fields ϱ_α, v_i and T reads

$$f^{(0)}_\alpha \left\{ \frac{\mathcal{D}\varrho_\alpha}{\varrho_\alpha} + \frac{\mathcal{D}T}{T}\left(\frac{m_\alpha \xi_\alpha^2}{2kT} - \frac{3}{2}\right) + \frac{m_\alpha}{kT}\xi^\alpha_i\left(\mathcal{D}v_i - F_i\right) \right.$$
$$\left. + \xi^\alpha_i \left[\frac{1}{\varrho_\alpha}\frac{\partial \varrho_\alpha}{\partial x_i} + \frac{1}{T}\frac{\partial T}{\partial x_i}\left(\frac{m_\alpha \xi_\alpha^2}{2kT} - \frac{3}{2}\right) + \frac{m_\alpha}{kT}\xi^\alpha_j \frac{\partial v_j}{\partial x_i}\right] \right\} = 0. \tag{8.56}$$

By following the same methodology of Section 2.6.2, the coefficients of the polynomial equation (8.56) in the variable ξ^α_i must be zero, so that

$$\frac{\mathcal{D}\varrho_\alpha}{\varrho_\alpha} - \frac{3}{2}\frac{\mathcal{D}T}{T} = 0, \qquad \frac{\mathcal{D}T}{T}\delta_{ij} + \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) = 0, \tag{8.57}$$

$$\mathcal{D}v_i - F_i + \frac{kT}{m_\alpha}\left(\frac{1}{\varrho_\alpha}\frac{\partial \varrho_\alpha}{\partial x_i} - \frac{3}{2}\frac{1}{T}\frac{\partial T}{\partial x_i}\right) = 0, \qquad \frac{\partial T}{\partial x_i} = 0. \tag{8.58}$$

In order to investigate (8.57) and (8.58), one takes the trace and the traceless parts of equation $(8.57)_2$ and obtains

$$\frac{3}{2}nk\mathcal{D}T + p\frac{\partial v_i}{\partial x_i} = 0, \qquad \frac{\partial v_{\langle i}}{\partial x_{j\rangle}} = 0. \tag{8.59}$$

Next, by eliminating $\mathcal{D}T$ from $(8.57)_1$ through the use of $(8.59)_1$, it follows

$$\mathcal{D}\varrho_\alpha + \varrho_\alpha \frac{\partial v_i}{\partial x_i} = 0. \tag{8.60}$$

The comparison of (8.60) with the balance of mass density (8.8) of the component α implies that the diffusion flux must be zero at equilibrium, i.e., $J_i^\alpha|_E = 0$. Likewise, from the comparison of $(8.59)_1$ with the balance of the internal energy density of the mixture (8.24) and by considering $\varrho\varepsilon|_E = 3nkT/2$, it follows that the values at equilibrium of the pressure tensor and of the heat flux vector read $p_{ij}|_E = p\,\delta_{ij}$ and $q_i|_E = 0$, respectively. One extends the terminology adopted for a single fluid and says that the thermodynamic fluxes at equilibrium for an Eulerian fluid mixture are characterized by: $J_i^\alpha|_E = 0$, $p_{ij}|_E = p\,\delta_{ij}$ and $q_i|_E = 0$.

The last comparison refers to the balance of momentum density of the mixture (8.15) and $(8.58)_1$. By taking into account $(8.58)_2$ and the constitutive equation $p_{ij}|_E = p\,\delta_{ij}$, it follows that in equilibrium

$$\frac{1}{\varrho}\frac{\partial n}{\partial x_i} = \frac{1}{\varrho_\alpha}\frac{\partial n_\alpha}{\partial x_i}. \tag{8.61}$$

From the above relationship, one can build the so-called generalized diffusion force of the constituent α, namely,

$$d_i^\alpha \equiv \frac{\partial}{\partial x_i}\left(\frac{n_\alpha}{n}\right) + \left(\frac{n_\alpha}{n} - \frac{\varrho_\alpha}{\varrho}\right)\frac{\partial \ln p}{\partial x_i} = \frac{1}{p}\frac{\partial p_\alpha}{\partial x_i} - \frac{\varrho_\alpha}{\varrho p}\frac{\partial p}{\partial x_i}. \tag{8.62}$$

The generalized diffusion forces have the properties: **(a)** they vanish at equilibrium and **(b)** there exist only $(n-1)$ generalized diffusion forces, which are linearly independent, i.e.,

$$d_i^\alpha|_E = 0 \quad \forall\,\alpha = 1, 2, \ldots, n, \qquad \sum_{\alpha=1}^{n} d_i^\alpha = 0. \tag{8.63}$$

Hence, the equilibrium state of a fluid mixture is characterized by the vanishing of the thermodynamic forces:

$$\left.\frac{\partial T}{\partial x_i}\right|_E = 0, \qquad \left.\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}\right|_E = 0, \qquad d_i^\alpha|_E = 0 \quad \forall\,\alpha = 1, 2, \ldots, n. \tag{8.64}$$

Exercise

8.8 By following the methodology described above concerning the comparison of the equations show that at equilibrium $J_i^\alpha|_E = 0$, $p_{ij}|_E = p\,\delta_{ij}$, $q_i|_E = 0$ and $\varrho_\alpha \partial n/\partial x_i = \varrho\,\partial n_\alpha/\partial x_i$.

8.6 Grad's Distribution Function

In order to determine Grad's distribution function for the constituent α, one expands the distribution function f_α in series of the peculiar velocity ξ_i^α, namely,

$$f_\alpha = f_\alpha^{(0)}\left(a^\alpha + a_i^\alpha \xi_i^\alpha + a_{ij}^\alpha \xi_i^\alpha \xi_j^\alpha + a_{ijj}^\alpha \xi_\alpha^2 \xi_i^\alpha\right), \tag{8.65}$$

where the coefficients a^α, a_i^α, a_{ij}^α and a_{ijj}^α do not depend on the peculiar velocities and are determined from the definition of the fields mass density ϱ_α, diffusion flux J_i^α, pressure tensor p_{ij}^α and heat flux vector q_i^α of the constituent α, namely,

$$\varrho_\alpha = \int m_\alpha f_\alpha d\mathbf{c}_\alpha, \qquad J_i^\alpha = \int m_\alpha \xi_i^\alpha f_\alpha d\mathbf{c}_\alpha, \tag{8.66}$$

$$p_{ij}^\alpha = \int m_\alpha C_i^\alpha C_j^\alpha f_\alpha d\mathbf{c}_\alpha, \qquad q_i^\alpha = \int \frac{1}{2} m_\alpha C_\alpha^2 C_i^\alpha f_\alpha d\mathbf{c}_\alpha. \tag{8.67}$$

In a linearized theory, the pressure tensor $(8.67)_1$ and the heat flux vector $(8.67)_2$ can be written in terms of the peculiar velocity $\xi_i^\alpha = C_i^\alpha + u_i^\alpha$ as

$$p_{ij}^\alpha = \int m_\alpha \left(\xi_i^\alpha \xi_j^\alpha - \xi_i^\alpha u_j^\alpha - \xi_j^\alpha u_i^\alpha\right) f_\alpha d\mathbf{c}_\alpha, \tag{8.68}$$

$$q_i^\alpha = \int \frac{1}{2} m_\alpha \left(\xi_\alpha^2 \xi_i^\alpha - \xi_\alpha^2 u_i^\alpha - 2\xi_i^\alpha \xi_r^\alpha u_r^\alpha\right) f_\alpha d\mathbf{c}_\alpha, \tag{8.69}$$

by neglecting all products of the diffusion velocity u_i^α.

For the determination of the coefficients a^α, a_i^α, a_{ij}^α and a_{ijj}^α, the insertion of the distribution function (8.65) into (8.66), (8.68) and (8.69) and the integration of the resulting equations lead to the following coupled system of algebraic equations:

$$1 = a^\alpha + \frac{kT}{m_\alpha} a_{rr}^\alpha, \qquad J_i^\alpha = \varrho_\alpha \frac{kT}{m_\alpha}\left[a_i^\alpha + 5\frac{kT}{m_\alpha} a_{ijj}^\alpha\right], \tag{8.70}$$

$$p_{ij}^\alpha = \varrho_\alpha \frac{kT}{m_\alpha}\left[a^\alpha \delta_{ij} + \frac{kT}{m_\alpha}(2a_{ij}^\alpha + a_{rr}^\alpha \delta_{ij})\right], \tag{8.71}$$

$$q_i^\alpha = \frac{5}{2}\varrho_\alpha \frac{kT}{m_\alpha}\left\{\frac{kT}{m_\alpha} a_i^\alpha + 7\left(\frac{kT}{m_\alpha}\right)^2 a_{ijj}^\alpha - \left[a^\alpha + \frac{5kT}{3m_\alpha} a_{rr}^\alpha\right] u_i^\alpha\right\}. \tag{8.72}$$

Above, all products of $a_{\langle ij\rangle}^\alpha$ and a_{ijj}^α by u_i^α were neglected, since they are of the same order.

By solving the system of algebraic equations (8.70)–(8.72) for the coefficients a^α, a_i^α, a_{ij}^α and a_{ijj}^α and by substituting the results into (8.65), one obtains Grad's distribution function for the constituent α for a mixture of monatomic rarefied gases:

$$f_\alpha = n_\alpha\left(\frac{\beta_\alpha}{\pi}\right)^{\frac{3}{2}} \exp\left(-\beta_\alpha\xi_\alpha^2\right)\left\{1 + 2\beta_\alpha\frac{J_i^\alpha\xi_i^\alpha}{\varrho_\alpha} + \frac{2\beta_\alpha^2}{\varrho_\alpha}\left[p_{\langle ij\rangle}^\alpha\xi_i^\alpha\xi_j^\alpha \right.\right.$$
$$\left.\left. + \frac{4}{5}q_i^\alpha\xi_i^\alpha\left(\beta_\alpha\xi_\alpha^2 - \frac{5}{2}\right)\right]\right\}. \tag{8.73}$$

Note that in Grad's distribution function above the temperature is the temperature of the mixture which is the same for all constituents. In this chapter the case where each constituent has its own temperature will not be treated.

Once Grad's distribution function (8.73) is known, one may calculate the entropy flux of the mixture in a linearized theory. In order achieve this objective, one determines first the linearized expression for the entropy flux of the constituent α by inserting Grad's distribution function (8.73) into its definition $(8.27)_2$ and by integrating the resulting equation. After some rearrangements, by neglecting all non-linear terms and using the approximation $\ln(1+x) \approx x$ (which is valid for all $x \ll 1$), it follows that $\varphi_i^\alpha = q_i^\alpha/T$, i.e., the entropy flux of the constituent α is proportional to the corresponding heat flux vector divided by the temperature of the mixture.

In a linearized theory, the heat flux vector of the mixture (8.22) reduces to

$$q_i = \sum_{\alpha=1}^{n} q_i^\alpha + \sum_{\alpha=1}^{n}\left(\varrho_\alpha\varepsilon_\alpha + p_\alpha\right)u_i^\alpha, \tag{8.74}$$

and the entropy flux of the mixture (8.27) can be written as

$$\varphi_i = \frac{q_i}{T} - \sum_{\alpha=1}^{n}\frac{\mu_\alpha}{T}J_i^\alpha = \frac{q_i}{T} - \frac{1}{T}\sum_{\alpha=1}^{n-1}\frac{\mu_\alpha - \mu_n}{T}J_i^\alpha, \tag{8.75}$$

due to the relationship $\varphi_i^\alpha = q_i^\alpha/T$ and the expression $(8.54)_1$ for the chemical potential of the constituent α. Note that the linearized expression for the entropy flux of the mixture (8.75) is the same as the one used in Section 8.3, namely, (8.36).

Exercises

8.9 Obtain (8.70)–(8.72).

8.10 Show that the entropy flux of the constituent α is given by $\varphi_i^\alpha = q_i^\alpha/T$.

8.7 The Combined Chapman–Enskog–Grad Method

The objective of this section is to calculate the constitutive equations for the diffusion fluxes J_i^α, for the pressure tensor p_{ij} and for the heat flux vector q_i of the mixture by using the combined Chapman–Enskog–Grad method (see Section 4.3).

To begin with, the insertion of Grad's distribution function (8.73) into the Boltzmann equation (8.1) leads to

$$\begin{aligned} f_\alpha^{(0)}\Bigg\{ & \frac{\mathcal{D}\varrho_\alpha}{\varrho_\alpha}+\frac{\mathcal{D}T}{T}\left(\frac{m_\alpha\xi_\alpha^2}{2kT}-\frac{3}{2}\right)+\frac{m_\alpha}{kT}\xi_i^\alpha\left(\mathcal{D}v_i-F_i\right) \\ & +\xi_i^\alpha\left[\frac{1}{\varrho_\alpha}\frac{\partial\varrho_\alpha}{\partial x_i}+\frac{1}{T}\frac{\partial T}{\partial x_i}\left(\frac{m_\alpha\xi_\alpha^2}{2kT}-\frac{3}{2}\right)+\frac{m_\alpha}{kT}\xi_j^\alpha\frac{\partial v_j}{\partial x_i}\right]\Bigg\}=\mathsf{I}_\alpha. \qquad (8.76)\end{aligned}$$

As usual in this method, only the Maxwellian distribution function was considered on the left-hand side of the Boltzmann equation, whereas on its right-hand side only linear terms were taken into account. The term I_α—which is a function of the thermodynamic fluxes J_i^α, p_{ij} and q_i—reads

$$\begin{aligned}\mathsf{I}_\alpha=\sum_{\beta=1}^{n}\Bigg\{ & \frac{J_k^\alpha}{\varrho_\alpha}\frac{m_\alpha}{kT}\mathcal{I}_{\alpha\beta}\left[\xi_k^\alpha\right]+\frac{J_k^\beta}{\varrho_\beta}\frac{m_\beta}{kT}\mathcal{I}_{\alpha\beta}\left[\xi_k^\beta\right]+\frac{p_{\langle kl\rangle}^\alpha}{2\varrho_\alpha}\left(\frac{m_\alpha}{kT}\right)^2\mathcal{I}_{\alpha\beta}\left[\xi_k^\alpha\xi_l^\alpha\right] \\ & +\frac{p_{\langle kl\rangle}^\beta}{2\varrho_\beta}\left(\frac{m_\beta}{kT}\right)^2\mathcal{I}_{\alpha\beta}\left[\xi_k^\beta\xi_l^\beta\right]+\frac{2}{5}\frac{q_k^\alpha}{\varrho_\alpha}\left(\frac{m_\alpha}{kT}\right)^2\mathcal{I}_{\alpha\beta}\left[\left(\frac{m_\alpha\xi_\alpha^2}{2kT}-\frac{5}{2}\right)\xi_k^\alpha\right] \\ & +\frac{2}{5}\frac{q_k^\beta}{\varrho_\beta}\left(\frac{m_\beta}{kT}\right)^2\mathcal{I}_{\alpha\beta}\left[\left(\frac{m_\beta\xi_\beta^2}{2kT}-\frac{5}{2}\right)\xi_k^\beta\right]\Bigg\}, \qquad (8.77)\end{aligned}$$

where $\mathcal{I}_{\alpha\beta}[\phi_\alpha]$ represent the integrals

$$\mathcal{I}_{\alpha\beta}[\phi_\alpha]=\int f_\alpha^{(0)}f_\beta^{(0)}(\phi_\alpha'-\phi_\alpha)g_{\beta\alpha}b\,db\,d\varepsilon\,d\mathbf{c}_\beta. \qquad (8.78)$$

It is easy to verify that for arbitrary functions $\varphi_\beta\equiv\varphi(\mathbf{x},\mathbf{c}_\beta,t)$ and $\phi_\alpha\equiv\phi(\mathbf{x},\mathbf{c}_\alpha,t)$ $(\alpha,\beta=1,2,\dots,n)$, the following relationship involving the integrals $\mathcal{I}_{\alpha\beta}[\phi_\alpha]$ holds

$$\begin{aligned}\int\varphi_\beta\mathcal{I}_{\alpha\beta}[\phi_\alpha]d\mathbf{c}_\alpha &= \int\varphi_\beta f_\alpha^{(0)}f_\beta^{(0)}(\phi_\alpha'-\phi_\alpha)g_{\beta\alpha}b\,db\,d\varepsilon\,d\mathbf{c}_\beta d\mathbf{c}_\alpha \\ =\int\phi_\alpha f_\alpha^{(0)}f_\beta^{(0)}(\varphi_\beta'-\varphi_\beta)g_{\beta\alpha}b\,db\,d\varepsilon\,d\mathbf{c}_\beta d\mathbf{c}_\alpha &= \int\phi_\alpha\mathcal{I}_{\alpha\beta}[\varphi_\beta]d\mathbf{c}_\alpha. \qquad (8.79)\end{aligned}$$

The above relationship can be extended to the sums, yielding

$$\sum_{\alpha,\beta=1}^{n}\int\varphi_\beta\left(\mathcal{I}_{\alpha\beta}[\phi_\alpha]+\mathcal{I}_{\alpha\beta}[\phi_\beta]\right)d\mathbf{c}_\alpha$$
$$=\sum_{\alpha,\beta=1}^{n}\int(\phi_\alpha+\phi_\beta)(\varphi_\beta'-\varphi_\beta)f_\alpha^{(0)}f_\beta^{(0)}g_{\beta\alpha}b\,db\,d\varepsilon\,d\mathbf{c}_\alpha d\mathbf{c}_\beta$$
$$=\sum_{\alpha,\beta=1}^{n}\int\phi_\beta(\varphi_\alpha'+\varphi_\beta'-\varphi_\alpha-\varphi_\beta)f_\alpha^{(0)}f_\beta^{(0)}g_{\beta\alpha}b\,db\,d\varepsilon\,d\mathbf{c}_\alpha d\mathbf{c}_\beta. \qquad (8.80)$$

From (8.76), one can obtain the balance equations for an Eulerian fluid mixture, namely,

$$\mathcal{D}\varrho_\alpha+\varrho_\alpha\frac{\partial v_i}{\partial x_i}=0,\qquad \varrho\mathcal{D}v_i+\frac{\partial p}{\partial x_i}=\varrho F_i,\qquad \frac{3}{2}nk\mathcal{D}T+p\frac{\partial v_i}{\partial x_i}=0. \qquad (8.81)$$

The above equations are used to eliminate the material time derivatives of ϱ_α, v_i and T from (8.76), yielding

$$f_\alpha^{(0)}\left\{\frac{m_\alpha}{kT}\xi_k^\alpha\xi_l^\alpha\frac{\partial v_{\langle k}}{\partial x_{l\rangle}}+\frac{1}{T}\frac{\partial T}{\partial x_k}\xi_k^\alpha\left(\frac{m_\alpha\xi_\alpha^2}{2kT}-\frac{5}{2}\right)+\frac{n}{n_\alpha}\xi_k^\alpha d_k^\alpha\right\}=\mathsf{I}_\alpha. \qquad (8.82)$$

Note that the left-hand side of (8.82) is function of the thermodynamic forces: velocity gradient deviator $\partial v_{\langle k}/\partial x_{l\rangle}$, temperature gradient $\partial T/\partial x_k$ and generalized diffusion forces d_k^α.

From (8.82), one can obtain the constitutive equations for the thermodynamic fluxes: diffusion flux J_i^α of the constituent α, pressure tensor p_{ij} and heat flux vector q_i of the mixture.

Exercises

8.11 Show that the relationships (8.79) and (8.80) are valid.

8.12 Obtain from (8.76) the balance equations for an Eulerian fluid (8.81).

8.8 The Navier–Stokes Law

In order determine the constitutive equation for the pressure tensor of the mixture, one proceeds as follows: the multiplication of (8.82) by $\beta_\alpha\xi_{\langle i}^\alpha\xi_{j\rangle}^\alpha/n_\alpha$, the integration of the resulting equation over all values of $\mathbf{c}_\alpha$ and the use of (4.75), yielding

$$-2\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}=\sum_{\beta=1}^{n}K_{\alpha\beta}p^{\beta}_{\langle ij\rangle}, \tag{8.83}$$

where the matrices $K_{\alpha\beta}$ are given by

$$K_{\alpha\beta}\overset{(\alpha\neq\beta)}{=}-\frac{m_\alpha m_\beta}{10n_\alpha n_\beta(kT)^3}\int\xi^\alpha_{\langle p}\xi^\alpha_{q\rangle}\mathcal{I}_{\alpha\beta}[\xi^\beta_{\langle p}\xi^\beta_{q\rangle}]d\mathbf{c}_\alpha, \tag{8.84}$$

$$K_{\alpha\alpha}=-\frac{m_\alpha^2}{10n_\alpha^2(kT)^3}\sum_{\beta=1}^{n}\int\xi^\alpha_{\langle p}\xi^\alpha_{q\rangle}\left\{\mathcal{I}_{\alpha\beta}[\xi^\alpha_{\langle p}\xi^\alpha_{q\rangle}]+\mathcal{I}_{\alpha\alpha}[\xi^\alpha_{\langle p}\xi^\alpha_{q\rangle}]\right\}d\mathbf{c}_\alpha. \tag{8.85}$$

The symbol $\overset{(\alpha\neq\beta)}{=}$ means that the equality is valid for all $\alpha\neq\beta$. Next, one solves the system of equations (8.83) for the pressure deviator $p^\alpha_{\langle ij\rangle}$ of the constituent α and obtains

$$p^\alpha_{\langle ij\rangle}=-2\sum_{\beta=1}^{n}(K^{-1})_{\alpha\beta}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \tag{8.86}$$

where $(K^{-1})_{\alpha\beta}$ is the inverse of the matrix $K_{\alpha\beta}$.

Since the linearized expression for the pressure tensor of the mixture is given by $p_{ij}=\sum_{\alpha=1}^{n}p^\alpha_{ij}$ (see (8.20)), it follows that the expression for the pressure deviator of the mixture reads

$$p_{\langle ij\rangle}=-2\mu\frac{\partial v_{\langle i}}{\partial x_{j\rangle}},\qquad\text{where}\qquad\mu=\sum_{\alpha,\beta=1}^{n}(K^{-1})_{\alpha\beta} \tag{8.87}$$

is the coefficient of shear viscosity of the mixture. The relationship $(8.87)_1$ represents Navier–Stokes' law for the mixture.

Exercise

8.13 Obtain (8.83) which relates the pressure tensor of the constituent α to the velocity gradient deviator.

8.9 The Laws of Fick and Fourier

For the determination of the constitutive equations for the diffusion flux J^α_i of the constituent α and for the heat flux vector q_i of the mixture, one proceeds as follows: first, (8.82) is multiplied by ξ^α_i/n_α and afterwards the resulting equation is integrated over all values of $\mathbf{c}_\alpha$. By making use of (4.79), one obtains that

$$-\frac{p}{\varrho_\alpha}d_i^\alpha = \sum_{\beta=1}^n A_{\alpha\beta}J_i^\beta - \sum_{\beta=1}^n \frac{m_\beta}{kT}F_{\alpha\beta}q_i^\beta, \tag{8.88}$$

where the matrices $A_{\alpha\beta}$ and $F_{\alpha\beta}$ read

$$A_{\alpha\beta} \overset{(\alpha\neq\beta)}{=} -\frac{1}{3n_\alpha n_\beta kT}\int \xi_k^\alpha \mathcal{I}_{\alpha\beta}[\xi_k^\beta]d\mathbf{c}_\alpha, \tag{8.89}$$

$$A_{\alpha\alpha} = -\frac{1}{3n_\alpha^2 kT}\sum_{\beta=1}^n \int \xi_k^\alpha \left\{\mathcal{I}_{\alpha\beta}[\xi_k^\alpha] + \mathcal{I}_{\alpha\alpha}[\xi_k^\alpha]\right\} d\mathbf{c}_\alpha, \tag{8.90}$$

$$F_{\alpha\beta} \overset{(\alpha\neq\beta)}{=} \frac{2}{15n_\alpha n_\beta kT}\int \xi_k^\alpha \mathcal{I}_{\alpha\beta}\left[\left(\frac{m_\beta\xi_\beta^2}{2kT} - \frac{5}{2}\right)\xi_k^\beta\right] d\mathbf{c}_\alpha, \tag{8.91}$$

$$\begin{aligned} F_{\alpha\alpha} &= \frac{2}{15n_\alpha^2 kT}\sum_{\beta=1}^n \int \xi_k^\alpha \Bigg\{\mathcal{I}_{\alpha\beta}\left[\left(\frac{m_\alpha\xi_\alpha^2}{2kT} - \frac{5}{2}\right)\xi_k^\alpha\right] \\ &+ \mathcal{I}_{\alpha\alpha}\left[\left(\frac{m_\alpha\xi_\alpha^2}{2kT} - \frac{5}{2}\right)\xi_k^\alpha\right]\Bigg\} d\mathbf{c}_\alpha. \end{aligned} \tag{8.92}$$

Next, the multiplication of (8.82) by $\beta_\alpha\left(\beta_\alpha\xi_\alpha^2 - 5/2\right)\xi_i^\alpha/n_\alpha$ leads to

$$\frac{5}{2}\frac{1}{T}\frac{\partial T}{\partial x_i} = \frac{5}{2}\sum_{\beta=1}^n \frac{m_\alpha}{kT}F_{\beta\alpha}J_i^\beta - \sum_{\beta=1}^n H_{\alpha\beta}q_i^\beta, \tag{8.93}$$

by following the same methodology above. Here, the matrices $H_{\alpha\beta}$ are given by

$$H_{\alpha\beta} \overset{(\alpha\neq\beta)}{=} -\frac{2m_\alpha m_\beta}{15n_\alpha n_\beta (kT)^3}\int \left(\frac{m_\alpha\xi_\alpha^2}{2kT} - \frac{5}{2}\right)\xi_k^\alpha \mathcal{I}_{\alpha\beta}\left[\left(\frac{m_\beta\xi_\beta^2}{2kT} - \frac{5}{2}\right)\xi_k^\beta\right] d\mathbf{c}_\alpha, \tag{8.94}$$

$$\begin{aligned} H_{\alpha\alpha} = -\frac{2m_\alpha^2}{15n_\alpha^2 (kT)^3}\sum_{\beta=1}^n \int \left(\frac{m_\alpha\xi_\alpha^2}{2kT} - \frac{5}{2}\right)\xi_k^\alpha \Bigg\{\mathcal{I}_{\alpha\beta}\left[\left(\frac{m_\alpha\xi_\alpha^2}{2kT} - \frac{5}{2}\right)\xi_k^\alpha\right] \\ + \mathcal{I}_{\alpha\alpha}\left[\left(\frac{m_\alpha\xi_\alpha^2}{2kT} - \frac{5}{2}\right)\xi_k^\alpha\right]\Bigg\} d\mathbf{c}_\alpha. \end{aligned} \tag{8.95}$$

From the system of equations (8.88) and (8.93), one may obtain the constitutive equations for the heat flux vector q_i^α and for the diffusion flux J_i^α of constituent α as functions of the temperature gradient $\partial T/\partial x_i$ and of the generalized diffusion forces d_i^α.

First, one should note that due to the constraints

$$\sum_{\alpha=1}^{n} d_i^\alpha = 0 \qquad \text{and} \qquad \sum_{\alpha=1}^{n} J_i^\alpha = 0, \qquad \text{so that} \qquad \sum_{\alpha=1}^{n-1} J_i^\alpha = -J_i^n, \tag{8.96}$$

there exist only $(n-1)$ linearly independent equations (8.88) and $(n-1)$ linearly independent diffusion fluxes. Because there are only $(n-1)$ linearly independent equations that can be obtained from (8.88), the subtraction of the n-th from the α-th equation leads to a system of $n-1$ coupled equations, which reads

$$\begin{aligned} -p\left(\frac{d_i^\alpha}{\varrho_\alpha}-\frac{d_i^n}{\varrho_n}\right) &= -T\frac{\partial}{\partial x_i}\left(\frac{\mu_\alpha-\mu_n}{T}\right)-\frac{5}{2}\left(\frac{k}{m_\alpha}-\frac{k}{m_n}\right)\frac{\partial T}{\partial x_i} \\ &= \sum_{\beta=1}^{n-1}(A_{\alpha\beta}-A_{n\beta}-A_{\alpha n}+A_{nn})J_i^\beta-\sum_{\beta=1}^{n}\frac{m_\beta}{kT}(F_{\alpha\beta}-F_{n\beta})q_i^\beta, \end{aligned} \tag{8.97}$$

due to the constraint $(8.96)_3$. The determination of the second equality above is left as an exercise.

By using $(8.96)_3$, it follows from (8.93) a system of n coupled equations, namely,

$$\frac{5}{2}\frac{1}{T}\frac{\partial T}{\partial x_i}=\frac{5}{2}\sum_{\beta=1}^{n-1}\frac{m_\alpha}{kT}(F_{\beta\alpha}-F_{n\alpha})J_i^\beta-\sum_{\beta=1}^{n}H_{\alpha\beta}q_i^\beta. \tag{8.98}$$

The system of equations (8.97) and (8.98) can now be solved for the heat flux vectors q_i^β $(\beta=1,2,\dots,n)$ and for the diffusion fluxes J_i^β $(\beta=1,2,\dots,n-1)$. Indeed, as a first step, the multiplication of (8.98) by the inverse matrix $(H^{-1})_{\gamma\alpha}$ and the sum over all values of α leads to

$$q_i^\gamma=\frac{5}{2}\sum_{\alpha=1}^{n}(H^{-1})_{\gamma\alpha}\left(-\frac{1}{T}\frac{\partial T}{\partial x_i}\right)+\frac{5}{2}\sum_{\alpha=1}^{n}\sum_{\beta=1}^{n-1}(H^{-1})_{\gamma\alpha}\frac{m_\alpha}{kT}(F_{\beta\alpha}-F_{n\alpha})J_i^\beta. \tag{8.99}$$

Next, one obtains through the substitution of the heat flux vector (8.99) into (8.97) and by performing some rearrangements:

$$\begin{aligned} &-T\frac{\partial}{\partial x_i}\left(\frac{\mu_\alpha-\mu_n}{T}\right)+\frac{5}{2}\Bigg\{\sum_{\beta,\gamma=1}^{n}\frac{m_\beta}{kT}(F_{\alpha\beta}-F_{n\beta})(H^{-1})_{\beta\gamma} \\ &+T\left(\frac{k}{m_\alpha}-\frac{k}{m_n}\right)\Bigg\}\left(-\frac{1}{T}\frac{\partial T}{\partial x_i}\right)=\sum_{\beta=1}^{n-1}\Big\{(A_{\alpha\beta}-A_{n\beta}-A_{\alpha n}+A_{nn}) \\ &-\frac{5}{2}\sum_{\delta,\gamma=1}^{n}\frac{m_\delta}{kT}(F_{\alpha\delta}-F_{n\delta})(H^{-1})_{\delta\gamma}\frac{m_\gamma}{kT}(F_{\beta\gamma}-F_{n\gamma})\Big\}J_i^\beta. \end{aligned} \tag{8.100}$$

By solving the above equation for the diffusion flux, it follows Fick's law

$$J_i^\alpha = -\frac{D_\alpha}{T}\frac{\partial T}{\partial x_i} - T\sum_{\beta=1}^{n-1} D'_{\alpha\beta}\frac{\partial}{\partial x_i}\left(\frac{\mu_\beta-\mu_n}{T}\right). \tag{8.101}$$

The expression (8.101) is equal to the one proposed within the framework of the thermodynamic theory of irreversible processes (see (8.39)). The coefficients related to the diffusion $D'_{\alpha\beta}$ and thermal–diffusion effect D_α read

$$\begin{aligned}(D'^{-1})_{\alpha\beta} = \Bigg\{&(A_{\alpha\beta}-A_{n\beta}-A_{\alpha n}+A_{nn})\\ &-\frac{5}{2}\sum_{\delta,\gamma=1}^{n}\frac{m_\delta}{kT}(F_{\alpha\delta}-F_{n\delta})(H^{-1})_{\delta\gamma}\frac{m_\gamma}{kT}(F_{\beta\gamma}-F_{n\gamma})\Bigg\},\end{aligned} \tag{8.102}$$

$$D_\alpha = \frac{5}{2}\sum_{\beta=1}^{n-1} D'_{\alpha\beta}\left\{T\left(\frac{k}{m_\beta}-\frac{k}{m_n}\right)+\sum_{\delta,\gamma=1}^{n}\frac{m_\delta}{kT}(F_{\beta\delta}-F_{n\delta})(H^{-1})_{\delta\gamma}\right\}. \tag{8.103}$$

In a linearized theory, the heat flux vector of the mixture (8.22) becomes

$$q_i = \sum_{\alpha=1}^{n} q_i^\alpha + \sum_{\alpha=1}^{n-1}\frac{5}{2}\left(\frac{k}{m_\alpha}-\frac{k}{m_n}\right)TJ_i^\alpha. \tag{8.104}$$

Now, the insertion of (8.99) and (8.101) into the above expression leads to Fourier's law:

$$q_i = -\frac{\lambda'}{T}\frac{\partial T}{\partial x_i} - T\sum_{\alpha=1}^{n-1} D'_\alpha\frac{\partial}{\partial x_i}\left(\frac{\mu_\alpha-\mu_n}{T}\right), \tag{8.105}$$

and one recognizes also its equivalence with (8.38) of the thermodynamic theory of irreversible processes. The coefficients associated with the thermal conductivity λ' and diffusion–thermal effect D'_α are given by

$$\begin{aligned}\lambda' = \frac{5}{2}\sum_{\alpha,\beta=1}^{n}(H^{-1})_{\alpha\beta} + \frac{5}{2}\sum_{\beta=1}^{n-1}D_\beta\Bigg[&\left(\frac{k}{m_\beta}-\frac{k}{m_n}\right)T\\ &+\sum_{\alpha,\gamma=1}^{n}(H^{-1})_{\gamma\alpha}\frac{m_\alpha}{kT}(F_{\beta\alpha}-F_{n\alpha})\Bigg],\end{aligned} \tag{8.106}$$

$$D'_\alpha = \frac{5}{2}\sum_{\beta=1}^{n-1}D'_{\beta\alpha}\left[\left(\frac{k}{m_\beta}-\frac{k}{m_n}\right)T+\sum_{\delta,\gamma=1}^{n}\frac{m_\delta}{kT}(F_{\beta\delta}-F_{n\delta})(H^{-1})_{\gamma\delta}\right]. \tag{8.107}$$

The thermal conductivity coefficient of the mixture λ is defined as the ratio of the heat flux vector and the temperature gradient when there is no diffusion, i.e., when the diffusion fluxes vanish ($J_i^\alpha = 0$). In this case, one obtains from (8.99) and (8.104) that

$$\lambda = \frac{5}{2}\frac{1}{T}\sum_{\alpha,\beta=1}^{n}(H^{-1})_{\alpha\beta}. \tag{8.108}$$

By inspecting (8.89) and (8.94), one may infer that the matrices $A_{\alpha\beta}$ and $H_{\alpha\beta}$ are symmetric. Hence, the matrix associated with the diffusion coefficients (8.102) is a also a symmetric matrix, i.e.,

$$D'_{\alpha\beta} = D'_{\beta\alpha}. \tag{8.109}$$

The symmetry of $D'_{\alpha\beta}$ implies—by comparing (8.103) and (8.107)—that the diffusion–thermal coefficient is equal to the thermal–diffusion coefficient, namely,

$$D'_\alpha = D_\alpha. \tag{8.110}$$

The equations (8.109) and (8.110) indicate the validity of the Onsager reciprocity relations for mixtures of monatomic ideal gases within the framework of the kinetic theory of gases.

Exercises

8.14 Obtain (8.88) and (8.93).

8.15 By using $(8.51)_2$ and (8.62) show that

$$\begin{aligned} -p\left(\frac{d_i^\alpha}{\varrho_\alpha} - \frac{d_i^n}{\varrho_n}\right) &= -\frac{1}{\varrho_\alpha}\frac{\partial p_\alpha}{\partial x_i} + \frac{1}{\varrho_n}\frac{\partial p_n}{\partial x_i} \\ &= -T\frac{\partial}{\partial x_i}\left(\frac{\mu_\alpha - \mu_n}{T}\right) - \frac{5}{2}\left(\frac{k}{m_\alpha} - \frac{k}{m_n}\right)\frac{\partial T}{\partial x_i}. \end{aligned}$$

8.16 Show that the matrix $D'_{\alpha\beta}$ is symmetric.

8.10 Matrices as Functions of the Collision Integrals

The aim of this section is to express the matrices $A_{\alpha\beta}$, $F_{\alpha\beta}$, $H_{\alpha\beta}$ and $K_{\alpha\beta}$ in terms of the collision integrals

$$\varOmega_{\alpha\beta}^{(l,r)} = \int_0^\infty \int_0^\infty \left(1 - \cos^l \chi_{\beta\alpha}\right)\gamma_{\beta\alpha}^{2r+3} e^{-\gamma_{\beta\alpha}^2} b\, db\, d\gamma_{\beta\alpha}, \tag{8.111}$$

where $\chi_{\beta\alpha}$ denotes the scattering angle corresponding to a binary collision of the molecules α and β. Furthermore, $\gamma_{\beta\alpha}$ is the dimensionless relative velocity

$$\gamma_{\beta\alpha} = \sqrt{\frac{m_\alpha m_\beta}{2kT(m_\alpha + m_\beta)}}\, g_{\beta\alpha}. \tag{8.112}$$

The computation of the matrices proceeds in the same manner as the one adopted for the single gas (see Section 3.2.2). As an example, the calculation of the matrix $A_{\alpha\beta}$, defined by (8.89), will be performed. First, by using the definition of $\mathcal{I}_{\alpha\beta}$ given by (8.78) and by inserting the Maxwellian distribution function (8.53) into (8.89) leads to

$$A_{\alpha\beta} = -\frac{1}{3}\frac{1}{kT}\frac{(m_\alpha m_\beta)^{\frac{3}{2}}}{(2\pi kT)^3}\int \xi_k^\alpha e^{-\frac{m_\alpha \xi_\alpha^2}{2kT}} e^{-\frac{m_\beta \xi_\beta^2}{2kT}} (\xi_k'^\beta - \xi_k^\beta) g_{\beta\alpha} b\, db\, d\varepsilon\, d\mathbf{c}_\beta d\mathbf{c}_\alpha. \tag{8.113}$$

Next, the velocity variables are changed by introducing the relative velocity $g_i^{\beta\alpha}$ and the center of mass velocity $G_i^{\alpha\beta}$, defined by

$$g_i^{\beta\alpha} = \xi_i^\beta - \xi_i^\alpha, \qquad G_i^{\alpha\beta} = \frac{m_\alpha \xi_i^\alpha + m_\beta \xi_i^\beta}{m_\alpha + m_\beta}, \tag{8.114}$$

whose inverse transformations read

$$\xi_i^\beta = G_i^{\alpha\beta} + \frac{m_\alpha}{m_\alpha + m_\beta} g_i^{\beta\alpha}, \qquad \xi_i^\alpha = G_i^{\alpha\beta} - \frac{m_\beta}{m_\alpha + m_\beta} g_i^{\beta\alpha}. \tag{8.115}$$

By taking into account the above change of velocity variables and the relationship $d\mathbf{c}_\alpha d\mathbf{c}_\beta = d\mathbf{g}_{\beta\alpha} d\mathbf{G}_{\alpha\beta}$, (8.113) becomes

$$\begin{aligned} A_{\alpha\beta} = &-\frac{1}{3}\frac{1}{kT}\frac{(m_\alpha m_\beta)^{\frac{3}{2}}}{(2\pi kT)^3}\frac{m_\alpha}{m_\alpha + m_\beta}\int \left(G_k^{\alpha\beta} - \frac{m_\beta}{m_\alpha + m_\beta} g_k^{\beta\alpha}\right)\left(g_k'^{\beta\alpha} - g_k^{\beta\alpha}\right) \\ &\times \exp\left[-\frac{(m_\alpha + m_\beta)G_{\alpha\beta}^2}{2kT} - \frac{m_\alpha m_\beta g_{\beta\alpha}^2}{2kT(m_\alpha + m_\beta)}\right] g_{\beta\alpha} b\, db\, d\varepsilon\, d\mathbf{g}_{\beta\alpha} d\mathbf{G}_{\alpha\beta}, \end{aligned} \tag{8.116}$$

since $\mathbf{G}'_{\alpha\beta} = \mathbf{G}_{\alpha\beta}$ due to the momentum conservation law. Now, by considering $g_k'^{\beta\alpha} g_k^{\beta\alpha} = g_{\beta\alpha}^2 \cos\chi_{\beta\alpha}$, one can get through the integration over all values of $\mathbf{G}_{\alpha\beta}$ and over the spherical angles of $\mathbf{g}_{\beta\alpha}$ the expression

$$A_{\alpha\beta} \overset{(\alpha\neq\beta)}{=} -\frac{16}{3}\sqrt{\frac{2\pi kT}{m_\alpha m_\beta (m_\alpha + m_\beta)}}\, \Omega_{\alpha\beta}^{(1,1)}. \tag{8.117}$$

By following the same methodology, one can obtain the other expressions for the remaining matrices:

$$A_{\alpha\alpha} = \frac{16}{3}\sqrt{\frac{\pi kT}{m_\alpha^3}}\left[\sum_{\beta=1}^{n}\sqrt{\frac{2m_\beta}{m_\alpha+m_\beta}}\frac{n_\beta}{n_\alpha}\varOmega_{\alpha\beta}^{(1,1)} - \varOmega_{\alpha\alpha}^{(1,1)}\right], \tag{8.118}$$

$$F_{\alpha\beta} \overset{(\alpha\neq\beta)}{=} \frac{32}{15}\sqrt{\frac{2\pi m_\alpha kT}{m_\beta(m_\alpha+m_\beta)^3}}\left[\varOmega_{\alpha\beta}^{(1,2)} - \frac{5}{2}\varOmega_{\alpha\beta}^{(1,1)}\right], \tag{8.119}$$

$$\begin{aligned} F_{\alpha\alpha} &= -\frac{16}{15}\sqrt{\frac{\pi kT}{m_\alpha^3}}\left[\sum_{\beta=1}^{n}\sqrt{\frac{8m_\beta^3}{(m_\alpha+m_\beta)^3}}\frac{n_\beta}{n_\alpha}\left(\varOmega_{\alpha\beta}^{(1,2)} - \frac{5}{2}\varOmega_{\alpha\beta}^{(1,1)}\right)\right. \\ &- \left.\left(\varOmega_{\alpha\alpha}^{(1,2)} - \frac{5}{2}\varOmega_{\alpha\alpha}^{(1,1)}\right)\right], \end{aligned} \tag{8.120}$$

$$H_{\alpha\beta} \overset{(\alpha\neq\beta)}{=} -\frac{32}{15}\sqrt{\frac{2\pi(m_\alpha m_\beta)^3}{(kT)^3(m_\alpha+m_\beta)^5}}\left[\frac{55}{4}\varOmega_{\alpha\beta}^{(1,1)} - 5\varOmega_{\alpha\beta}^{(1,2)} + \varOmega_{\alpha\beta}^{(1,3)} - 2\varOmega_{\alpha\beta}^{(2,2)}\right], \tag{8.121}$$

$$\begin{aligned} H_{\alpha\alpha} &= \frac{32}{15}\sqrt{\frac{2\pi}{(kT)^3}}\left\{\sum_{\beta=1}^{n}\sqrt{\frac{m_\alpha^5 m_\beta}{(m_\alpha+m_\beta)^5}}\frac{n_\beta}{n_\alpha}\left[\left(\frac{25}{4}\frac{m_\beta^2}{m_\alpha^2} + \frac{15}{2}\right)\varOmega_{\alpha\beta}^{(1,1)}\right.\right. \\ &- \left. 5\frac{m_\beta^2}{m_\alpha^2}\varOmega_{\alpha\beta}^{(1,2)} + \frac{m_\beta^2}{m_\alpha^2}\varOmega_{\alpha\beta}^{(1,3)} + 2\frac{m_\beta}{m_\alpha}\varOmega_{\alpha\beta}^{(2,2)}\right] \\ &- \left.\frac{\sqrt{2m_\alpha}}{8}\left(\frac{55}{4}\varOmega_{\alpha\alpha}^{(1,1)} - 5\varOmega_{\alpha\alpha}^{(1,2)} + \varOmega_{\alpha\alpha}^{(1,3)} - 2\varOmega_{\alpha\alpha}^{(2,2)}\right)\right\}, \end{aligned} \tag{8.122}$$

$$K_{\alpha\beta} \overset{(\alpha\neq\beta)}{=} -\frac{16}{15}\sqrt{\frac{2\pi m_\alpha m_\beta}{kT(m_\alpha+m_\beta)^3}}\left[10\varOmega_{\alpha\beta}^{(1,1)} - 3\varOmega_{\alpha\beta}^{(2,2)}\right], \tag{8.123}$$

$$\begin{aligned} K_{\alpha\alpha} &= \frac{16}{15}\sqrt{\frac{2\pi}{kT}}\left\{\sum_{\beta=1}^{n}\sqrt{\frac{m_\alpha m_\beta}{(m_\alpha+m_\beta)^3}}\frac{n_\beta}{n_\alpha}\left[3\frac{m_\beta}{m_\alpha}\varOmega_{\alpha\beta}^{(2,2)} + 10\varOmega_{\alpha\beta}^{(1,1)}\right]\right. \\ &+ \left.\frac{1}{4}\sqrt{\frac{2}{m_\alpha}}\left(3\varOmega_{\alpha\alpha}^{(2,2)} - 10\varOmega_{\alpha\alpha}^{(1,1)}\right)\right\}. \end{aligned} \tag{8.124}$$

For a complete evaluation of the above matrices, one has to know the values of the collision integrals $\varOmega_{\alpha\beta}^{(l,r)}$, which depend on the potentials of molecular interaction. For the hard-sphere potential, the collision integrals read

$$\varOmega_{\alpha\beta}^{(1,1)} = \frac{\mathsf{d}_{\alpha\beta}^2}{2}, \qquad \varOmega_{\alpha\beta}^{(1,2)} = \frac{3\mathsf{d}_{\alpha\beta}^2}{2}, \qquad \varOmega_{\alpha\beta}^{(1,3)} = 6\mathsf{d}_{\alpha\beta}^2, \qquad \varOmega_{\alpha\beta}^{(2,2)} = \mathsf{d}_{\alpha\beta}^2, \tag{8.125}$$

where $\mathsf{d}_{\alpha\beta} = (\mathsf{d}_\alpha + \mathsf{d}_\beta)/2$ is the mean molecular diameter of the spheres. For the centers of repulsion potential $\varPhi(r_{\alpha\beta}) = \kappa_{\alpha\beta}/(\nu-1)r_{\alpha\beta}^{\nu-1}$, they read

$$\Omega^{(1,1)}_{\alpha\beta} = \left(\frac{\kappa_{\alpha\beta}}{2kT}\right)^{\frac{2}{\nu-1}} \frac{A_1(\nu)}{2}\,\Gamma\left(\frac{3\nu-5}{\nu-1}\right), \tag{8.126}$$

$$\Omega^{(1,2)}_{\alpha\beta} = \left(\frac{\kappa_{\alpha\beta}}{2kT}\right)^{\frac{2}{\nu-1}} \frac{A_1(\nu)}{2}\,\Gamma\left(\frac{4\nu-6}{\nu-1}\right), \tag{8.127}$$

$$\Omega^{(1,3)}_{\alpha\beta} = \left(\frac{\kappa_{\alpha\beta}}{2kT}\right)^{\frac{2}{\nu-1}} \frac{A_1(\nu)}{2}\,\Gamma\left(\frac{5\nu-7}{\nu-1}\right), \tag{8.128}$$

$$\Omega^{(2,2)}_{\alpha\beta} = \left(\frac{\kappa_{\alpha\beta}}{2kT}\right)^{\frac{2}{\nu-1}} \frac{A_2(\nu)}{2}\,\Gamma\left(\frac{4\nu-6}{\nu-1}\right). \tag{8.129}$$

Exercises

8.17 Obtain the expressions (8.119) and (8.123).

8.18 Show that the collision integrals for the hard-sphere potential and for the centers of repulsion potential reduce to (8.125) and (8.126)–(8.129), respectively.

8.11 Binary Mixtures

In this section, the transport coefficients of a binary mixture will be analyzed. For an easy comparison of the expressions for the transport coefficients, the notation adopted here will follow the one used in the book by Chapman and Cowling.

8.11.1 Coefficients of Shear Viscosity and Thermal Conductivity

For a binary mixture, the shear viscosity coefficient $(8.87)_2$ reduces to

$$\mu = \frac{K_{11}+K_{22}-2K_{12}}{K_{11}K_{22}-K_{12}^2}. \tag{8.130}$$

By adopting the same symbols as those of Chapman and Cowling[2], the shear viscosity—thanks to (8.123) and (8.124)—can be written as

$$\mu = \frac{\mathsf{x}_1^2 R_1 + \mathsf{x}_2^2 R_2 + \mathsf{x}_1\mathsf{x}_2 R_{12}'}{\mathsf{x}_1^2 R_1/\mu_1 + \mathsf{x}_2^2 R_2/\mu_2 + \mathsf{x}_1\mathsf{x}_2 R_{12}}. \tag{8.131}$$

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[2] The expressions for some symbols adopted in this and in the next section differ from the book by Chapman and Cowling, since their collision integral $\Omega_{12}^{(l,r)}$ is defined with the factor $\sqrt{2\pi kT(m_1+m_2)/m_1m_2}$.

where $\mathsf{x}_1 = n_1/n$ and $\mathsf{x}_2 = 1 - \mathsf{x}_1 = n_2/n$ are molar fractions. Moreover, it introduced the symbols

$$\mu_\alpha = \frac{5}{16}\frac{1}{\Omega_{\alpha\alpha}^{(2,2)}}\sqrt{\frac{m_\alpha kT}{\pi}}, \quad R_1 = \frac{m_1}{m_2}A + \frac{2}{3}, \quad R_2 = \frac{m_2}{m_1}A + \frac{2}{3}, \tag{8.132}$$

$$R_{12} = \frac{E}{2\mu_1\mu_2} + \frac{4A}{3E}\frac{(m_1+m_2)^2}{m_1m_2}, \quad R_{12}' = \frac{E}{2\mu_1} + \frac{E}{2\mu_2} + \frac{4}{3} - 2A, \tag{8.133}$$

$$A = \frac{\Omega_{12}^{(2,2)}}{5\Omega_{12}^{(1,1)}}, \quad E = \sqrt{\frac{2kT(m_1+m_2)^3}{\pi m_1 m_2}}\frac{1}{16\Omega_{12}^{(1,1)}}. \tag{8.134}$$

Note that μ_α is the shear viscosity of the single constituent α.

The thermal conductivity coefficient for a binary mixture is obtained from (8.108) and reads

$$\lambda = \frac{5}{2}\frac{1}{T}\frac{H_{11} + H_{22} - 2H_{12}}{H_{11}H_{22} - H_{12}^2}, \tag{8.135}$$

or on the basis of (8.121) and (8.122), one may write

$$\lambda = \frac{\mathsf{x}_1^2\lambda_1 Q_1 + \mathsf{x}_2^2\lambda_2 Q_2 + \mathsf{x}_1\mathsf{x}_2 Q_{12}'}{\mathsf{x}_1^2 Q_1 + \mathsf{x}_2^2 Q_2 + \mathsf{x}_1\mathsf{x}_2 Q_{12}}. \tag{8.136}$$

In this case, the above abbreviations are given by

$$\lambda_\alpha = \frac{15}{4}\frac{k}{m_\alpha}\mu_\alpha, \qquad P_\alpha = \frac{15}{4}\frac{kE}{\lambda_\alpha}, \qquad B = \frac{5\Omega_{12}^{(1,2)} - \Omega_{12}^{(1,3)}}{5\Omega_{12}^{(1,1)}}, \tag{8.137}$$

$$Q_1 = \frac{P_1}{m_1+m_2}\left[m_1^2(5-4B) + 8Am_1m_2 + 6m_2^2\right], \tag{8.138}$$

$$Q_2 = \frac{P_2}{m_1+m_2}\left[m_2^2(5-4B) + 8Am_1m_2 + 6m_1^)\right], \tag{8.139}$$

$$Q_{12} = 3(m_1-m_2)^2(5-4B) + 4Am_1m_2(11-4B) + 2P_1P_2, \tag{8.140}$$

$$Q_{12}' = \frac{15}{2}kE\left[P_1 + P_2 + \frac{m_1m_2}{m_1+m_2}(11-4B-8A)\right], \tag{8.141}$$

where λ_α is the thermal conductivity of the single constituent α.

The expressions for the coefficients of shear viscosity (8.131) and thermal conductivity (8.136) refer to their first approximations in Sonine polynomials.

Exercise

8.19 Obtain the expression (8.131) for the shear viscosity coefficient.

8.11.2 Coefficients of Diffusion and Thermal–Diffusion Ratio

For the determination of the coefficients associated with the diffusion and cross effects, one writes Fick's law for a binary mixture as

$$J_i^1 = -\frac{n^2 m_1 m_2}{\varrho} D_{12}\left[d_i^1 + \frac{k_T}{T}\frac{\partial T}{\partial x_i}\right], \qquad \text{with} \qquad J_i^2 = -J_i^1. \tag{8.142}$$

where D_{12} denotes the diffusion coefficient, while k_T is the thermal–diffusion ratio. Furthermore, according to (8.62), the generalized diffusion force for a binary mixture becomes

$$d_i^1 = \frac{\partial \mathsf{x}_1}{\partial x_i} + \left(\mathsf{x}_1 - \frac{\varrho_1}{\varrho}\right)\frac{\partial \ln p}{\partial x_i}, \qquad \text{with} \qquad d_i^2 = -d_i^1. \tag{8.143}$$

From (8.142) and (8.143), one may infer that the diffusion flux—which is the responsible of the mass transfer—is due to: **(a)** a flux associated with the gradient of the molar fraction ($\partial \mathsf{x}_1/\partial x_i$) that tends to reduce the non-homogeneity of the mixture when the molar fraction is non-uniform; **(b)** a flux due to the pressure gradient ($\partial \ln p/\partial x_i$) where the heavy molecules tend to diffuse to places with large pressures like in the case of centrifuges and **(c)** a flux due to a temperature gradient ($\partial T/\partial x_i$), which is related with the thermal–diffusion processes.

From the system of equations (8.97) and (8.98), one obtains the following expressions for the diffusion coefficient D_{12} and thermal–diffusion ratio k_T in terms of the matrices $A_{\alpha\beta}$, $F_{\alpha\beta}$ and $H_{\alpha\beta}$:

$$D_{12} = \frac{p\varrho^2}{m_1^2 m_2^2 n^2 n_1 n_2}\left\{(A_{11} - 2A_{12} + A_{22}) - \frac{5}{2}\left[\left(\frac{m_1}{kT}\right)^2 \frac{(F_{11}-F_{21})^2 H_{22}}{H_{11}H_{22} - H_{12}^2}\right.\right.$$
$$\left.\left. + \left(\frac{m_2}{kT}\right)^2 \frac{(F_{12}-F_{22})^2 H_{11}}{H_{11}H_{22} - H_{12}^2} - 2\frac{m_1 m_2}{(kT)^2}\frac{(F_{12}-F_{22})(F_{11}-F_{21})H_{12}}{H_{11}H_{22} - H_{12}^2}\right]\right\}^{-1}, \tag{8.144}$$

$$k_T = \frac{5\varrho_1\varrho_2}{2kTp\varrho}\left[\frac{m_1(F_{11}-F_{21})(H_{22}-H_{12})}{H_{11}H_{22} - H_{12}^2} + \frac{m_2(F_{12}-F_{22})(H_{11}-H_{12})}{H_{11}H_{22} - H_{12}^2}\right]. \tag{8.145}$$

By considering the representations of the matrices $A_{\alpha\beta}$, $F_{\alpha\beta}$ and $H_{\alpha\beta}$ given by (8.118)—(8.122), the diffusion coefficient and the thermal–diffusion ratio may be written as

$$D_{12} = \frac{3E}{2(m_1+m_2)n}\frac{1}{1-\varDelta}, \tag{8.146}$$

$$k_T = \frac{5C\mathsf{x}_1\mathsf{x}_2}{\mathsf{x}_1^2 Q_1 + \mathsf{x}_2^2 Q_2 + \mathsf{x}_1\mathsf{x}_2 Q_{12}}(\mathsf{x}_1 S_1 - \mathsf{x}_2 S_2), \tag{8.147}$$

where the following abbreviations were introduced

$$\Delta = \frac{5C^2}{(m_1+m_2)} \frac{\mathsf{x}_1^2 m_1^2 P_1 + \mathsf{x}_2^2 m_2^2 P_2 + \mathsf{x}_1\mathsf{x}_2 P_{12}}{\mathsf{x}_1^2 Q_1 + \mathsf{x}_2^2 Q_2 + \mathsf{x}_1\mathsf{x}_2 Q_{12}}, \tag{8.148}$$

$$C = \frac{2}{5}\frac{\Omega_{12}^{(1,2)}}{\Omega_{12}^{(1,1)}} - 1, \quad P_{12} = \left[3(m_1-m_2)^2 + 4m_1m_2A\right](m_1+m_2), \tag{8.149}$$

$$S_1 = m_1P_1 - m_2[3(m_2-m_1) + 4m_1A], \tag{8.150}$$

$$S_2 = m_2P_2 - m_1[3(m_1-m_2) + 4m_2A]. \tag{8.151}$$

The expression (8.147) represents the first approximation in Sonine polynomials of the thermal–diffusion ratio, while (8.146) stands for the second approximation of the diffusion coefficient. The first approximation of the diffusion coefficient is obtained by considering $\Delta = 0$, so that it reduces to

$$D_{12} = \frac{3E}{2(m_1+m_2)n}. \tag{8.152}$$

The first and second approximations to the self-diffusion coefficient may be obtained by taking $m_1 = m_2 = m$, $\mathsf{x}_1 = 1$ and $\mathsf{x}_2 = 0$ into (8.146), yielding

$$D = \frac{3}{16n}\sqrt{\frac{kT}{m\pi}}\frac{1}{\Omega^{(1,1)}}, \qquad D = \frac{3}{16n}\sqrt{\frac{kT}{m\pi}}\frac{1}{\Omega^{(1,1)}}\frac{1}{1-\frac{5C^2}{11+8A-4B}}, \tag{8.153}$$

respectively.

Exercise

8.20 Obtain (8.147) for the thermal–diffusion ratio.

8.11.3 Coefficients for Some Intermolecular Potentials

For hard-sphere potentials, the coefficients A, B, C and E reduce to

$$A = \frac{2}{5}, \qquad B = \frac{3}{5}, \qquad C = \frac{1}{5}, \qquad E = \sqrt{\frac{2kT(m_1+m_2)^3}{\pi m_1 m_2}}\frac{1}{8\mathsf{d}_{12}^2}, \tag{8.154}$$

by taking into account the values of the collision integrals given by (8.125).

The transport coefficients for argon–neon gas mixture of hard-spherical particles are plotted in Figures 8.1 and 8.2 as functions of the temperature

T and of the molar fraction of the argon gas x_1. The values adopted for the diameters of the argon and neon gas were $\mathsf{d}_1 = 3.00 \times 10^{-10}$ m and $\mathsf{d}_2 = 2.11 \times 10^{-10}$ m, respectively.

In the same way as a single gas of hard-spherical particles, the coefficients of shear viscosity and thermal conductivity of the mixture depend on the square root of the temperature. Furthermore, both coefficients decrease by increasing the molar fraction, since the shear viscosity and the thermal conductivity for the neon gas is larger than the corresponding ones for the argon gas. These behaviors can be observed in Figure 8.1.

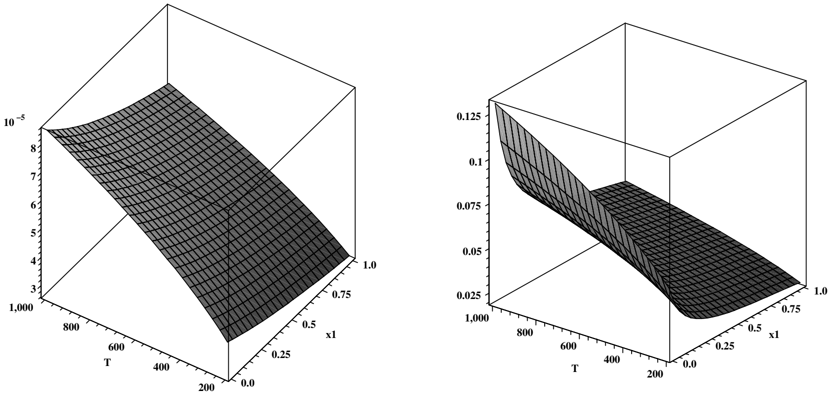

Fig. 8.1 Transport coefficients versus temperature T and molar fraction x_1 for argon-neon gas mixture. Left frame: shear viscosity μ; right frame: thermal conductivity λ.

For hard-sphere potentials, the thermal–diffusion ratio does not depend on the temperature so that in the left-frame of Figure 8.2 it is plotted only as a function of the molar fraction x_1. One may infer from this figure that the thermal–diffusion ratio vanishes when $\mathsf{x}_1 = 0$ and $\mathsf{x}_1 = 1$, i.e., in the case of a single gas. Furthermore, for this case, the thermal–diffusion ratio is a positive quantity indicating that the heavier molecules tend to go toward the cooler region, whereas the lighter molecules into the warmer region.

The diffusion coefficient for the hard-sphere potential is proportional to $\sqrt{T}/n$. In the right-frame of Figure 8.2 the behavior of the diffusion coefficient as function of the temperature and of the molar fraction for one mole of gas mixture where $n = 2.6 \times 10^{25}$ molecules/m^3 is shown. One may observe from this figure that the diffusion coefficient increases by increasing the molar fraction, due to the fact that the self-diffusion coefficient for the argon gas is larger than the one for the neon gas.

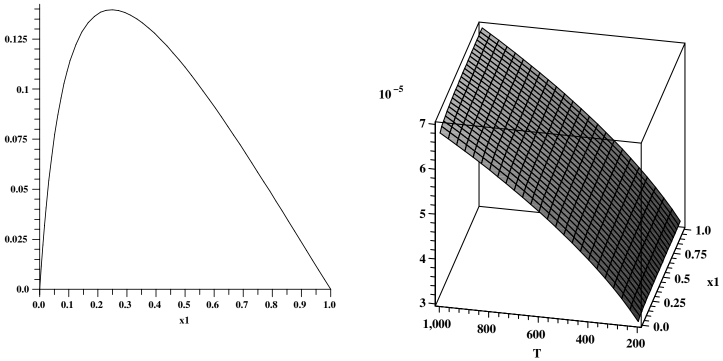

Fig. 8.2 Transport coefficients for argon–neon gas mixture. Left frame: thermal–diffusion ratio k_T versus molar fraction x_1; right frame: diffusion coefficient D_{12} versus temperature T and molar fraction x_1.

For the centers of repulsion potential, the coefficients A, B, C and E read

$$A = \frac{A_2(\nu)(3\nu-5)}{5A_1(\nu)(\nu-1)}, \qquad B = \frac{(3\nu-5)(\nu+1)}{5(\nu-1)^2}, \qquad C = \frac{\nu-5}{5(\nu-1)}, \tag{8.155}$$

$$E = \sqrt{\frac{2kT(m_1+m_2)^3}{\pi m_1 m_2}}\left(\frac{2kT}{\kappa_{12}}\right)^{\frac{2}{\nu-1}} \frac{1}{8A_1(\nu)\Gamma(\frac{3\nu-5}{\nu-1})}. \tag{8.156}$$

It is worth to notice that for Maxwellian molecules $\nu = 5$ so that $C = 0$. In this case, one may infer from (8.146) and (8.147) that the diffusion coefficient reduces to its first approximation in Sonine polynomials, and the thermal–diffusion ratio vanishes.

Exercise

8.21 Obtain the coefficients (8.154) and draw the curves of Figures 8.1 and 8.2.

8.12 Appendix

One important thermodynamic potential is the Gibbs function,[3] because during a natural process at constant pressure p and at constant temperature T,

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[3] Also known in the literature as Gibbs free energy or Gibbs energy.

it decreases and attains its minimum at equilibrium. The Gibbs function is defined by $G = E - TS + pV$, where E is the internal energy, S the entropy and V the volume of the thermodynamic system.

Let $\mathcal{M}_\alpha$ denotes the total mass of constituent α in a fluid mixture of n constituents. The Gibbs function of the mixture is a function of the pressure p and temperature T of the mixture, and of all masses of the constituents, i.e., $G = G(p, T, \mathcal{M}_1, \mathcal{M}_2, \dots, \mathcal{M}_n)$. The differential of the Gibbs function reads

$$dG = \frac{\partial G}{\partial p} dp + \frac{\partial G}{\partial T} dT + \sum_{\alpha=1}^{n} \frac{\partial G}{\partial \mathcal{M}_\alpha} d\mathcal{M}_\alpha = V dp - S dT + \sum_{\alpha=1}^{n} \mu_\alpha d\mathcal{M}_\alpha, \quad (8.157)$$

where μ_α denotes the chemical potential of the constituent α.

The Gibbs function is an extensive quantity such that if one increases the masses of all constituents in the same proportion, the same will happen with the Gibbs function. Mathematically, one may say that the Gibbs function is a linear homogeneous function of the masses of the constituents and written as

$$G(T, p, \lambda\mathcal{M}_1, \lambda\mathcal{M}_2, \dots, \lambda\mathcal{M}_n) = \lambda G(T, p, \mathcal{M}_1, \mathcal{M}_2, \dots, \mathcal{M}_n), \quad (8.158)$$

where λ is a positive parameter. The differentiation of the above equation with respect to the parameter λ and by considering afterwards $\lambda = 1$ leads to

$$G(T, p, \mathcal{M}_1, \mathcal{M}_2, \dots, \mathcal{M}_n) = \sum_{\alpha=1}^{n} \frac{\partial G}{\partial \mathcal{M}_\alpha} \mathcal{M}_\alpha = \sum_{\alpha=1}^{n} \mu_\alpha \mathcal{M}_\alpha. \quad (8.159)$$

One may write (8.157) and (8.159) with regard to specific quantities defined in terms of the total mass of all constituents $\mathcal{M} = \sum_{\alpha=1}^{n} \mathcal{M}_\alpha$, namely,

$$g = \frac{G}{\mathcal{M}}, \qquad s = \frac{G}{\mathcal{M}}, \qquad \varepsilon = \frac{E}{\mathcal{M}}, \qquad \varrho = \frac{\mathcal{M}}{V}, \qquad \mathsf{c}_\alpha = \frac{\mathcal{M}_\alpha}{\mathcal{M}} = \frac{\varrho_\alpha}{\varrho}, \quad (8.160)$$

where c_α denotes the mass concentration of constituent α which fulfills the constraint $\sum_{\alpha=1}^{n} \mathsf{c}_\alpha = 1$. These equations read

$$dg = \frac{dp}{\varrho} - s dT + \sum_{\alpha=1}^{n} \mu_\alpha d\mathsf{c}_\alpha, \qquad g = \varepsilon - Ts + \frac{p}{\varrho} = \sum_{\alpha=1}^{n} \mu_\alpha \mathsf{c}_\alpha. \quad (8.161)$$

In terms of the specific entropy, $(8.161)_1$ becomes

$$ds = \frac{1}{T}\left(d\varepsilon - \frac{p}{\varrho^2} d\varrho - \sum_{\alpha=1}^{n} \mu_\alpha d\mathsf{c}_\alpha\right) = \frac{1}{T}\left(d\varepsilon - \frac{p}{\varrho^2} d\varrho - \sum_{\alpha=1}^{n-1} (\mu_\alpha - \mu_n) d\mathsf{c}_\alpha\right), \quad (8.162)$$

which represents the Gibbs equation. The last equality of the above equation follows from the constraint $\sum_{\alpha=1}^{n} d\mathsf{c}_\alpha = 0$, since

$$\sum_{\alpha=1}^{n} \mu_\alpha d\mathsf{c}_\alpha = \sum_{\alpha=1}^{n-1} \mu_\alpha d\mathsf{c}_\alpha + \mu_n d\mathsf{c}_n = \sum_{\alpha=1}^{n-1} \mu_\alpha d\mathsf{c}_\alpha - \mu_n \sum_{\alpha=1}^{n-1} d\mathsf{c}_\alpha. \tag{8.163}$$

Chapter 9
Chemically Reacting Gas Mixtures

9.1 Thermodynamics of Chemically Reacting Systems

9.1.1 Extent of Reaction and Affinity

Consider the following independent reactions in the gaseous phase:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3, \qquad O_2 + 2H_2 \rightleftharpoons 2H_2O, \qquad H_2 + Cl \rightleftharpoons HCl + H.$$

The above expressions indicate the amounts of the elements which correspond to the reagents and products of the reactions. For example, in the formation of ammonia, 1 mole of N_2 with 3 moles of H_2 results in 2 moles of NH_3. From now on, only a single uncoupled chemical reaction will be analyzed.

In general, a chemical reaction is represented by the stoichiometric relationship $\sum_{\alpha=1}^{n} \nu_\alpha A_\alpha = 0$, where A_α is the chemical symbol of the element α and ν_α its stoichiometric coefficient. The stoichiometric coefficient is considered negative for the reagents and positive for the products of a chemical reaction.

For each reaction there exists a parameter which specifies the changes of the number of the molecules N_α of each constituent, namely, the extent of reaction ξ, which is also known as the degree of advancement of a reaction. For a general chemical reaction of n constituents, one has

$$\frac{dN_1}{\nu_1} = \frac{dN_2}{\nu_2} = \ldots = \frac{dN_n}{\nu_n} = V d\xi, \qquad \text{or} \qquad dN_\alpha = \nu_\alpha V d\xi, \tag{9.1}$$

where V is the volume occupied by the mixture. The multiplication of $(9.1)_2$ by the mass of a molecule m_α leads to

$$d\mathcal{M}_\alpha = d(m_\alpha N_\alpha) = m_\alpha \nu_\alpha V d\xi, \qquad \text{so that} \qquad d\mathcal{M} = \sum_{\alpha=1}^{n} m_\alpha \nu_\alpha V d\xi, \tag{9.2}$$

where $\mathcal{M} = \sum_{\alpha=1}^{n} \mathcal{M}_\alpha$ is the total mass of the mixture. Because the total mass of a closed system is constant, one obtains the mass conservation law for a chemical reaction:

$$\sum_{\alpha=1}^{n} m_\alpha \nu_\alpha = 0. \tag{9.3}$$

The insertion of $(9.2)_1$ into the differential expression of the Gibbs function (8.157) leads to

$$dG = V dp - S dT + \sum_{\alpha=1}^{n} m_\alpha \nu_\alpha \mu_\alpha V d\xi. \tag{9.4}$$

For natural processes at constant pressure and at constant temperature, the Gibbs function decreases and attains its minimum at equilibrium. Hence, it follows from the above equation that the chemical equilibrium is characterized by the relationship

$$\sum_{\alpha=1}^{n} m_\alpha \nu_\alpha \mu_\alpha^{\mathrm{eq}} = 0. \tag{9.5}$$

From now on, the index "eq" will denote the equilibrium value of a quantity.

For chemically reacting systems, it is necessary to include into the balance of mass density of each constituent a contribution which takes into account the mass production of the constituent due to the chemical reaction. This contribution comes by observing that one may write $(9.2)_1$ as

$$d\mathsf{c}_\alpha = d\left(\frac{\mathcal{M}_\alpha}{\mathcal{M}}\right) = \frac{m_\alpha \nu_\alpha V}{\mathcal{M}} d\xi = \frac{m_\alpha \nu_\alpha}{\varrho} d\xi. \tag{9.6}$$

From the above expression, one concludes that the balance equation $(8.34)_1$ for the concentration c_α of the constituent α should read

$$\varrho \mathcal{D} \mathsf{c}_\alpha + \frac{\partial J_i^\alpha}{\partial x_i} = m_\alpha \nu_\alpha \frac{d\xi}{dt} \equiv \tau_\alpha. \tag{9.7}$$

The rate of change of the extent of reaction $d\xi/dt$ is called reaction velocity.

By summing the mass production density τ_α over all constituents, it follows the conservation of mixture's mass density $\sum_{\alpha=1}^{n} \tau_\alpha = 0$, which is a consequence of the mass conservation law (9.3).

The influence of a chemical reaction in the entropy production density is now analyzed. For this end, let us consider an Eulerian fluid mixture which is characterized by the constitutive equations $J_i^\alpha|_E = 0$, $p_{ij}|_E = p\,\delta_{ij}$ and $q_i|_E = 0$. Hence, by following the same methodology of Section 8.3, one obtains from (8.33) and (9.7):

$$\varrho \mathcal{D} s = -\sum_{\alpha=1}^{n} \frac{m_\alpha \nu_\alpha \mu_\alpha}{T} \frac{d\xi}{dt} = \varsigma \geqslant 0. \tag{9.8}$$

The affinity $\mathcal{A}$ of a chemical reaction is defined by

$$\mathcal{A} = -\sum_{\alpha=1}^{n} m_\alpha \nu_\alpha \mu_\alpha \qquad \text{such that} \qquad \mathcal{A}|_E = 0, \tag{9.9}$$

which is a consequence of (9.3). By taking into account the definition of the affinity, the entropy production density due to the chemical reactions can be written as

$$\varsigma = \frac{\mathcal{A}}{T}\frac{d\xi}{dt} \geqslant 0. \tag{9.10}$$

From the above inequality, one concludes that the affinity and the reaction velocity always have the same sign. The signs of the reaction velocity and of the affinity are better understood when one considers a typical chemical reaction, for example, the reaction $H_2 + Cl \rightleftharpoons HCl + H$. The sign of the reaction velocity indicates the direction of the reaction, so that **(a)** if the net conversion of the reaction is from $H_2 + Cl$ to $HCl + H$, the reaction velocity and the affinity are positive and the reaction proceeds to the right $H_2 + Cl \rightarrow HCl + H$ and **(b)** if the net conversion is from $HCl + H$ to $H_2 + Cl$, the reaction velocity and the affinity are negative and the reaction proceeds to the left $H_2 + Cl \leftarrow HCl + H$.

Exercise

9.1 Obtain the inequality (9.8).

9.1.2 Chemical Potentials

The chemical potentials for gases whose molecules have internal variables associated with their energy states differ from the ones for monatomic gases, which was obtained in the last chapter and given by $(8.51)_2$.

Although in this chapter the analysis of the chemical reactions will be restricted to gases where the internal energy states of the molecules associated with the rotational, vibrational, electronic and nuclei states will not be taken into account, the chemical bonds of the molecules must be considered in order to treat the chemical reactions properly.

The chemical compounds are formed through the combination of two or more atoms so that a stable compound has a lower total energy when compared with the one of the separated atoms, and in order to separate the atoms from a molecule, an external energy must be supplied. Hence, to take into account the chemical binding energy, one writes the internal energy of the constituent α of the gaseous chemically reacting mixture as

$$U_\alpha = \frac{3}{2}N_\alpha kT + N_\alpha \epsilon_\alpha. \tag{9.11}$$

The energy ϵ_α refers to the binding energy of a molecule of the constituent α and it is supposed that all constituents are at the same temperature T, which is the temperature of the mixture.

In analyzing chemical reactions, one should also take care the exact value of the constant $\mathtt{b}_\alpha$, which appears in the expression for the entropy $(8.52)_2$. Indeed, on the basis of the statistical mechanics[1], the value of this constant is given by $\mathtt{b}_\alpha = (h/m_\alpha)^3/e$, where h denotes Planck's constant and e is the base of the natural logarithm. Hence, the expression for the entropy should read

$$S_\alpha = N_\alpha k\left[\frac{3}{2}\ln T - \ln n_\alpha + \frac{5}{2} + \frac{3}{2}\ln\left(\frac{2\pi k m_\alpha}{h^2}\right)\right], \tag{9.12}$$

which is known as the Sackur–Tetrode equation.[2]

The determination of the chemical potential of constituent α proceeds as follows. First, one builds the Gibbs function $G_\alpha = U_\alpha - TS_\alpha + p_\alpha V$ of constituent α, by using (9.11), (9.12) and the thermal equation of state $p_\alpha V = N_\alpha kT$, yielding

$$G_\alpha = N_\alpha kT\left[\frac{\epsilon_\alpha}{kT} + \ln n_\alpha - \frac{3}{2}\ln T - \frac{3}{2}\ln\left(\frac{2\pi k m_\alpha}{h^2}\right)\right]. \tag{9.13}$$

Next, from the definition of the Gibbs function of the mixture and the relationship (8.159), one has $G = \sum_{\alpha=1}^n G_\alpha = \sum_{\alpha=1}^n \mu_\alpha \mathcal{M}_\alpha$ such that

$$\mu_\alpha = \frac{kT}{m_\alpha}\left[\frac{\epsilon_\alpha}{kT} + \ln n_\alpha - \frac{3}{2}\ln T - \frac{3}{2}\ln\left(\frac{2\pi k m_\alpha}{h^2}\right)\right]. \tag{9.14}$$

Exercise

9.2 Build the Gibbs function G_α and obtain the chemical potential (9.14).

9.1.3 The Law of Mass Action

The reactions that will be analyzed in this chapter refer to the bimolecular reactions $A_1 + A_2 \rightleftharpoons A_3 + A_4$ or the symmetric reactions $A + A \rightleftharpoons B + B$. Examples of bimolecular reactions are: $H_2 + Cl \rightleftharpoons HCl + H$; $H + D_2 \rightleftharpoons HD + D$; $O + N_2 \rightleftharpoons NO + N$; $OH + H_2 \rightleftharpoons H_2O + H$, etc. The symmetric reactions

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[1] See e.g., D.A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976).

[2] Otto Sackur (1880–1914) German physical chemist. Hugo Martin Tetrode (1895–1931) Dutch scientist.

can be considered as a first stage of the Lindemann–Hinshelwood mechanism[3] for isomeric reactions, i.e., those where the constituents are isomers.

Consider the generic bimolecular reaction $\nu_1 A_1 + \nu_2 A_2 \rightleftharpoons \nu_3 A_3 + \nu_4 A_4$ where the stoichiometric coefficients are $\nu_1 = \nu_2 = -\nu_3 = -\nu_4 = -1$. For this kind of reaction, the chemical equilibrium condition (9.5) together with the expression for the chemical potential (9.14) leads to

$$\frac{n_3^{\text{eq}} n_4^{\text{eq}}}{n_1^{\text{eq}} n_2^{\text{eq}}} = \left(\frac{m_3 m_4}{m_1 m_2}\right)^{\frac{3}{2}} e^{-Q/kT} \equiv K(T). \tag{9.15}$$

The above equation is known as law of mass action, and $K(T)$ is the so-called equilibrium constant. Furthermore, $Q = \epsilon_3 + \epsilon_4 - \epsilon_1 - \epsilon_2$ denotes the difference of the chemical binding energies of the products and the reactants of the chemical reaction, which is identified with the heat of reaction. The law of mass action was proposed in 1867 by Guldberg and Waage.[4]

If the heat of reaction is negative, the energy is released to the surroundings and the process is called exothermic. Examples of exothermic processes are all combustion reactions. In the case where the heat of reaction is positive, the energy is gained from its surroundings and the process is denominated endothermic. The vaporization of water is an example of an endothermic process. If the chemically reacting system is enclosed by diathermic walls, the heat flows to the system for endothermic reactions and from the system for exothermic reactions, whereas if the walls are adiabatic, the temperature will increase for an exothermic process and decrease for an endothermic one.

One may obtain from the law of mass action (9.15), through its differentiation with respect to temperature, the van't Hoff equation[5] (or van't Hoff isochore), namely,

$$\frac{d \ln K(T)}{dT} = \frac{Q}{kT^2}. \tag{9.16}$$

From the van't Hoff equation, one may analyze the displacements from equilibrium of a chemical reaction on the basis of Le Châtelier's principle.[6] This principle can be stated as: any depart from equilibrium of a thermodynamic variable will induce a rearrangement of the system in order to prevent the imposed modification.

For an exothermic reaction, it follows from the van't Hoff equation that $d \ln K(T)/dT < 0$ and an increase of the temperature implies in a decrease of the equilibrium constant. For this case, one concludes from the law of mass action (9.15) that the numerator must decrease and the denominator must increase. Hence, for exothermic reactions, the increase of the temperature will

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[3] See e.g., P.W. Atkins, *Physical Chemistry* 5th. edition (Oxford University Press, Oxford, 1994).

[4] Cato Maximilian Guldberg (1836–1902) Norwegian mathematician and chemist; Peter Waage (1833–1900) Norwegian chemist.

[5] Jacobus Henricus van't Hoff (1852–1911) Dutch physical chemist.

[6] Henri Louis Le Châtelier (1850–1936) French chemist.

favor the reactants, i.e., the reaction proceeds from right to left. A similar analysis can be done for an endothermic reaction and one may infer that the increase of the temperature will favor the products of the reaction, i.e., the reaction proceeds from left to right.

The affinity (9.9) of the reaction may be expressed as

$$\mathcal{A} = kT \ln\left(\frac{n_1 n_2 n_3^{\mathrm{eq}} n_4^{\mathrm{eq}}}{n_3 n_4 n_1^{\mathrm{eq}} n_2^{\mathrm{eq}}}\right), \tag{9.17}$$

by using the expression for the chemical potentials given by (9.14).

Exercise

9.3 Perform the same analysis on the direction of the reaction when the temperature of an endothermic or an exothermic reaction decreases.

9.1.4 The Arrhenius Equation

By introducing the reaction rate coefficients for the forward direction k_f and reverse direction k_r, one may represent a bimolecular reaction as

$$A_1 + A_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A_3 + A_4, \tag{9.18}$$

and write the law of mass action (9.15) as

$$\frac{n_3^{\mathrm{eq}} n_4^{\mathrm{eq}}}{n_1^{\mathrm{eq}} n_2^{\mathrm{eq}}} = K(T) = \frac{\mathsf{k}_f(T)}{\mathsf{k}_r(T)}. \tag{9.19}$$

The above equation written as $\mathsf{k}_f(T) n_1^{\mathrm{eq}} n_2^{\mathrm{eq}} = \mathsf{k}_r(T) n_3^{\mathrm{eq}} n_4^{\mathrm{eq}}$ indicates that in equilibrium the reactions in the forward and reverse directions occur with the same probability. This equilibrium property is known as the principle of detailed balance, which is also a consequence of the principle of microscopic reversibility.

A chemical reaction will occur only if the relative translational energy of two colliding molecules becomes larger than a critical value, which is known as the activation energy. Hence, the activation energy refers to the minimum energy which is necessary to start a chemical reaction.

One may represent the activation energy as the height of the energy barrier which separates the potential energy of the reactants from the potential energy of products of a reaction. In Figure 9.1, a portrait of the formation energies of the reactants $\epsilon_1 + \epsilon_2$ and products $\epsilon_3 + \epsilon_4$ of a chemical reaction is shown. In this figure, the activation energy of the forward reaction

ϵ_f, the activation energy of the reverse reaction ϵ_r and the heat of reaction which is connected with the difference of the activation energies through the expression $Q = \epsilon_f - \epsilon_r$ is also portrayed.

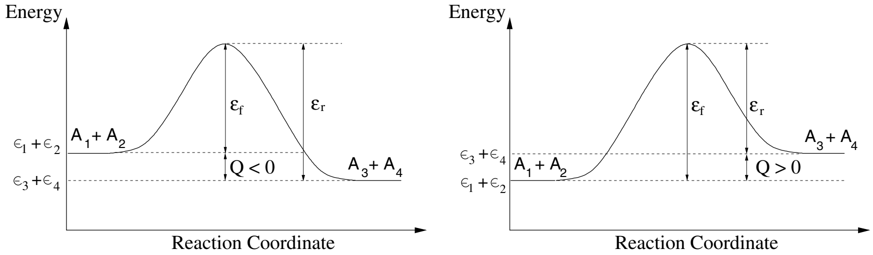

Fig. 9.1 Portrait of the formation and activation energies and heat of reaction

By using the relationship $Q = \epsilon_f - \epsilon_r$, the van't Hoff equation (9.16) can be expressed as

$$\frac{d\ln \mathsf{k}_f}{dT} - \frac{d\ln \mathsf{k}_r}{dT} = \frac{\epsilon_f - \epsilon_r}{kT^2}, \tag{9.20}$$

which can be split into two equations

$$\frac{d\ln \mathsf{k}_f}{dT} = \frac{\epsilon_f}{kT^2} + F(T), \qquad \frac{d\ln \mathsf{k}_r}{dT} = \frac{\epsilon_r}{kT^2} + F(T). \tag{9.21}$$

In the above equations, $F(T)$ is an arbitrary function of the temperature.

From the integration of $(9.21)_1$ with respect to temperature it follows

$$\ln \mathsf{k}_f = -\frac{\epsilon_f}{kT} + \int F(T)dT + \ln A, \tag{9.22}$$

where A is a constant of integration. Now, by setting the arbitrary function $F(T)$ equal to zero, one obtains the Arrhenius equation[7]

$$\mathsf{k}_f = A\, e^{-\epsilon_f/kT}, \tag{9.23}$$

which expresses the dependence of the reaction rate coefficient on temperature. The pre-exponential factor is usually assumed to be a constant. At the end of the 19th century, several scientists contributed to the explanation of the theory of chemical reactions by proposing equations for the reaction rate coefficient. The major contributions are due to van't Hoff in 1884 and to Arrhenius who in 1889 furnished a physical interpretation of the equation which bears his name.

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[7] Svante August Arrhenius (1859–1927) Swedish chemist.

One may also determine the entropy production density for a chemically reacting system. For that end, one writes the reaction velocity as a difference between the forward and reverse reaction rate coefficients, i.e.,

$$\frac{d\xi}{dt} = \mathsf{k}_f n_1 n_2 - \mathsf{k}_r n_3 n_4. \tag{9.24}$$

It is easy to see that the reaction velocity vanishes at equilibrium due to principle of detailed balance. Furthermore, in terms of the reaction rate, coefficients the affinity (9.17) reads

$$\mathcal{A} = kT \ln\left(\frac{\mathsf{k}_f n_1 n_2}{\mathsf{k}_r n_3 n_4}\right), \tag{9.25}$$

thanks to (9.19). Hence, the substitution of (9.24) and (9.25) into the inequality (9.10) leads to

$$\varsigma = k \ln\left(\frac{\mathsf{k}_f n_1 n_2}{\mathsf{k}_r n_3 n_4}\right)\left(\mathsf{k}_f n_1 n_2 - \mathsf{k}_r n_3 n_4\right). \tag{9.26}$$

The above expression for the entropy production density is only a function of the forward and reverse reaction rate coefficients and is positive semidefinite thanks to the relationship $(x-1)\ln x \geqslant 0$, which is valid for all $x > 0$. At equilibrium, the principle of detailed balance holds and the entropy production density vanishes.

Exercise

9.4 In general, the pre-exponential factors depend on the temperature. What arguments one has to use in order to obtain the modified Arrhenius equation $\mathsf{k}_f = BT^n\, e^{-\epsilon_f/kT}$—where B and n are constants—from (9.22)?

9.2 Boltzmann Equations

Consider a simple reversible bimolecular gas reaction characterized by the chemical law $A_1 + A_2 \rightleftharpoons A_3 + A_4$ where only binary encounters between the molecules are taken into account. Two types of binary collisions are then considered, namely, the elastic and the reactive ones.

For a reactive collision, the conservation laws of mass, linear momentum and total energy read

$$m_1 + m_2 = m_3 + m_4, \tag{9.27}$$

$$m_1\mathbf{c}_1 + m_2\mathbf{c}_2 = m_3\mathbf{c}_3 + m_4\mathbf{c}_4, \tag{9.28}$$

$$\epsilon_1 + \frac{1}{2}m_1c_1^2 + \epsilon_2 + \frac{1}{2}m_2c_2^2 = \epsilon_3 + \frac{1}{2}m_3c_3^2 + \epsilon_4 + \frac{1}{2}m_4c_4^2, \tag{9.29}$$

where m_α denotes the mass and ϵ_α the binding energy of the molecule $\alpha = 1,\dots,4$. Moreover, $(\mathbf{c}_1,\mathbf{c}_2)$ are the velocities of the reactants and $(\mathbf{c}_3,\mathbf{c}_4)$ are the velocities of the products of the forward reaction.

The conservation law for the total energy (9.29) can be written in terms of the relative velocities $g_{\beta\alpha} = |\mathbf{g}_{\beta\alpha}| = |\mathbf{c}_\beta - \mathbf{c}_\alpha|$ and of the heat of reaction Q as

$$\frac{1}{2}m_{12}g_{21}^2 = \frac{1}{2}m_{34}g_{43}^2 + Q, \tag{9.30}$$

where $m_{\alpha\beta} = m_\alpha m_\beta/(m_\alpha + m_\beta)$ denotes the reduced mass.

For an elastic collision of two molecules—say α and β—with pre-collision velocities $(\mathbf{c}_\alpha,\mathbf{c}_\beta)$ and post-collision velocities $(\mathbf{c}'_\alpha,\mathbf{c}'_\beta)$, the linear momentum and the energy conservation laws are given by (1.91) and (1.92), respectively.

A state of a reacting gaseous mixture in the μ-phase space spanned by the positions $\mathbf{x}$ and velocities $\mathbf{c}_\alpha$ of the molecules is characterized by the set of distribution functions $f_\alpha \equiv f(\mathbf{x},\mathbf{c}_\alpha,t)$ with $\alpha = 1,\dots,4$. The distribution functions are defined in such a manner that $f_\alpha d\mathbf{x}d\mathbf{c}_\alpha$ gives at time t the number of α molecules in the volume element $d\mathbf{x}d\mathbf{c}_\alpha$ around the position $\mathbf{x}$ and the velocity $\mathbf{c}_\alpha$.

The distribution function f_α of constituent α is assumed to satisfy a Boltzmann equation—which in the absence of external forces—reads

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha\frac{\partial f_\alpha}{\partial x_i} = \sum_{\beta=1}^{4}\int \left(f'_\alpha f'_\beta - f_\alpha f_\beta\right) g_{\beta\alpha}\sigma_{\beta\alpha}d\varOmega\, d\mathbf{c}_\beta + \mathcal{Q}_\alpha^R. \tag{9.31}$$

The right-hand side of the above equation has two terms. The first one referring to the elastic interactions among the constituents where $\sigma_{\alpha\beta}$ is a differential elastic cross section and $d\varOmega = \sin\chi d\chi d\varepsilon$ is an element of solid angle. The second term on the right-hand side of (9.31)—namely $\mathcal{Q}_\alpha^R$—refers to the reactive collisions, and in the following its expression will be determined. The collision operator for the constituent labeled by the index 1 is obtained as follows. The number of reactive collisions for the forward reaction $A_1 + A_2 \rightharpoonup A_3 + A_4$ per unit of volume and time is given by $(f_1\, f_2\, g_{21}\, \sigma_{12}^\star\, d\varOmega^\star\, d\mathbf{c}_1\, d\mathbf{c}_2)$, where $\sigma_{12}^\star$ represents the reactive differential cross section and $d\varOmega^\star$ is an element of solid angle which relates the orientation of the post-collisional relative velocity $\mathbf{g}_{43}$ with respect to the pre-collisional one $\mathbf{g}_{21}$. In the same manner, the number of collisions for the reverse reaction $A_1 + A_2 \leftharpoondown A_3 + A_4$ reads $(f_3\, f_4\, g_{43}\, \sigma_{34}^\star\, d\varOmega^\star\, d\mathbf{c}_3\, d\mathbf{c}_4)$.

For a fixed value of the heat of reaction, it follows from (9.30) that $m_{12}g_{21}dg_{21} = m_{34}g_{43}dg_{43}$ and one can prove that

$$d\mathbf{c}_3\,d\mathbf{c}_4=\frac{m_{12}g_{43}}{m_{34}g_{21}}\,d\mathbf{c}_1\,d\mathbf{c}_2. \tag{9.32}$$

Furthermore, from the principle of microscopic reversibility, one obtains a relationship between the differential cross sections (see (5.13)). For the case where the heat of reaction could be considered as a small quantity, this connection reads

$$(m_{12}g_{21})^2\sigma_{12}^\star=(m_{34}g_{43})^2\sigma_{34}^\star. \tag{9.33}$$

Hence, by taking into account (9.32) and (9.33), one may write the following relationship

$$f_3\,f_4\,g_{43}\,\sigma_{34}^\star\,d\Omega^\star\,d\mathbf{c}_3\,d\mathbf{c}_4=f_3\,f_4\left(\frac{m_{12}}{m_{34}}\right)^3 g_{21}\,\sigma_{12}^\star\,d\Omega^\star\,d\mathbf{c}_1\,d\mathbf{c}_2. \tag{9.34}$$

From the difference of the expressions (9.34) and $(f_1\,f_2\,g_{21}\,\sigma_{12}^\star\,d\Omega^\star\,d\mathbf{c}_1\,d\mathbf{c}_2)$ divided by $d\mathbf{c}_1$ and the integration of the resulting equation over all values of $d\mathbf{c}_2$ and $d\Omega^\star$, one obtains the reactive collision term for the constituent labeled by the index 1, namely,

$$\mathcal{Q}_{1(2)}^R=\int\left[f_3f_4\left(\frac{m_{12}}{m_{34}}\right)^3-f_1f_2\right]\sigma_{12}^\star g_{21}d\Omega^\star d\mathbf{c}_{2(1)}. \tag{9.35}$$

Note that the reactive collision term for the constituent labeled by the index 2 is similar being represented in the above equation by the parentheses. Likewise, the reactive collision terms for the constituents labeled by the indexes 3 and 4 read

$$\mathcal{Q}_{3(4)}^R=\int\left[f_1f_2\left(\frac{m_{34}}{m_{12}}\right)^3-f_3f_4\right]\sigma_{34}^\star g_{43}d\Omega^\star d\mathbf{c}_{4(3)}. \tag{9.36}$$

Exercises

9.5 Obtain (9.30).

9.6 Show that the relationship (9.32) holds.

9.3 Transfer and Balance Equations

As usual, the transfer equation for the constituent α is obtained from (9.31) by multiplying both sides of it by an arbitrary function $\psi_\alpha\equiv\psi(\mathbf{x},\mathbf{c}_\alpha,t)$ and integrating the resulting equation over all values of $\mathbf{c}_\alpha$. After some rearrangements, the transfer equation can be written as

$$\frac{\partial}{\partial t}\int \psi_\alpha f_\alpha d\mathbf{c}_\alpha + \frac{\partial}{\partial x_i}\int \psi_\alpha c_i^\alpha f_\alpha d\mathbf{c}_\alpha - \int \left(\frac{\partial \psi_\alpha}{\partial t} + c_i^\alpha \frac{\partial \psi_\alpha}{\partial x_i}\right) f_\alpha d\mathbf{c}_\alpha$$
$$= \sum_{\beta=1}^{4}\int (\psi_\alpha' - \psi_\alpha) f_\alpha f_\beta g_{\beta\alpha}\sigma_{\beta\alpha} d\Omega\, d\mathbf{c}_\beta d\mathbf{c}_\alpha$$
$$-\nu_\alpha\left\{\int \psi_\alpha \left[f_3 f_4 \left(\frac{m_{12}}{m_{34}}\right)^3 - f_1 f_2\right]\sigma_{12}^\star g_{21} d\Omega^\star d\mathbf{c}_1 d\mathbf{c}_2\right\}. \quad (9.37)$$

By summing the above equation over all the constituents, one obtains the transfer equation for the mixture

$$\frac{\partial}{\partial t}\sum_{\alpha=1}^{4}\int \psi_\alpha f_\alpha d\mathbf{c}_\alpha + \frac{\partial}{\partial x_i}\sum_{\alpha=1}^{4}\int \psi_\alpha c_i^\alpha f_\alpha d\mathbf{c}_\alpha - \sum_{\alpha=1}^{4}\int \left(\frac{\partial \psi_\alpha}{\partial t} + c_i^\alpha \frac{\partial \psi_\alpha}{\partial x_i}\right) f_\alpha d\mathbf{c}_\alpha$$
$$= \frac{1}{4}\sum_{\alpha,\beta=1}^{4}\int (\psi_\alpha + \psi_\beta - \psi_\alpha' - \psi_\beta')(f_\alpha' f_\beta' - f_\alpha f_\beta) g_{\beta\alpha}\sigma_{\beta\alpha} d\Omega\, d\mathbf{c}_\beta d\mathbf{c}_\alpha$$
$$+\int (\psi_1 + \psi_2 - \psi_3 - \psi_4)\left[f_3 f_4 \left(\frac{m_{12}}{m_{34}}\right)^3 - f_1 f_2\right]\sigma_{12}^\star g_{21} d\Omega^\star d\mathbf{c}_1 d\mathbf{c}_2. \quad (9.38)$$

In the above equation, the symmetry properties of the collision terms have been used. The first integral terms on the right-hand sides of the transfer equations (9.37) and (9.38) represent the corresponding production terms due to the effects of the elastic collisions, whereas the second ones are related to the actions of the chemical reactions.

The macroscopic description of a reacting gas mixture undergoing a simple reversible bimolecular reaction can be characterized by the basic fields

$$\varrho_\alpha = \int m_\alpha f_\alpha\, d\mathbf{c}_\alpha = m_\alpha n_\alpha \quad - \quad \text{mass density}, \quad (9.39)$$

$$\varrho_\alpha v_i^\alpha = \int m_\alpha c_i^\alpha f_\alpha\, d\mathbf{c}_\alpha \quad - \quad \text{momentum density}, \quad (9.40)$$

$$\varrho_\alpha \widetilde{u}_\alpha = \int \left(\frac{m_\alpha}{2} c_\alpha^2 + \epsilon_\alpha\right) f_\alpha\, d\mathbf{c}_\alpha \quad - \quad \text{energy density}. \quad (9.41)$$

By introducing the peculiar velocity $C_i^\alpha = c_i^\alpha - v_i^\alpha$, one may decompose the energy density of the constituent α as

$$\varrho_\alpha \widetilde{u}_\alpha = \frac{1}{2}\varrho_\alpha v_\alpha^2 + \varrho_\alpha \varepsilon_\alpha + n_\alpha \epsilon_\alpha, \qquad \text{where} \qquad \varrho_\alpha \varepsilon_\alpha = \frac{1}{2}\int m_\alpha C_\alpha^2 f_\alpha d\mathbf{c}_\alpha \quad (9.42)$$

is the internal energy density of constituent α associated with the translational degrees of freedom. Note that the energy density $\varrho_\alpha \widetilde{u}_\alpha$ differs from that of a mixture of monatomic gases (8.7) through the inclusion of the term $n_\alpha \epsilon_\alpha$, which is associated with the binding energy of the molecule α.

As usual, the balance equations for the fields (9.39)–(9.41) are obtained from the transfer equation (9.37) by choosing ψ_α equal to:

(a) *Balance of mass density* ($\psi_\alpha = m_\alpha$):

$$\frac{\partial \varrho_\alpha}{\partial t} + \frac{\partial \varrho_\alpha v_i^\alpha}{\partial x_i} = \tau_\alpha, \tag{9.43}$$

where the mass production density of the constituent α is given by

$$\tau_\alpha \equiv m_\alpha \nu_\alpha \frac{d\xi}{dt} = -m_\alpha \nu_\alpha \int \left[f_3 f_4 \left(\frac{m_{12}}{m_{34}} \right)^3 - f_1 f_2 \right] \sigma_{12}^\star g_{21} d\Omega^\star d\mathbf{c}_1 d\mathbf{c}_2. \tag{9.44}$$

By taking into account the expression (9.24) for the reaction velocity in terms of the forward k_f and reverse k_r reaction rate coefficients, one obtains

$$\mathsf{k}_f = \frac{1}{n_1 n_2} \int f_1 f_2 \sigma_{12}^\star g_{21} d\Omega^\star d\mathbf{c}_1 d\mathbf{c}_2, \tag{9.45}$$

$$\mathsf{k}_r = \frac{1}{n_3 n_4} \int f_3 f_4 \left(\frac{m_{12}}{m_{34}} \right)^3 \sigma_{12}^\star g_{21} d\Omega^\star d\mathbf{c}_1 d\mathbf{c}_2. \tag{9.46}$$

(b) *Balance of momentum density* ($\psi_\alpha = m_\alpha c_i^\alpha$):

$$\frac{\partial \varrho_\alpha v_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j} (\varrho_\alpha v_i^\alpha v_j^\alpha + p_{ij}^\alpha) = \pi_i^\alpha, \tag{9.47}$$

where the pressure tensor and the momentum production density of the constituent α read

$$p_{ij}^\alpha = \int m_\alpha C_i^\alpha C_j^\alpha f_\alpha d\mathbf{c}_\alpha, \tag{9.48}$$

$$\begin{aligned} \pi_i^\alpha = & \sum_{\beta=1}^{4} \int m_\alpha (c_i'^\alpha - c_i^\alpha) f_\alpha f_\beta g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega \, d\mathbf{c}_\beta d\mathbf{c}_\alpha \\ & - \nu_\alpha \left\{ \int m_\alpha c_i^\alpha \left[f_3 f_4 \left(\frac{m_{12}}{m_{34}} \right)^3 - f_1 f_2 \right] \sigma_{12}^\star g_{21} d\Omega^\star d\mathbf{c}_1 d\mathbf{c}_2 \right\}. \end{aligned} \tag{9.49}$$

(c) *Balance of energy density* ($\psi_\alpha = m_\alpha c_\alpha^2/2 + \epsilon_\alpha$):

$$\begin{aligned} \frac{\partial}{\partial t} \left[\varrho_\alpha \left(\varepsilon_\alpha + \frac{1}{2} v_\alpha^2 + \frac{\epsilon_\alpha}{m_\alpha} \right) \right] + \frac{\partial}{\partial x_i} \Bigg[q_i^\alpha + p_{ji}^\alpha v_j^\alpha & \\ + \varrho_\alpha \left(\varepsilon_\alpha + \frac{1}{2} v_\alpha^2 + \frac{\epsilon_\alpha}{m_\alpha} \right) v_i^\alpha \Bigg] &= \zeta_\alpha, \end{aligned} \tag{9.50}$$

where the heat flux vector and the energy production density of the constituent α are given by

$$q_i^\alpha = \int \frac{m_\alpha}{2} C_\alpha^2 C_i^\alpha f_\alpha d\mathbf{c}_\alpha, \tag{9.51}$$

$$\begin{aligned} \zeta_\alpha &= \sum_{\beta=1}^{4} \int \frac{m_\alpha}{2}(c_\alpha'^2 - c_\alpha^2) f_\alpha f_\beta g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega\, d\mathbf{c}_\beta d\mathbf{c}_\alpha \\ &- \nu_\alpha \left\{ \int \left(\frac{m_\alpha}{2} c_\alpha^2 + \epsilon_\alpha \right) \left[f_3 f_4 \left(\frac{m_{12}}{m_{34}} \right)^3 - f_1 f_2 \right] \sigma_{12}^\star g_{21} d\Omega^\star d\mathbf{c}_1 d\mathbf{c}_2 \right\}. \end{aligned} \tag{9.52}$$

The balance equations for the mass density, momentum density and energy density of the mixture are obtained from (9.43), (9.47) and (9.50) through a summation over all constituents, yielding

$$\frac{\partial \varrho}{\partial t} + \frac{\partial \varrho v_i}{\partial x_i} = 0, \tag{9.53}$$

$$\frac{\partial \varrho v_i}{\partial t} + \frac{\partial}{\partial x_j} \left(p_{ij} + \varrho v_i v_j \right) = 0, \tag{9.54}$$

$$\frac{\partial}{\partial t} \left[\varrho \left(\widetilde{\varepsilon} + \frac{1}{2} v^2 \right) \right] + \frac{\partial}{\partial x_i} \left[\varrho \left(\widetilde{\varepsilon} + \frac{1}{2} v^2 \right) v_i + \widetilde{q}_i + p_{ij} v_j \right] = 0. \tag{9.55}$$

The sums of the production terms of the constituents vanish due to the conservation laws of mass, momentum and energy for the mixture, i.e.,

$$\sum_{\alpha=1}^{4} \tau_\alpha = 0, \qquad \sum_{\alpha=1}^{4} \pi_i^\alpha = 0, \qquad \sum_{\alpha=1}^{4} \zeta_\alpha = 0. \tag{9.56}$$

The mixture's quantities which have appeared in (9.53)–(9.55) are related to the corresponding ones of the constituents by

$$\varrho = \sum_{\alpha=1}^{4} \varrho_\alpha \qquad \varrho v_i = \sum_{\alpha=1}^{4} \varrho_\alpha v_i^\alpha, \qquad p_{ij} = \sum_{\alpha=1}^{4} \left(p_{ij}^\alpha + \varrho_\alpha u_i^\alpha u_j^\alpha \right), \tag{9.57}$$

$$\varrho\, \widetilde{\varepsilon} = \sum_{\alpha=1}^{4} \varrho_\alpha \left(\varepsilon_\alpha + \frac{\epsilon_\alpha}{\underline{m_\alpha}} + \frac{1}{2} u_\alpha^2 \right), \tag{9.58}$$

$$\widetilde{q}_i = \sum_{\alpha=1}^{4} \left[q_i^\alpha + \varrho_\alpha \left(\varepsilon_\alpha + \frac{\epsilon_\alpha}{\underline{m_\alpha}} + \frac{1}{2} u_\alpha^2 \right) u_i^\alpha + p_{ji}^\alpha u_j^\alpha \right]. \tag{9.59}$$

where u_i^α denotes the diffusion velocity of the constituent α, namely,

$$u_i^\alpha = \frac{1}{n_\alpha} \int \xi_i^\alpha f_\alpha d\mathbf{c}_\alpha, \tag{9.60}$$

whereas $\xi_i^\alpha = v_i^\alpha - v_i$ is a peculiar velocity. Note that the expressions given in (9.57) are same as those for mixtures of monatomic gases (see Section 8.2), but the relationships (9.58) and (9.59) differ due to the presence of the underlined terms. In chemically reacting systems, the internal energy of the mixture depends also on the binding energies of the molecules, and the heat flux of the mixture has a term $n_\alpha \epsilon_\alpha u_i^\alpha$, which corresponds to the transport of the binding energies of the molecules in the diffusive motion.

The balance equation for the internal energy density of the mixture follows from (9.55) by eliminating the time derivative of the velocity through the use of (9.54), yielding

$$\frac{\partial \varrho \widetilde{\varepsilon}}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho \widetilde{\varepsilon} v_i + \widetilde{q}_i\right) + p_{ij}\frac{\partial v_i}{\partial x_j} = 0. \tag{9.61}$$

Another balance equation which is important is that of the entropy density of the mixture, which is obtained from the transfer equation for the mixture (9.38) by taking $\psi_\alpha = -k\ln(\mathsf{b}_\alpha f_\alpha / m_\alpha^3)$. Hence, it follows

$$\frac{\partial \varrho s}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho s v_i + \varphi_i\right) = \varsigma_E + \varsigma_R. \tag{9.62}$$

Above, the entropy density ϱs and the entropy flux φ_i of the mixture are defined by

$$\varrho s = \sum_{\alpha=1}^{4} \varrho_\alpha s_\alpha, \qquad \varrho_\alpha s_\alpha = -k\int f_\alpha \ln\left(\frac{\mathsf{b}_\alpha f_\alpha}{m_\alpha^3}\right) d\mathbf{c}_\alpha, \tag{9.63}$$

$$\varphi_i = \sum_{\alpha=1}^{4}\left(\varphi_i^\alpha + \varrho_\alpha s_\alpha u_i^\alpha\right), \qquad \varphi_i^\alpha = -k\int f_\alpha \ln\left(\frac{\mathsf{b}_\alpha f_\alpha}{m_\alpha^3}\right) C_i^\alpha d\mathbf{c}_\alpha. \tag{9.64}$$

Furthermore, ς_E and ς_R are the entropy production densities due to the elastic collisions and chemical reactions, respectively. They are given by

$$\varsigma_E = -\frac{k}{4}\sum_{\alpha,\beta=1}^{4}\int f_\alpha' f_\beta' \left(1 - \frac{f_\alpha f_\beta}{f_\alpha' f_\beta'}\right)\ln\left(\frac{f_\alpha f_\beta}{f_\alpha' f_\beta'}\right) g_{\beta\alpha}\sigma_{\beta\alpha} d\Omega\, d\mathbf{c}_\beta d\mathbf{c}_\alpha, \tag{9.65}$$

$$\begin{aligned}\varsigma_R = {} & -k\left(\frac{m_{12}}{m_{34}}\right)^3 \int f_3 f_4 \left[1 - \left(\frac{m_{34}}{m_{12}}\right)^3 \frac{f_1 f_2}{f_3 f_4}\right] \\ & \times \ln\left[\left(\frac{m_{34}}{m_{12}}\right)^3 \frac{f_1 f_2}{f_3 f_4}\right] \sigma_{12}^\star g_{21} d\Omega^\star d\mathbf{c}_1 d\mathbf{c}_2.\end{aligned} \tag{9.66}$$

From the above equations, one may infer that both ς_E and ς_R are nonnegative quantities, since one has $(1-x)\ln x \leqslant 0$, for any positive x, i.e., the total entropy production density of the reacting mixture is a positive semi-definite quantity $\varsigma_E + \varsigma_R \geqslant 0$. Note that the elastic and the reactive collisions separately contribute to the increase of the entropy of the mixture, since both lead to semi-positive entropy production densities.

Exercises

9.7 Obtain the transfer equations (9.37) and (9.38).

9.8 Obtain the balance equations for entropy density of the mixture (9.62).

9.4 Models for Differential Cross Sections

In this chapter, it will be assumed that the elastic differential cross sections correspond to a hard-sphere potential, namely,

$$\sigma_{\alpha\beta} = \frac{1}{4}\mathsf{d}_{\alpha\beta}^2, \qquad \mathsf{d}_{\alpha\beta} = \frac{1}{2}\left(\mathsf{d}_\alpha + \mathsf{d}_\beta\right), \tag{9.67}$$

where d_α and d_β are the diameters of the colliding spheres.

Three different reactive differential cross sections will be analyzed here: two of them take into account the barrier represented by the activation energy and the other one arises from an attractive interaction potential, and the chemical reaction proceeds without the need to go beyond an energy barrier.

One kind of reactive differential cross section which considers the barrier of the activation energy is known as the step cross section and it is given by

$$\sigma_{12}^\star = \begin{cases} 0, & \frac{m_{12}g_{21}^2}{2} < \epsilon_f \\ \frac{1}{4}\mathsf{d}_f^2, & \frac{m_{12}g_{21}^2}{2} \geqslant \epsilon_f \end{cases}, \qquad \sigma_{34}^\star = \begin{cases} 0, & \frac{m_{34}g_{43}^2}{2} < \epsilon_r \\ \frac{1}{4}\mathsf{d}_r^2, & \frac{m_{34}g_{43}^2}{2} \geqslant \epsilon_r \end{cases}. \tag{9.68}$$

Hence, a chemical reaction happens whenever the relative translational energy of the forward reaction $m_{12}g_{21}^2/2$ is larger than the forward activation energy ϵ_f and whenever the relative translational energy of the reverse reaction $m_{34}g_{43}^2/2$ is larger than the reverse activation energy $\epsilon_r = \epsilon_f - Q$. The quantities d_f and d_r represent reactive diameters of the forward and reverse reactions, respectively. The reactive diameters are connected with the molecular diameters by the relationships $\mathsf{d}_f = \mathsf{s}_f\mathsf{d}_{12}$ and $\mathsf{d}_r = \mathsf{s}_r d_{34}$ where s_f and s_r are called steric factors of the forward and reverse reactions, respectively. In most of the cases, the steric factor is lesser than one so that the reactive cross section is smaller than the elastic one, as indicated schematically by Figure 9.2.

Another kind of reactive differential cross section which takes into account the barrier of the activation energy is the so-called line-of-centers model, which is defined through the relationships

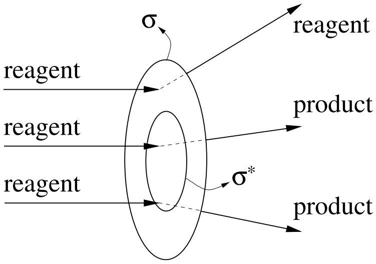

Fig. 9.2 Schematic representation of elastic and reactive cross sections.

$$\sigma^\star_{12}=\begin{cases}0, & \frac{m_{12}g_{21}^2}{2}<\epsilon_f\\ \frac{1}{4}\mathsf{d}_f^2\left(1-\frac{2\epsilon_f}{m_{12}g_{21}^2}\right), & \frac{m_{12}g_{21}^2}{2}\geqslant\epsilon_f\end{cases}, \tag{9.69}$$

$$\sigma^\star_{34}=\begin{cases}0, & \frac{m_{34}g_{43}^2}{2}<\epsilon_r\\ \frac{1}{4}\mathsf{d}_r^2\left(1-\frac{2\epsilon_r}{m_{34}g_{43}^2}\right), & \frac{m_{34}g_{43}^2}{2}\geqslant\epsilon_r\end{cases}. \tag{9.70}$$

The same restrictions on the relative translational energies which are valid for the step cross section hold here.

There exist chemical reactions which proceeds without going beyond an energy barrier so that the differential cross section results from an attractive interaction potential of the form $V=-K/r^n$. The differential cross sections for these reactive collisions are given by

$$\sigma^\star_{12}=\frac{\mathsf{d}_f^2}{4}\left(\frac{m_{12}g_{21}^2}{2kT_0}\right)^{n-1/2}, \qquad \sigma^\star_{34}=\frac{\mathsf{d}_r^2}{4}\left(\frac{m_{34}g_{43}^2}{2kT_0}\right)^{n-1/2}. \tag{9.71}$$

In the above equation, T_0 is a characteristic temperature, and the exponent n may range from $-3/2$ to $1/2$, with the particular values $1/2$, 0 and $1/6$ which correspond to hard-spheres, ion-molecule and neutral reaction type, respectively.

9.5 Equilibrium Distribution Function

In Section 8.4, it was shown that the state of equilibrium of a non-reacting gas mixture was characterized by the Maxwellian distribution functions

$$f_\alpha^{(0)}=n_\alpha\left(\frac{m_\alpha}{2\pi kT}\right)^{\frac{3}{2}}e^{-m_\alpha\xi_\alpha^2/2kT}, \qquad \alpha=1,\dots,n. \tag{9.72}$$

The above distribution functions render the elastic collision terms of the Boltzmann equation (9.31) to vanish, but not the reactive collision terms (9.35) and (9.36). The reason of the last statement is due to the fact that the particle number densities in the distribution functions (9.72) are not the equilibrium ones, which characterize the chemical equilibrium and are related by the law of mass action (9.15). Hence, the equilibrium distribution functions of chemically reacting gas are given by

$$f_\alpha^{\mathrm{eq}} = n_\alpha^{\mathrm{eq}} \left(\frac{m_\alpha}{2\pi kT}\right)^{\frac{3}{2}} e^{-m_\alpha \xi_\alpha^2/2kT}, \qquad \alpha = 1, \dots, 4. \tag{9.73}$$

From the knowledge of the Maxwellian distribution functions, one can calculate, the equilibrium value of the forward reaction rate coefficient for a given reactive differential cross section. Indeed, the insertion of the expressions for the Maxwellian distribution functions (9.72) into the definition of the forward reaction rate coefficient (9.45) leads to

$$\mathsf{k}_f^{(0)} = \frac{(m_1 m_2)^{\frac{3}{2}}}{(2\pi kT)^3} \int \exp\left[-\frac{(m_1+m_2)G_{12}^2}{2kT} - \frac{m_{12} g_{21}^2}{2kT}\right] \sigma_{12}^\star g_{21} d\Omega^\star d\mathbf{g}_{21} d\mathbf{G}_{12}, \tag{9.74}$$

by introducing the relative velocity $\mathbf{g}_{21}$ and the center of mass velocity $\mathbf{G}_{12}$ defined by (8.114). For the differential cross section of the line-of-centers model (9.69), one obtains from the above equation through the integration over the element of solid angle $d\Omega^\star$ and over the center of mass velocity:

$$\mathsf{k}_f^{(0)} = \sqrt{\frac{8\pi kT}{m_{12}}} \mathsf{d}_f^2 \int_{\epsilon_f^\star}^\infty \left(1 - \frac{\epsilon_f^\star}{x}\right) x dx, \quad \text{where} \quad \epsilon_f^\star = \frac{\epsilon_f}{kT}, \quad x = \frac{m_{12} g_{21}^2}{2kT}, \tag{9.75}$$

where $\epsilon_f^\star$ is the forward activation energy in units of the thermal energy kT and x is a new variable of integration. From (9.75), one obtains through the integration over the variable x the following expression:

$$\mathsf{k}_f^{(0)} = A_{12} e^{-\epsilon_f^\star}, \qquad A_{12} = \sqrt{\frac{8\pi kT}{m_{12}}} \mathsf{d}_f^2, \tag{9.76}$$

which is the Arrhenius equation. Note that the pre-exponential factor of the Arrhenius equation A_{12} depends on the square root of the temperature.

By following the same methodology, one obtains that the pre-exponential factor of the Arrhenius equation for the step cross section (9.68) reads

$$A_{12} = \sqrt{\frac{8\pi kT}{m_{12}}} \mathsf{d}_f^2 (1 + \epsilon_f^\star). \tag{9.77}$$

It is obvious that the expression for the forward reaction rate coefficient in the case of a differential cross section without barriers (9.71) does not follow the Arrhenius equation, since in this case one obtains that

$$\mathsf{k}_f^{(0)} = \sqrt{\frac{8\pi kT}{m_{12}}}\,\mathsf{d}_f^2\left(\frac{T}{T_0}\right)^{n-1/2}\Gamma\left(n+\frac{3}{2}\right). \tag{9.78}$$

Exercises

9.9 Show that the reactive collision terms (9.35) and (9.36) vanish when the distribution function is given by (9.73).

9.10 Obtain the expressions for the forward reaction rate coefficients (9.77) and (9.78).

9.11 Calculate the equilibrium value of the reverse reaction rate coefficient (9.46) by using the line-of-centers differential cross section (9.70) and show that the equilibrium condition $\mathsf{k}_f^{(0)} n_1^{\rm eq} n_2^{\rm eq} = \mathsf{k}_r^{(0)} n_3^{\rm eq} n_4^{\rm eq}$ leads to the following relationship between the steric factors:

$$\mathsf{s}_f\,\sqrt{m_{12}}\,\mathsf{d}_{12} = \mathsf{s}_r\,\sqrt{m_{34}}\,\mathsf{d}_{34}.$$

9.6 Transport Coefficients for $H_2 + Cl \rightleftharpoons HCl + H$

The objective of this section is to analyze the transport properties of bimolecular reactions by using the Boltzmann equation and the scheme of the presentation follows the work.[8] It will be considered that the elastic differential cross section is modeled by the hard-sphere potential, whereas the reactive one refers to the line-of-centers model. First, the non-equilibrium distribution functions are determined through the Chapman–Enskog method and afterwards, an analysis of the transport coefficients for the bimolecular reacting mixture $H_2 + Cl \rightleftharpoons HCl + H$ is performed.

9.6.1 Chapman–Enskog Method

In order to obtain the transport coefficients of a bimolecular reaction from the Boltzmann equation, it will be considered that the system is nearby a chemical equilibrium state, so that the frequencies of the reacting collisions have the same order of magnitude as those of the elastic ones. In this specific case—which is very typical at the last stage of a chemical reaction—it is supposed that there exists just one relaxation time, despite the fact that the collisions have different nature. These kinds of reactions are known as fast reactions and are characterized by the condition that the affinity is considered

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[8] A.W. Silva, G.M. Alves & G.M. Kremer, "Transport phenomena in a reactive quaternary gas mixture", *Physica A*, **374**, 533-549 (2007).

as a small quantity in comparison with the thermal energy of the mixture kT, i.e., $|\mathcal{A}|/kT < 1$. It is interesting to point out the difference between the former case and the one where the reactions are considered far from the chemical equilibrium and which are known as slow reactions. This latter case refers to the initial stage of a chemical reaction and is characterized by the condition that the frequencies of the elastic collisions are larger than those of the reactive ones and that the affinity is much larger than the thermal energy of the mixture, i.e., $|\mathcal{A}|/kT \gg 1$. In Section 9.8.1, the case of slow reactions will be analyzed for the symmetric reaction $A + A \rightleftharpoons B + B$.

For the determination of the non-equilibrium distribution function f_α by using the Chapman–Enskog methodology, one should write the distribution function of constituent α as

$$f_\alpha = f_\alpha^{(0)} + f_\alpha^{(1)} = f_\alpha^{(0)}\left(1 + \phi_\alpha\right), \tag{9.79}$$

where $f_\alpha^{(0)}$ stands for the Maxwellian distribution function (9.72), whereas $f_\alpha^{(1)} = f_\alpha^{(0)}\phi_\alpha$ refers to its deviation from the thermal and mechanical equilibrium state. It is important to call attention to the fact that the Maxwellian distribution function $f_\alpha^{(0)}$ does not refer to a chemical equilibrium. Indeed, the ratio between the Maxwellian distribution functions for the four constituents leads to

$$\frac{f_1^{(0)} f_2^{(0)}}{f_3^{(0)} f_4^{(0)}} = \frac{n_1 n_2}{n_3 n_4}\left(\frac{m_{12}}{m_{34}}\right)^{\frac{3}{2}} e^{-Q^\star} = \left(\frac{m_{12}}{m_{34}}\right)^3 e^{\mathcal{A}^\star} \approx \left(\frac{m_{12}}{m_{34}}\right)^3 \left(1 + \mathcal{A}^\star\right), \tag{9.80}$$

due to (9.15) and (9.17) and by considering processes nearby the chemical equilibrium state where the affinity has a small value with respect to the thermal energy of the mixture, i.e., $|\mathcal{A}/kT| < 1$. Above, the starred quantities $Q^\star = Q/kT$ and $\mathcal{A}^\star = \mathcal{A}/kT$ were introduced, which represent the heat of reaction and the affinity in units of kT, respectively.

The deviation ϕ_α from the Maxwellian distribution function $f_\alpha^{(0)}$ in (9.79) is considered as a small quantity for processes close to equilibrium—i.e., $|\phi_\alpha| < 1$—and it is constrained by the following relationships:

$$\int f_\alpha^{(0)} \phi_\alpha d\mathbf{c}_\alpha = 0, \qquad \sum_{\alpha=1}^{4} \int m_\alpha c_i^\alpha f_\alpha^{(0)} \phi_\alpha d\mathbf{c}_\alpha = 0, \tag{9.81}$$

$$\sum_{\alpha=1}^{4} \int \left(\frac{1}{2} m_\alpha c_\alpha^2 + \epsilon_\alpha\right) f_\alpha^{(0)} \phi_\alpha d\mathbf{c}_\alpha = 0. \tag{9.82}$$

The determination of the deviation ϕ_α proceeds by applying the Chapman–Enskog methodology (see Section 3.2), i.e., the Maxwellian distribution function (9.72) is inserted into the left-hand side of the Boltzmann equation (9.31), whereas on its right-hand side, the representation (9.79) is introduced. By neglecting all products of the deviations, it follows

$$\begin{aligned}\frac{\partial f_\alpha^{(0)}}{\partial t}+c_i^\alpha\frac{\partial f_\alpha^{(0)}}{\partial x_i}&=f^{(0)}\left\{\frac{\mathcal{D}n_\alpha}{n_\alpha}-\left(\frac{3}{2}-\frac{m_\alpha\xi_\alpha^2}{2kT}\right)\frac{\mathcal{D}T}{T}+\frac{m_\alpha}{kT}\xi_i^\alpha\mathcal{D}v_i\right.\\&\left.+\,\xi_i^\alpha\left[\frac{1}{n_\alpha}\frac{\partial n_\alpha}{\partial x_i}-\left(\frac{3}{2}-\frac{m_\alpha\xi_\alpha^2}{2kT}\right)\frac{1}{T}\frac{\partial T}{\partial x_i}+\frac{m_\alpha}{kT}\xi_j^\alpha\frac{\partial v_j}{\partial x_i}\right]\right\}\\&=\sum_{\beta=1}^{4}\int f_\alpha^{(0)}f_\beta^{(0)}\left(\phi_\beta'+\phi_\alpha'-\phi_\beta-\phi_\alpha\right)g_{\beta\alpha}\sigma_{\beta\alpha}d\Omega\,d\mathbf{c}_\beta+\widetilde{\mathcal{Q}}_\alpha^R,\end{aligned}\tag{9.83}$$

where $\mathcal{D}$ denotes the material time derivative, and the reactive collision term $\widetilde{\mathcal{Q}}_\alpha^R$ reads

$$\widetilde{\mathcal{Q}}_\alpha^R=\nu_\alpha\int f_\alpha^{(0)}f_\gamma^{(0)}\left(\mathcal{A}^\star+\phi_1+\phi_2-\phi_3-\phi_4\right)\sigma_{\alpha\gamma}^\star g_{\alpha\gamma}d\Omega^\star d\mathbf{c}_\gamma.\tag{9.84}$$

In the above expression, there exists a correspondence between the indexes, namely, $\alpha=1,2,3,4$ are related to $\gamma=2,1,4,3$. The expression (9.84) for $\alpha=1$ is obtained as follows:

$$\begin{aligned}\widetilde{\mathcal{Q}}_1^R&=\int\left[f_3^{(0)}f_4^{(0)}\left(\frac{m_{12}}{m_{34}}\right)^3(1+\phi_3+\phi_4)-f_1^{(0)}f_2^{(0)}(1+\phi_1+\phi_2)\right]\sigma_{12}^\star g_{21}d\Omega^\star d\mathbf{c}_2\\&=\int f_1^{(0)}f_2^{(0)}\left[(1-\mathcal{A}^\star)(1+\phi_3+\phi_4)-(1+\phi_1+\phi_2)\right]\sigma_{12}^\star g_{21}d\Omega^\star d\mathbf{c}_2\\&=\nu_1\int f_1^{(0)}f_2^{(0)}\left[(\mathcal{A}^\star+\phi_1+\phi_2-\phi_3-\phi_4)\right]\sigma_{12}^\star g_{21}d\Omega^\star d\mathbf{c}_2,\end{aligned}\tag{9.85}$$

where in the second equality (9.80) was used and in the third one, the products of the affinity with the deviations were neglected. The determination of the expressions for the other constituents proceeds in the same manner.

The next step in the Chapman–Enskog method is the elimination of the material time derivatives by using the balance equations of partial particle number densities, hydrodynamic velocity and temperature of the mixture for a non-viscous, non-heat conducting and non-diffusive mixture of reacting gases, which refers to an Eulerian gas mixture. The constitutive equations in this case read

$$\varrho\,\widetilde{\varepsilon}=\frac{3}{2}nkT+\sum_{\alpha=1}^{4}n_\alpha\epsilon_\alpha,\qquad p_{ij}=p\,\delta_{ij},\qquad q_i=0,\tag{9.86}$$

$$u_i^\alpha=0,\qquad\tau_\alpha=m_\alpha\nu_\alpha\mathcal{A}^\star n_1n_2\mathsf{k}_f^{(0)},\tag{9.87}$$

where $\mathsf{k}_f^{(0)}$ denotes the forward reaction rate coefficient calculated through the Maxwellian distribution function (9.72) and whose expression is given by the Arrhenius equation (9.76). Hence, the balance equations—obtained from (9.43), (9.54) and (9.55) and the above constitutive equations—read

$$\mathcal{D}n_\alpha + n_\alpha \frac{\partial v_i}{\partial x_i} = \nu_\alpha \mathcal{A}^\star n_1 n_2 \mathsf{k}_f^{(0)}, \tag{9.88}$$

$$\varrho \mathcal{D} v_i + \frac{\partial p}{\partial x_i} = 0, \tag{9.89}$$

$$\frac{3}{2} nk\mathcal{D}T + p\frac{\partial v_i}{\partial x_i} = -Q\mathcal{A}^\star n_1 n_2 \mathsf{k}_f^{(0)}. \tag{9.90}$$

Once the material time derivatives are eliminated from (9.83) by using the balance equations (9.88)–(9.90), the following coupled system of four linear integral equations, for the deviations ϕ_1, ϕ_2, ϕ_3 and ϕ_4, is obtained

$$f_\alpha^{(0)} \Bigg\{ \xi_i^\alpha \xi_j^\alpha \frac{m_\alpha}{kT} \frac{\partial v_{\langle i}}{\partial x_{j\rangle}} + \frac{\xi_i^\alpha}{T}\left(\frac{m_\alpha \xi_\alpha^2}{2kT} - \frac{5}{2}\right)\frac{\partial T}{\partial x_i} + \frac{n}{n_\alpha}\xi_i^\alpha d_i^\alpha - \Bigg[\nu_\alpha \frac{n_1 n_2 \mathsf{k}_f^{(0)}}{n_\alpha}$$
$$+ \frac{n_1 n_2 \mathsf{k}_f^{(0)}}{n} Q^\star \left(1 - \frac{m_\alpha \xi_\alpha^2}{3kT}\right) + \nu_\alpha \int f_\gamma^{(0)} g_{\gamma\alpha} \sigma_{\gamma\alpha}^\star d\Omega^\star d\mathbf{c}_\gamma \Bigg] \mathcal{A}^\star \Bigg\}$$
$$= \sum_{\beta=1}^{4} \int f_\alpha^{(0)} f_\beta^{(0)} \left(\phi_\alpha' + \phi_\beta' - \phi_\alpha - \phi_\beta\right) g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega^\star \, d\mathbf{c}_\beta$$
$$+ \nu_\alpha \int f_\alpha^{(0)} f_\gamma^{(0)} \left(\phi_1 + \phi_2 - \phi_3 - \phi_4\right) \sigma_{\alpha\gamma}^\star g_{\gamma\alpha} d\Omega^\star d\mathbf{c}_\gamma. \tag{9.91}$$

One infers from the left-hand side of (9.91) that each ϕ_α is a function of four thermodynamic forces, namely, **(i)** the affinity $\mathcal{A}^\star$, which is a scalar; **(ii)** the gradient of temperature $\partial T/\partial x_i$ and the generalized diffusion forces d_i^α, which are vectors and **(iii)** the velocity gradient deviator $\partial v_{\langle i}/\partial x_{j\rangle}$, which is a second-order tensor. Hence, it is assumed that the deviations ϕ_α—which are in the right-hand side of (9.91)—depend linearly on these four forces and are represented by

$$\phi_\alpha = -\frac{A_i^\alpha}{T}\frac{\partial T}{\partial x_i} - B_{ij}^\alpha \frac{\partial v_{\langle i}}{\partial x_{j\rangle}} - \sum_{\beta=1}^{4} F_i^{\alpha\beta} d_i^\beta - E_\alpha \frac{\mathcal{A}}{kT}, \qquad \alpha = 1, \dots, 4, \tag{9.92}$$

where A_i^α, B_{ij}^α, $F_i^{\alpha\beta}$ and E_α are unknown functions of the peculiar velocity ξ_i^α, of the particle number densities n_α and of mixture's temperature T. The representations of the vectorial and tensorial functions read

$$A_i^\alpha = A_\alpha \xi_i^\alpha, \qquad B_{ij} = B_\alpha \xi_i^\alpha \xi_j^\alpha, \qquad F_i^{\alpha\beta} = F_{\alpha\beta}\xi_i^\alpha, \tag{9.93}$$

where A_α, B_α and $F_{\alpha\beta}$ are scalar coefficients that depend on $(n_\alpha, T, \xi_\alpha^2)$.

In order to determine the scalar coefficients A_α, B_α, $F_{\alpha\beta}$ and E_α from the system of integral equations (9.91), the methodology described in the book by Chapman and Cowling is applied and extended to a reactive mixture.

First, in order to take into account the constraint on the generalized diffusion forces $\sum_{\alpha=1}^4 d_i^\alpha = 0$, one has to impose a condition on the coefficients $F_{\alpha\beta}$, which can be written as

$$\sum_{\beta=1}^4 \varrho_\beta F_{\alpha\beta} = 0, \qquad \text{so that} \qquad \sum_{\beta=1}^4 F_{\alpha\beta}\xi_i^\alpha d_i^\beta = \frac{1}{p}\sum_{\beta=1}^4 F_{\alpha\beta}\xi_i^\alpha \frac{\partial p_\beta}{\partial x_i}, \tag{9.94}$$

due to (8.62). Hence, the deviation (9.92) becomes

$$\phi_\alpha = -\frac{A_\alpha}{T}\xi_i^\alpha \frac{\partial T}{\partial x_i} - B_\alpha \xi_i^\alpha \xi_j^\alpha \frac{\partial v_{\langle i}}{\partial x_{j\rangle}} - \frac{1}{p}\sum_{\beta=1}^4 F_{\alpha\beta}\xi_i^\alpha \frac{\partial p_\beta}{\partial x_i} - E_\alpha \frac{\mathcal{A}}{kT}, \qquad \alpha = 1, \dots, 4. \tag{9.95}$$

The substitution of the deviation on the constraints (9.81) and (9.82) leads to the following restrictions on the scalar coefficients:

$$\int f_\alpha^{(0)} E_\alpha d\mathbf{c}_\alpha = 0, \qquad \sum_{\alpha=1}^4 \int m_\alpha c_\alpha^2 f_\alpha^{(0)} E_\alpha d\mathbf{c}_\alpha = 0, \tag{9.96}$$

$$\sum_{\alpha=1}^4 \int m_\alpha \xi_\alpha^2 f_\alpha^{(0)} A_\alpha d\mathbf{c}_\alpha = 0, \qquad \sum_{\alpha=1}^4 \int m_\alpha \xi_\alpha^2 f_\alpha^{(0)} F_{\alpha\beta} d\mathbf{c}_\alpha = 0. \tag{9.97}$$

From the insertion of the representation (9.95) into the system of integral equations (9.91), one obtains systems of integral equations for each scalar coefficients A_α, B_α, $F_{\alpha\beta}$ and E_α by equating the coefficients of each thermodynamic force to zero, namely,

$$\left(\frac{m_\alpha \xi_\alpha^2}{2kT} - \frac{5}{2}\right) f_\alpha^{(0)}\, \xi_i^\alpha = -\sum_{\beta=1}^4 \mathcal{I}_{\alpha\beta}^E \left[A_\alpha\, \xi_i^\alpha + A_\beta\, \xi_i^\beta\right] - \mathcal{I}_\alpha^R \left[A_\alpha\, \xi_i^\alpha\right], \tag{9.98}$$

$$\frac{m_\alpha}{kT} f_\alpha^{(0)}\, \xi_{\langle i}^\alpha\, \xi_{j\rangle}^\alpha = -\sum_{\beta=1}^4 \mathcal{I}_{\alpha\beta}^E \left[B_\alpha\, \xi_{\langle i}^\alpha\, \xi_{j\rangle}^\alpha + B_\beta\, \xi_{\langle i}^\beta\, \xi_{j\rangle}^\beta\right] - \mathcal{I}_\alpha^R \left[B_\alpha\, \xi_{\langle i}^\alpha\, \xi_{j\rangle}^\alpha\right], \tag{9.99}$$

$$\frac{1}{\mathsf{x}_\alpha}\left[\delta_{\alpha\tau} - \frac{\varrho_\alpha}{\varrho}\right] f_\alpha^{(0)}\, \xi_i^\alpha = -\sum_{\beta=1}^4 \mathcal{I}_{\alpha\beta}^E \left[F_{\alpha\tau}\, \xi_i^\alpha + F_{\beta\tau}\, \xi_i^\beta\right] - \mathcal{I}_\alpha^R \left[F_{\alpha\tau}\, \xi_i^\alpha\right], \tag{9.100}$$

$$\left[\nu_\alpha \frac{n_1 n_2 \mathsf{k}_f^{(0)}}{n_\alpha} + \frac{n_1 n_2 \mathsf{k}_f^{(0)}}{n} Q^\star \Big(1 - \frac{m_\alpha \xi_\alpha^2}{3kT}\Big) + \nu_\alpha \int f_\gamma^{(0)} g_{\gamma\alpha} \sigma_{\gamma\alpha}^\star d\Omega^\star d\mathbf{c}_\gamma\right] f^{(0)}$$

$$= \sum_{\beta=1}^4 \mathcal{I}_{\alpha\beta}^E \left[E_\alpha + E_\beta\right] + \mathcal{I}_\alpha^R \left[E_\alpha\right]. \tag{9.101}$$

In the above equations, the elastic $\mathcal{I}_{\alpha\beta}^E$ and the reactive $\mathcal{I}_\alpha^R$ integrals are defined by

$$\mathcal{I}^E_{\alpha\beta}[\Phi_{\gamma\tau}] = \int f^{(0)}_\alpha f^{(0)}_\beta \left(\Phi'_{\gamma\tau} - \Phi_{\gamma\tau}\right) g_{\beta\alpha}\sigma_{\beta\alpha} d\Omega\, d\mathbf{c}_\beta, \tag{9.102}$$

$$\mathcal{I}^R_\alpha[\Phi_{\alpha\tau}] = \nu_\alpha \int f^{(0)}_\alpha f^{(0)}_\gamma \left(\Phi_{1\tau} + \Phi_{2\tau} - \Phi_{3\tau} - \Phi_{4\tau}\right) \sigma^\star_{\alpha\gamma} g_{\gamma\alpha} d\Omega^\star d\mathbf{c}_\gamma, \tag{9.103}$$

where $\alpha = 1, 2, 3, 4$ corresponds to $\gamma = 2, 1, 4, 3$.

In (9.100), $\mathsf{x}_\alpha = n_\alpha/n$ is the molar fraction of the constituent α and one may observe that this equation fulfils the condition $(9.94)_1$. Indeed, the multiplication of (9.100) by ϱ_γ and the sum of the resulting equation over all values of $\gamma = 1, \ldots, 4$ leads to an identity.

According to the Chapman–Enskog method (see Chapter 3), the scalar coefficients A_α, B_α, $F_{\alpha\beta}$ and E_α are expanded in terms of Sonine polynomials in such way that the problem of finding the function ϕ_α becomes the one of determining each coefficient in the expansions. With this purpose each system of integral equations—represented by (9.98) through (9.101)—is conveniently multiplied by a specific Sonine polynomial and the resulting equations are integrated over the velocity space. Afterwards, a system of algebraic equations for the expansion coefficients is obtained and the coefficients are determined. These steps will be omitted here since the resulting equations for the expansion coefficients are extremely lengthy. In the following sections, the general expressions for the transport coefficients will be given and the figures which show the behavior of the transport coefficients in an inert as well as in a chemically reacting quaternary gas mixture will be presented.

Exercises

9.12 Obtain the balance equation (9.90).

9.13 Obtain the system of integral equations (9.91) and (9.98)–(9.101).

9.14 Show that the multiplication of (9.100) by ϱ_γ and the sum of the resulting equation over all values of $\gamma = 1, \ldots, 4$ leads to an identity.

9.6.2 Transport Coefficients

Once the non-equilibrium distributions are known functions of the thermodynamic forces, one may obtain the constitutive equations for the reaction rate coefficient, diffusion velocities, pressure tensor and heat flux vector of the mixture and identify the transport coefficients of diffusion, thermal–diffusion, diffusion–thermal, thermal conductivity and shear viscosity. This will be analyzed afterwards.

Reaction Rate Coefficient

The forward and reverse reaction rate coefficients are obtained through the insertion of the distribution function (9.79) together with (9.95) into their definitions (9.45) and (9.46). By integrating the resulting equations and by neglecting all non-linear terms, one obtains

$$\begin{aligned}\mathsf{k}_f &= \frac{1}{n_1 n_2}\int f_1^{(0)} f_2^{(0)}\left[1-(E_1-E_2)\,\mathcal{A}^\star\right]\sigma_{12}^\star g_{21}\, d\Omega^\star d\mathbf{c}_1 d\mathbf{c}_2 \\ &= \mathsf{k}_f^{(0)} + \mathsf{k}_f^{(1)}\mathcal{A}^\star, \qquad (9.104)\\ \mathsf{k}_r &= \frac{1}{n_3 n_4}\int f_3 f_4 \left(\frac{m_{12}}{m_{34}}\right)^3 \left[1-(E_3-E_4)\,\mathcal{A}^\star\right]\sigma_{12}^\star g_{21}\, d\Omega^\star d\mathbf{c}_1 d\mathbf{c}_2 \\ &= \mathsf{k}_r^{(0)} + \mathsf{k}_r^{(1)}\mathcal{A}^\star. \qquad (9.105)\end{aligned}$$

In the above equations, $\mathsf{k}_f^{(0)}$ and $\mathsf{k}_r^{(0)}$ denote the equilibrium rate constants, whereas $\mathsf{k}_f^{(1)}$ and $\mathsf{k}_r^{(1)}$ represent the non-equilibrium ones.

The mass production density (9.44) can be written in terms of the rate constants as

$$\tau_\alpha = m_\alpha \nu_\alpha \left[\left(n_1 n_2 \mathsf{k}_f^{(0)} - n_3 n_4 \mathsf{k}_r^{(0)}\right) + \left(n_1^{\mathrm{eq}} n_2^{\mathrm{eq}} \mathsf{k}_f^{(1)} - n_3^{\mathrm{eq}} n_4^{\mathrm{eq}} \mathsf{k}_r^{(1)}\right)\mathcal{A}^\star\right]. \qquad (9.106)$$

Coefficient of Shear Viscosity

For the determination of the Navier–Stokes law, the non-equilibrium distribution function (9.79) with (9.95) is inserted into the definition of the pressure tensor—equations $(9.57)_3$ and (9.48)—and the resulting equation is integrated. If all non-linear terms are neglected, then

$$p_{ij} = p\delta_{ij} - 2\mu \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \qquad (9.107)$$

where the coefficient of shear viscosity μ is given by

$$\mu = \frac{1}{15}\sum_{\alpha=1}^{4}\int m_\alpha B_\alpha \xi_\alpha^4 f_\alpha^{(0)} d\mathbf{c}_\alpha. \qquad (9.108)$$

Coefficients of Diffusion and Thermal–Diffusion

The generalized Fick's law is obtained by the insertion of the non-equilibrium distribution function (9.79) with (9.95) into the definition of the diffusion velocity (9.60) of constituent α and the integration of the resulting equation, which leads to

$$u_i^\alpha = -\sum_{\beta=1}^{4} \varDelta_{\alpha\beta} \frac{1}{p}\frac{\partial p_\beta}{\partial x_i} - D_T^\alpha \frac{\partial \ln T}{\partial x_i}. \tag{9.109}$$

In the above equation, $\varDelta_{\alpha\beta}$ denotes a generalized diffusion coefficient, whereas D_T^α represents a thermal–diffusion coefficient. Their expressions are given by

$$\varDelta_{\alpha\beta} = \frac{1}{3n_\alpha}\int F_{\alpha\beta}\xi_\alpha^2 f_\alpha^{(0)} d\mathbf{c}_\alpha, \qquad D_T^\alpha = \frac{1}{3n_\alpha}\int A_\alpha \xi_\alpha^2 f_\alpha^{(0)} d\mathbf{c}_a. \tag{9.110}$$

Due to the constraints $(9.94)_1$ and $\sum_{\alpha=1}^4 \varrho_\alpha u_i^\alpha = 0$, it follows the restrictions

$$\sum_{\beta=1}^{4} \varrho_\beta \varDelta_{\alpha\beta} = 0, \qquad \sum_{\alpha=1}^{4} \varrho_\alpha \varDelta_{\alpha\beta} = 0, \qquad \sum_{\beta=1}^{4} \varrho_\alpha D_T^\alpha = 0. \tag{9.111}$$

Furthermore, the multiplication of (9.100) by $F_{\alpha\gamma}\xi_i^\alpha$ and the summation over all values of α of the resulting equation yields

$$3n\varDelta_{\tau\gamma} = -\sum_{\alpha=1}^{4}\int F_{\alpha\gamma}\xi_i^\alpha \left\{\sum_{\beta=1}^{4} \mathcal{I}_{\alpha\beta}^E\left[F_{\alpha\tau}\,\xi_i^\alpha + F_{\beta\tau}\,\xi_i^\beta\right] + \mathcal{I}_\alpha^R\left[F_{\alpha\tau}\,\xi_i^\alpha\right]\right\} d\mathbf{c}_\alpha, \tag{9.112}$$

due to $(9.97)_2$. From the above equation, one may obtain that the matrix of the generalized diffusion coefficients is symmetric, i.e., $\varDelta_{\tau\gamma} = \varDelta_{\gamma\tau}$, hence there exist $n(n-1)/2$ diffusion coefficients that are linearly independent in a mixture of n constituents. Besides, there exist only $n-1$ thermal diffusion coefficients.

If one makes use of the restrictions given in (9.111), the diffusion velocity (9.109) may be expressed as

$$u_i^\alpha = -\sum_{\beta=1}^{4} \varDelta_{\alpha\beta} d_i^\beta - D_T^\alpha \frac{\partial \ln T}{\partial x_i}. \tag{9.113}$$

Another way to express the generalized Fick's law follows by solving (9.113) for the generalized diffusion forces, yielding

$$d_i^\alpha + \kappa_T^\alpha \frac{\partial \ln T}{\partial x_i} = -\sum_{\beta=1}^{4} \frac{\mathsf{x}_\alpha \mathsf{x}_\beta}{D_{\alpha\beta}}\left(u_i^\alpha - u_i^\beta\right). \tag{9.114}$$

The proof of the above relationship is left as an exercise. The coefficient $D_{\alpha\beta}$ is identified as the diffusion coefficient and κ_T^α as the thermal–diffusion ratio.

Coefficients of Thermal Conductivity and Diffusion–Thermal

The determination of the generalized Fourier law proceeds in the same manner, i.e., by inserting the non-equilibrium distribution function (9.79) with (9.95) into the definition of the heat flux (9.51) of the constituent α and by using the definition of the heat flux of the mixture (9.59). Hence, it follows by integrating the resulting equation

$$\widetilde{q}_i = -\tilde{\lambda}\frac{\partial T}{\partial x_i} - T\sum_{\beta=1}^{4}\tilde{D}_\beta d_i^\beta, \tag{9.115}$$

where the coefficients associated with the thermal conductivity and the diffusion–thermal effect $\tilde{\lambda}$ and $\tilde{D}_\beta$ read

$$\tilde{\lambda} = \frac{1}{T}\sum_{\alpha=1}^{4}\left[\frac{1}{6}\int m_\alpha \xi_\alpha^4 A_\alpha f_\alpha^{(0)} d\mathbf{c}_\alpha + n_\alpha \epsilon_\alpha D_T^\alpha\right], \tag{9.116}$$

$$\tilde{D}_\beta = \frac{1}{T}\sum_{\alpha=1}^{4}\left[\frac{1}{6}\int m_\alpha \xi_\alpha^4 F_{\alpha\beta} f_\alpha^{(0)} d\mathbf{c}_\alpha + n_\alpha \epsilon_\alpha \Delta_{\alpha\beta}\right]. \tag{9.117}$$

The thermal conductivity λ is the coefficient of proportionality between the heat flux of the mixture and the gradient of temperature when the diffusion is absent. It is obtained from the substitution of the generalized diffusion fluxes d_i^α given by (9.114) into (9.115) and by considering the diffusion velocities u_i^α equal to zero, yielding

$$\lambda = \tilde{\lambda} - \sum_{\alpha=1}^{4}\tilde{D}_\alpha \kappa_T^\alpha. \tag{9.118}$$

Exercises

9.15 Show from the relationship (9.112) that the matrix of the generalized diffusion coefficients is symmetric, i.e., $\Delta_{\tau\gamma} = \Delta_{\gamma\tau}$.

9.16 Obtain the generalized Fick's law (9.114) from (9.113).

9.6.3 Quaternary Mixture H_2, Cl, HCl, H

Unfortunately, the transport coefficients can only be determined numerically, since their algebraic expressions are lengthy. In order to illustrate the behavior of the transport coefficients, the quaternary mixture of constituents H, H_2, Cl and HCl will be analyzed. First the results for the inert case are presented and afterwards mixtures where the chemical reactions occur are considered. Note that the internal degrees of the molecules—like the rotational and the vibrational modes—will not be considered. In the graphics below only the first approximation in Sonine polynomials for the scalar coefficients A_α, B_α, $F_{\alpha\beta}$ and E_α, which appear in the expression for the deviation ϕ_α of the distribution function (9.95), was taken into account.

Inert Mixture

The transport coefficients of inert gas mixtures can be obtained from the equations of the theory developed above—i.e., for reactive gas mixtures—just by setting the values of the steric factors equal to zero. In this case, the reactive cross sections vanish and only elastic encounters are considered.

Table 9.1 Molecular weights, viscosities and molecular diameters

Gas	H	H_2	Cl	HCl
M_α	1.008	2.016	35.453	36.461
μ_α ($\times 10^{-5}$ Pa s)	–	0.841	–	1.332
d_α ($\times 10^{-10}$ m)	1.06	2.78	1.99	4.55

In order to evaluate the coefficients of shear viscosity, thermal conductivity, diffusion and thermal–diffusion ratio, it is necessary to know some characteristic parameters for the constituents of the mixture, such as masses, diameters and molar fractions. In Table 9.1, the values of the molecular weights M_α and of the coefficients of shear viscosity μ_α at temperature $T = 293$ K are listed for the single constituents H, H_2, Cl and HCl.[9]

From the expression of the coefficient of shear viscosity valid for hard-sphere molecules—see $(3.54)_1$—namely,

$$\mu_\alpha = \frac{5}{16\mathsf{d}_\alpha^2}\sqrt{\frac{m_\alpha kT}{\pi}}, \tag{9.119}$$

one may calculate the diameters of the single constituents H_2 and HCl. For the constituent Cl, the diameter was considered as twice its atomic radius, whereas for the constituent H, its diameter was taken to be of order of two times the Bohr's atomic radius ($a_0 = 0.529 \times 10^{-10}$ m). Furthermore, it was considered that the total number of molecules in the mixture is approximately equal to 2.6 $\times 10^{25}$ molecules/m^3, which refers to one mole of an ideal gas mixture. With respect to the molar fractions, two sets of values were

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[9] Landolt-Börsnstein, *Transportphänomene I*, II. Band, 5. Teil, Bandteil a, (Springer-Verlag, Berlin, 1969).

considered: (a) $\mathsf{x}_{H_2} = \mathsf{x}_{Cl} = 0.1$ and $\mathsf{x}_H = \mathsf{x}_{HCl} = 0.4$ and (b) $\mathsf{x}_{H_2} = \mathsf{x}_{Cl} = 0.4$ and $\mathsf{x}_H = \mathsf{x}_{HCl} = 0.1$, by recalling that the sum of the molar fractions is equal to unity $\sum_{\alpha=1}^{4} \mathsf{x}_\alpha = 1$.

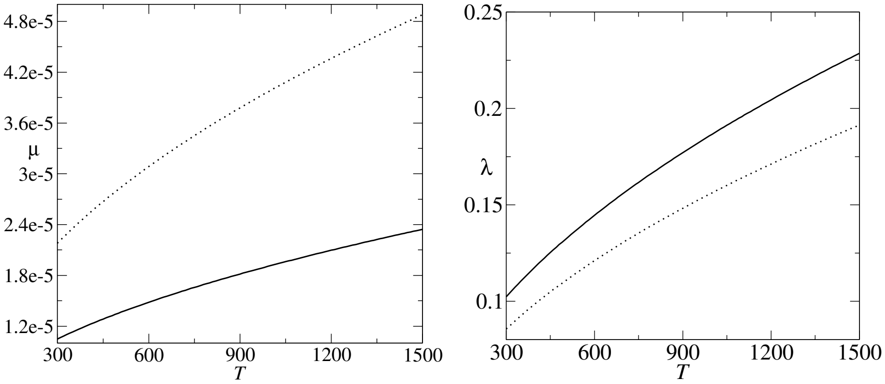

Fig. 9.3 Left frame: shear viscosity μ (Pa s); right frame: thermal conductivity λ (W/m K) as functions of temperature T (K). Straight lines $\mathsf{x}_{H_2} = \mathsf{x}_{Cl} = 0.1$ and $\mathsf{x}_H = \mathsf{x}_{HCl} = 0.4$; dotted lines $\mathsf{x}_{H_2} = \mathsf{x}_{Cl} = 0.4$ and $\mathsf{x}_H = \mathsf{x}_{HCl} = 0.1$.

In Figures 9.3 and 9.4, the behaviors of the coefficients of shear viscosity μ, thermal conductivity λ and diffusion $D_{\alpha\beta}$ are plotted as functions of the temperature. These figures show—as it was expected—that the transport coefficients increase with the temperature. The left and right frames of Figure 9.3 indicate that the coefficients of shear viscosity and thermal conductivity also depend on the molar fraction of the constituents.

For the case of the diffusion coefficients—which are represented in Figure 9.4—one can observe that $D_{\alpha\beta}$ is larger for the couple of molecules that has the smallest reduced mass $m_{\alpha\beta}$ and the smallest mean diameter $\mathsf{d}_{\alpha\beta}$. This is not surprising since the motion of these molecules through the gas mixture is easier than for those which are heavier and larger. Note that the first approximation in Sonine polynomials for the diffusion coefficient does not depend on the molar fractions of the constituents in the mixture (see Section 8.11).

In Table 9.2, the values of the thermal–diffusion ratios κ_T for the inert mixtures are given by considering the two sets of molar fractions. It can be observed that the values of κ_T for the heavier molecules is positive, which means that these particles diffuse toward cooler regions, whereas κ_T is negative for the lightest molecules which tend to diffuse into the hotter regions.

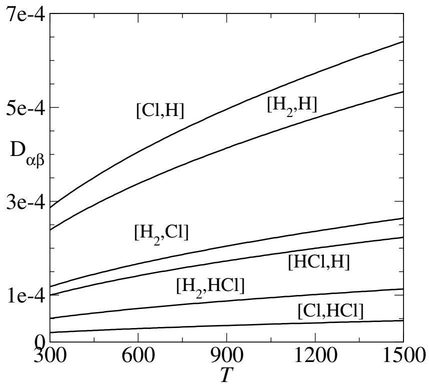

Fig. 9.4 Diffusion coefficients $D_{\alpha\beta}$ (m^2/s) as functions of temperature T (K) for the mixture H, H_2, HCl and Cl.

Table 9.2 Thermal–diffusion ratio for the inert mixture H_2, Cl, H and HCl

x_α		κ_T^α			
H_2, Cl	HCl, H	H_2	Cl	HCl	H
0.1	0.4	-0.0225	0.0132	0.1382	-0.1288
0.4	0.1	-0.0928	0.0823	0.0427	-0.0323

Reactive Mixture

In order to observe the effect of the chemical reactions on the transport coefficients, the reversible reaction $H_2 + Cl \rightleftharpoons HCl + H$ is now analyzed. In Table 9.3, the coefficient A of the Arrhenius equation $\mathsf{k}_f^{(0)} = Ae^{-\epsilon_f^\star}$, the forward and the reverse activation energies[10] are listed. The reference temperature for this reaction is 300 K, and the heat of reaction was obtained from the relationship $Q = \epsilon_f - \epsilon_r$.

Table 9.3 Arrhenius coefficients, forward and reverse activation energies, heat of reaction and forward steric factor

Reaction	A(m^3/mol s)	ϵ_f(kJ/mol)	ϵ_r(kJ/mol)	Q(kJ/mol)	s_f
$H_2 + Cl \rightharpoonup HCl + H$	7.94×10^7	23.03	18.84	4.19	0.648

By considering the chemical reactions as fast processes, it follows that the number of collisions that result in a forward reaction and its reverse reaction

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[10] Landolt-Börsnstein, *Transportphänomene II*, II. Band, 5. Teil, Bandteil b, (Springer-Verlag, Berlin, 1968).

are of the same order of magnitude as the number of elastic encounters. On account of this fact and from the observation that the activation energy is already an obstacle for the occurrence of a chemical reaction, one infers that the reactive cross section cannot be much smaller than the elastic one, which means that the steric factor plays an important role in the theory. The value of the steric factor for the forward reaction s_f was obtained from the Arrhenius equation (9.76), namely,

$$A_{12} = (\mathsf{s}_f d_{12})^2 \sqrt{\frac{8\pi kT}{m_{12}}}. \tag{9.120}$$

Note that with this choice, there is no free parameter for the analyzed reactions, and the transport coefficients depend only on the variables: the molar fractions of the constituents and the temperature of the mixture.

Furthermore, the equilibrium molar fractions must fulfill the condition of chemical equilibrium given by (9.15), which in terms of the molar fractions, reads

$$Q^\star = \ln\left[\left(\frac{m_{34}}{m_{12}}\right)^{3/2} \frac{\mathsf{x}_1^{eq}\mathsf{x}_2^{eq}}{\mathsf{x}_3^{eq}\mathsf{x}_4^{eq}}\right]. \tag{9.121}$$

Here, the case of an equimolar mixture of reagents and products were considered in which $\mathsf{x}_1 = \mathsf{x}_2$ and $\mathsf{x}_3 = \mathsf{x}_4$. Hence, from (9.121) and with the help of the relationship $\sum_{\alpha=1}^4 \mathsf{x}_\alpha = 1$, it follows that $\mathsf{x}_{H_2} = \mathsf{x}_{Cl} = 0.396$ and $\mathsf{x}_{HCl} = \mathsf{x}_H = 0.104$ for the reaction $H_2 + Cl \rightleftharpoons HCl + H$ at $T = 300$ K.

In the left frame of Figure 9.5, the equilibrium molar concentrations is plotted as a function of the temperature in the range 300 K $\leqslant T \leqslant$ 1500 K. Note that by considering the reaction heat as a constant, the molar fractions of the reagents decrease with the increasing of the temperature while those of the products increase. The equilibrium and the non-equilibrium rate

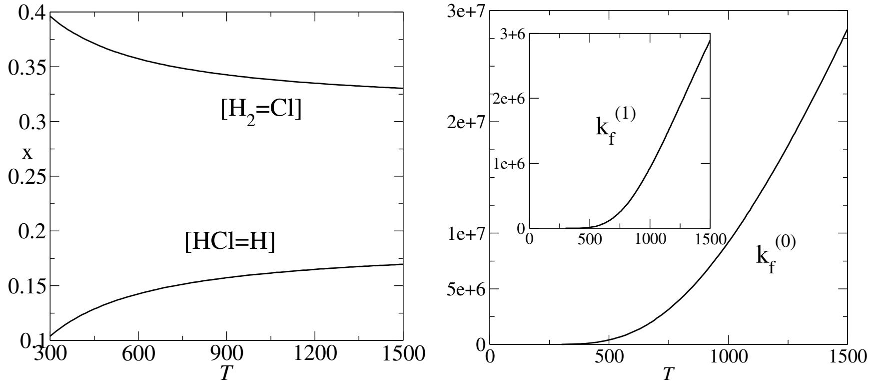

Fig. 9.5 Left frame: equilibrium molar fraction; right frame: rate constants (m^3/mol s) as functions of temperature T (K) for the reaction $H_2 + Cl \rightleftharpoons HCl + H$.

constants are graphically represented in the right frame of Figure 9.5 as functions of the temperature, and one concludes that the equilibrium rate constant is ten times larger than the non-equilibrium one.

In Figures 9.6–9.8, the behavior of the coefficients of shear viscosity μ, thermal conductivity λ, diffusion $D_{\alpha\beta}$ and thermal–diffusion ratio κ_T^α as functions of the temperature T for the reaction $H_2 + Cl \rightleftharpoons HCl + H$ is shown. One can observe from these figures that the behavior of these coefficients are similar, i.e., they tend to their inert values as the temperature decreases. This result indicates that the effect of the chemical reactions becomes negligible at lower temperatures which was expected, since in this situation the

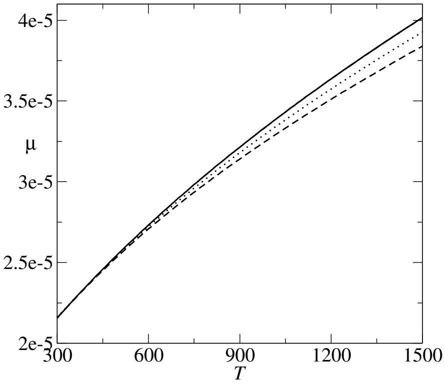

Fig. 9.6 Left frame: shear viscosity (Pa·s); right frame: thermal conductivity (W/m·K) as functions of temperature T (K). Straight lines: inert mixture; dotted lines: $H_2 + Cl \rightharpoonup HCl + H$; dashed lines: $H_2 + Cl \leftharpoondown HCl + H$.

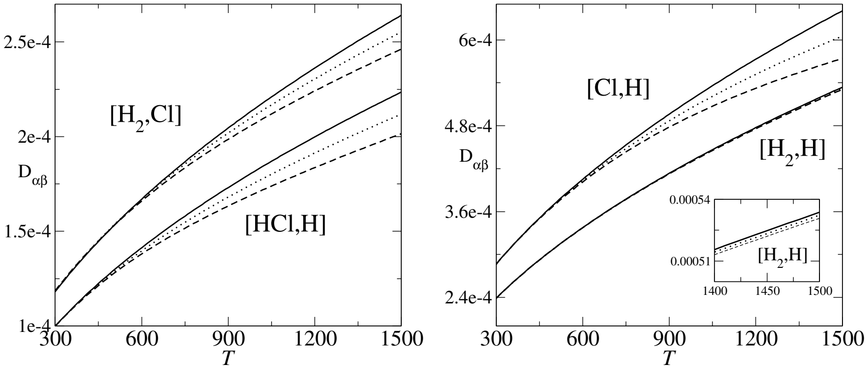

Fig. 9.7 Diffusion coefficients $D_{\alpha\beta}$ (m^2/s) as functions of the temperature T. Straight lines: inert mixture; dotted lines: $H_2 + Cl \rightharpoonup HCl + H$; dashed lines: $H_2 + Cl \leftharpoondown HCl + H$.

number of collisions that result in chemical reactions reduces due to a decrease of the exponential term $e^{-\epsilon_f^\star}$. One can also infer from these figures that all coefficients become smaller than the corresponding coefficients in the inert case. Moreover, this difference becomes more accentuated as the temperature increases. Besides, the coefficients are more affected at high temperatures when the reaction proceeds from left to right than the one from right to left. This fact can be easily understood since the steric factor and the reactive cross section of the former case are larger than those of the latter case (see Table 9.3).

If one compares the behavior of the shear viscosity with the thermal conductivity—left and right frames of Figure 9.6—one concludes that the latter is more affected by the reactions. This fact is a direct consequence of the influence of the binding energies on the energy transport (see (9.116) and (9.118)). With respect to the diffusion coefficients, one may observe from Figure 9.7 and the left frame of Figure 9.8 that the effect of the reaction is larger for the constituents which have heavier masses. As previously discussed in the inert case, one may infer from the right frame of Figure 9.8 that the thermal–diffusion ratios of the heavier molecules are positive, whereas those of the lighter molecules are negative.

One important fact to call attention is that in the calculation of the transport coefficients of shear viscosity, thermal conductivity, diffusion and thermal–diffusion ratio (Figures 9.6–9.8), the molar fractions were considered as a function of the temperature according to (9.121) (see also the left frame of Figure 9.5).

To sum up, one may conclude that all transport coefficients plotted in Figures 9.6–9.8 have a common characteristic for the analyzed reaction

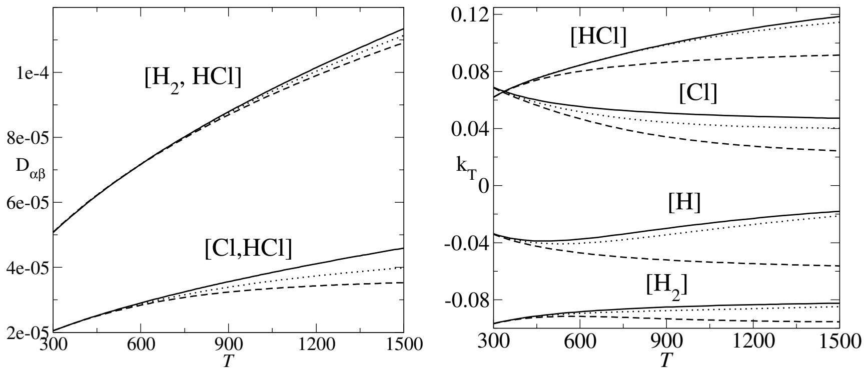

Fig. 9.8 Left frame: diffusion coefficients (m^2/s); right frame: thermal–diffusion ratio as function of the temperature T (K). Straight lines: inert mixture; dotted lines: $H_2 + Cl \rightharpoonup HCl + H$; dashed lines: $H_2 + Cl \leftharpoondown HCl + H$.

$H_2 + Cl \rightleftharpoons HCl + H$, namely, **(i)** all coefficients are smaller than the corresponding coefficients in the inert case; **(ii)** the coefficients are more affected at high temperatures when the reaction proceeds from left to right than the one from right to left; **(iii)** the coefficients tend to their inert values as the temperature decreases and **(iv)** the steric factor plays an important role concerning the effect of the chemical reactions on the transport coefficients.

Exercises

9.17 Obtain the steric factors of Table 9.3.

9.18 By using (9.121), plot the equilibrium molar fractions as functions of the temperature.

9.6.4 Remarks on the Reactive Contributions to the Transport Coefficients

One may conclude from the last section that the influence of the chemical reactions on the transport coefficients is small. As mentioned previously, there exist two factors that makes this influence to be small, namely, the barrier associated with the activation energy and the steric factor which reduces the reactive collision section. This means that the large part of the collisions results from elastic scattering, since only few particles go beyond the activation energy barrier.

In Figure 9.9, the distribution function of the relative velocity modulus versus the relative velocity modulus and the location of the forward

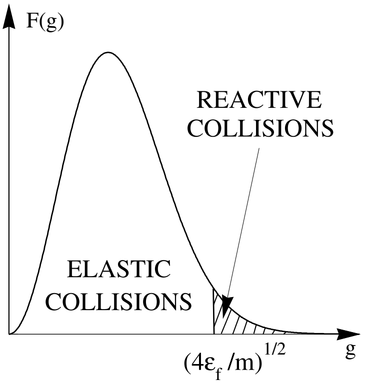

Fig. 9.9 Distribution function of the relative velocity modulus versus the relative velocity modulus.

activation energy are plotted schematically. This figure indicates that the reactive contributions turns out to be smaller than the elastic contributions. Therefore, the reactive collisions occur only for those pairs of molecules which have relative translational energy larger than the activation energy, whereas almost elastic collisions occur for low energy levels.

However, if one takes a look into the expression of the system of the Boltzmann equations (9.31) with the reactive collisional terms given by (9.35) and (9.36), one may conclude that the elastic and reactive collisions are counting twice when $g \geqslant \sqrt{4\epsilon_f/m}$. In this sense, there exists some overlapping for high energies since both the elastic and the reactive collisions are taken into account.

This is not a serious problem when one is dealing with chemical reactions with higher activation energies, but it turns out to be a critical problem when one is dealing with chemical reactions which proceed without going beyond an energy barrier and whose differential cross section is given by (9.71). In this case, one has to reformulate the system of the Boltzmann equations and this will be the subject of Section 9.8.2.

9.7 Trend to Equilibrium of $H_2 + Cl \rightleftharpoons HCl + H$

In this section, the trend to equilibrium of the chemical reaction $H_2 + Cl \rightleftharpoons HCl + H$ will be analyzed when the reactive mixture is displaced from its thermal–mechanical and chemical equilibrium state. In order to achieve this objective, one searches for the spatially homogeneous solutions of the system of balance equations (9.43), (9.47) and (9.50) which turns out to be a system of field equations—for the fields of mass density ϱ_α, hydrodynamic velocity v_i^α and temperature $T_\alpha = 2m_\alpha\varepsilon_\alpha/3k$—once one knows the constitutive equations for mass production density τ_α, momentum production density π_i^α and energy production density ζ_α. This will be the subject of the next analysis, which is based on the work.[11]

9.7.1 Determination of the Production Terms

For the determination of the production terms, one has to choose the elastic and reactive differential cross sections and the input distribution function of each constituent. The elastic differential cross section adopted here is the one which corresponds to a hard-sphere potential (9.67), whereas the reactive differential cross section refers to the line-of-centers model (9.69) and (9.70). The input distribution function is obtained from the Maxwellian distribution

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[11] G.M. Kremer, M.P. Bianchi & A.J. Soares, "Analysis of the trend to equilibrium of a chemically reacting system", *J. Phys. A*, **40**, 2553-2571 (2007).

function in the constituent rest frame with temperature T_α and velocity v_i^α, namely,

$$f_\alpha = n_\alpha \left(\frac{m_\alpha}{2\pi k T_\alpha} \right)^{\frac{3}{2}} \mathrm{e}^{-\frac{m_\alpha (c_i^\alpha - v_i^\alpha)^2}{2kT_\alpha}} . \tag{9.122}$$

The above distribution function is then approximated, through a first-order expansion around a Maxwellian distribution function in the mixture rest frame with temperature T, as follows

$$f_\alpha = n_\alpha \left(\frac{m_\alpha}{2\pi k T} \right)^{\frac{3}{2}} \mathrm{e}^{-\frac{m_\alpha \xi_\alpha^2}{2kT}} \left[1 + \frac{m_\alpha \xi_i^\alpha}{kT} u_i^\alpha + \left(\frac{m_\alpha \xi_\alpha^2}{2kT} - \frac{3}{2} \right) \varDelta_\alpha \right] . \tag{9.123}$$

The distribution function (9.123) thus represents a linearization of the Maxwellian distribution function (9.122), with respect to the diffusion velocity $u_i^\alpha = v_i^\alpha - v_i$ and the temperature difference $\varDelta_\alpha = (T_\alpha - T)/T$. It is relevant to observe that the individual particle number densities n_α are not correlated by the chemical equilibrium condition (9.5). For this reason, the input distribution function (9.123) can be regarded as a deviation from the thermal–mechanical equilibrium only. The dependence of the distribution function (9.123) on each species temperature allows to appreciate the mixture effects in a more detailed fashion for what concerns the reaction mechanism and the heat and the mass exchanges.

The computation of the production terms proceeds by inserting the distribution function (9.123) together with the differential cross sections (9.67), (9.69) and (9.70) into the definitions of the production terms (9.44), (9.49) and (9.52) and by integrating the resulting equations. By neglecting all nonlinear terms, one obtains the following expressions:

(a) *Mass production density*

$$\tau_\alpha = \nu_\alpha m_\alpha n_\alpha^{\mathrm{eq}} n_\gamma^{\mathrm{eq}} \mathsf{k}_\alpha^{(0)} \Bigg\{ \mathcal{A}^\star - \sum_{\beta=1}^{4} \nu_\beta (1 - M_\beta) \Bigg[\left(\epsilon_\beta^\star + \frac{1}{2} \right) + \nu_\beta Q^\star \left(1 - \delta_{\alpha\beta} - \delta_{\gamma\beta} \right) \Bigg] \varDelta_\beta \Bigg\}, \tag{9.124}$$

(b) *Momentum production density*

$$\pi_i^\alpha = -\frac{8}{3} \mathsf{d}_{\alpha\beta}^2 \sqrt{\frac{2\pi k T}{m_{\alpha\beta}}} n_\alpha n_\beta m_{\alpha\beta} (u_i^\alpha - u_i^\beta) + \tau_\alpha v_i - m_\alpha n_\alpha^{\mathrm{eq}} n_\gamma^{\mathrm{eq}} \mathsf{k}_\alpha^{(0)} \left[\nu_\alpha \sum_{\beta=1}^{4} \nu_\beta M_\beta u_i^\beta + \frac{2}{3} (\epsilon_\alpha^\star + 2) M_\gamma (u_i^\alpha - u_i^\gamma) \right], \tag{9.125}$$

(c) *Energy production density*

$$
\begin{aligned}
\zeta_\alpha = {} & 8\sqrt{\frac{2\pi kT}{m_{\alpha\beta}}}\, n_\alpha n_\beta kT \mathsf{d}^2_{\alpha\beta} M_\alpha M_\beta (\mathit{\Delta}_\beta - \mathit{\Delta}_\alpha) + v_i \pi_i^\alpha + \left(\frac{1}{2} m_\alpha v^2 + \epsilon_\alpha\right)\tau_\alpha \\
& + \frac{1}{2}\, kT n_\alpha^{\mathrm{eq}} n_\gamma^{\mathrm{eq}} \mathsf{k}_\alpha^{(0)} \nu_\alpha \Bigg\{ \Bigg[3M_\alpha + 2M_\gamma(\epsilon_\alpha^\star + 2) \Bigg] \mathcal{A}^\star - M_\alpha \sum_{\beta=1}^{4} \nu_\beta \Bigg[\frac{15}{2} M_\beta - \frac{9}{2} \\
& \qquad + 3(\epsilon_\beta^\star + 2)(1 - M_\beta)\left(1 - \frac{m_\gamma}{m_\alpha}\right) + 4(1 - M_\alpha)(\delta_{\alpha\beta} - \delta_{\gamma\beta})(\epsilon_\beta^\star + 2) \\
& \qquad + 3\nu_\beta Q^\star (1 - M_\beta)(1 - \delta_{\alpha\beta} - \delta_{\gamma\beta}) + 2\frac{m_\gamma}{m_\alpha}(1 - M_\beta)[{\epsilon_\beta^\star}^2 + 4\epsilon_\beta^\star + 6 \\
& \qquad + \nu_\beta (1 - \delta_{\alpha\beta} - \delta_{\gamma\beta}) Q^\star (\epsilon_\beta^\star + 2)] \Bigg] \mathit{\Delta}_\beta \Bigg\}. \qquad (9.126)
\end{aligned}
$$

Above, $\alpha = 1, 2, 3, 4$ corresponds to $\gamma = 2, 1, 4, 3$ and one has to identify: $\mathsf{k}_1^{(0)} = \mathsf{k}_2^{(0)} = \mathsf{k}_f^{(0)}$; $\mathsf{k}_3^{(0)} = \mathsf{k}_4^{(0)} = \mathsf{k}_r^{(0)}$; $\epsilon_1^\star = \epsilon_2^\star = \epsilon_f^\star$ and $\epsilon_3^\star = \epsilon_4^\star = \epsilon_r^\star$. Furthermore, the first approximation to the forward reaction rate coefficient is given by (9.76) and the abbreviation $M_\alpha = m_\alpha/(m_\alpha + m_\gamma)$ was introduced.

Exercises

9.19 Determine the distribution function (9.123) from (9.122).

9.20 Obtain the mass production density (9.124).

9.7.2 Constituents at Same Temperature

The thermodynamical description of a mixture whose constituents are at the same temperature—which is the temperature of the mixture—is determined from the knowledge of the space–time evolution of the basic fields of partial particle number densities n_α, partial velocities v_i^α and temperature of the mixture T. The field equations for these basic fields are given by the balance equations (9.43), (9.47) and (9.55), supplied by the constitutive equations for the constitutive quantities. In the spatially homogeneous case, the fields depend only on time, and for processes close to the equilibrium state, one can write the partial particle number densities as

$$
n_\alpha(t) = n_\alpha^{\mathrm{eq}}[1 + \overline{n}_\alpha(t)], \qquad (\alpha = 1, \ldots, 4) \qquad (9.127)
$$

where $\overline{n}_\alpha(t)$ is a small deviation from the equilibrium state. Without loss of generality, the x-axis is chosen for the perturbation of the partial velocities, or equivalently for the diffusion velocities, in such a fashion that

$$u_x^\alpha(t) = \overline{u}_\alpha(t), \qquad (\alpha = 1, \dots, 4) \quad \text{with} \quad \sum_{\alpha=1}^{4} m_\alpha n^{\text{eq}} \mathsf{x}_\alpha \overline{u}_\alpha(t) = 0, \quad (9.128)$$

where $\mathsf{x}_\alpha = n_\alpha^{\text{eq}}/n^{\text{eq}}$ represents the equilibrium molar fraction of constituent α. The quantity $\overline{u}_\alpha(t)$ is also considered as a small perturbation from equilibrium. Furthermore, the temperature field is written as

$$T(t) = T_{\text{eq}}[1 + \overline{T}(t)], \tag{9.129}$$

where $\overline{T}(t)$ is a small perturbation of the temperature field from the equilibrium temperature T_{eq}.

From the definition of the affinity (9.17) and the relationships (9.127) and (9.129), one can obtain that the affinity is given by

$$\frac{\mathcal{A}}{kT_{\text{eq}}} = \overline{n}_1(t) + \overline{n}_2(t) - \overline{n}_3(t) - \overline{n}_4(t). \tag{9.130}$$

The insertion of (9.124)–(9.126) together with (9.127)–(9.130) into the balance equations (9.43), (9.47) and (9.55) leads to a linearized system of differential equations for $\overline{n}_\alpha$, $\overline{u}_\alpha$ and $\overline{T}$, which reads

$$\mathsf{x}_\alpha \frac{d\overline{n}_\alpha}{dt} = \nu_\alpha \mathsf{x}_\alpha \zeta_{\alpha\gamma}^R (\overline{n}_1 + \overline{n}_2 - \overline{n}_3 - \overline{n}_4), \qquad \alpha = 1, \dots, 4; \tag{9.131}$$

$$\frac{d\overline{u}_\alpha}{dt} = -\sum_{\beta=1}^{4} \zeta_{\alpha\beta}^E M_\beta (\overline{u}_\alpha - \overline{u}_\beta) - \zeta_{\alpha\gamma}^R \Bigg[\nu_\alpha \sum_{\beta=1}^{4} \nu_\beta M_\beta \overline{u}_\beta + \frac{2}{3}(\epsilon_\alpha^\star + 2) M_\gamma (\overline{u}_\alpha - \overline{u}_\gamma) \Bigg], \qquad \alpha = 1, \dots, 4. \tag{9.132}$$

$$\frac{d\overline{T}}{dt} = -\frac{2}{3} \mathsf{x}_1 \zeta_{12}^R Q^\star (\overline{n}_1 + \overline{n}_2 - \overline{n}_3 - \overline{n}_4). \tag{9.133}$$

Note that it was considered $\varDelta_\alpha = 0$, since it was supposed that all constituents are at the same temperature. In the above equations $\zeta_{\alpha\beta}^E$ and $\zeta_{\alpha\gamma}^R$ are elastic and reactive collision frequencies defined by

$$\zeta_{\alpha\beta}^E = \frac{8}{3} \mathsf{d}_{\alpha\beta}^2 \sqrt{\frac{2\pi kT}{m_{\alpha\beta}}} n_\beta^{\text{eq}}, \qquad \zeta_{\alpha\gamma}^R = n_\gamma^{\text{eq}} \mathsf{k}_\alpha^{(0)}, \tag{9.134}$$

respectively.

Equations (9.131) together with (9.133) represent a coupled system of five linearized differential equations for the partial particle number densities and temperature of the mixture, while (9.132) represents a coupled system of three linearized differential equations for the partial diffusion velocities, since due to the constraint $(9.128)_2$ only three among the four equations (9.132) are linearly independent.

Here, the numerical simulations of the system of equations (9.131)–(9.133) are presented for the reaction $H_2{+}Cl \rightleftharpoons HCl{+}H$. The data used are the same as those used in Section 9.6 and it is considered that the mixture's equilibrium particle number density consists of one mole of an ideal gas for which $n = 2.6\times 10^{25}$ molecules/m^3. Furthermore, two equilibrium temperatures for the mixture are considered for the case of an equimolar mixture of reagents and products where $\mathsf{x}_1 = \mathsf{x}_2$ and $\mathsf{x}_3 = \mathsf{x}_4$, namely,

(a) $T_{\mathrm{eq}} = 500$ K, $\mathsf{x}_1^{\mathrm{eq}} = \mathsf{x}_2^{\mathrm{eq}} = 0.366$ and $\mathsf{x}_3^{\mathrm{eq}} = \mathsf{x}_4^{\mathrm{eq}} = 0.134$;
(b) $T_{\mathrm{eq}} = 600$ K, $\mathsf{x}_1^{\mathrm{eq}} = \mathsf{x}_2^{\mathrm{eq}} = 0.357$ and $\mathsf{x}_3^{\mathrm{eq}} = \mathsf{x}_4^{\mathrm{eq}} = 0.143$.

The above equilibrium molar fractions follow from the condition of chemical equilibrium (9.121).

Consider an isolated system where no energy exchanges are allowed. For this kind of system, the sum of the particle number densities (9.127) imposes that

$$\sum_{\alpha=1}^{4} n_\alpha(t) = \sum_{\alpha=1}^{4} n_\alpha^{\mathrm{eq}}, \qquad \text{so that} \qquad \sum_{\alpha=1}^{4} n_\alpha^{\mathrm{eq}}\overline{n}_\alpha(t) = 0. \tag{9.135}$$

Hence, one may fix three particle density perturbations among the four ones and calculate the fourth from (9.135)$_2$. Here, the values of $\overline{n}_1, \overline{n}_2, \overline{n}_4$ were fixed and determined the value of $\overline{n}_3$.

The system of linearized differential equations (9.131) and (9.133) were solved by imposing the following initial conditions where only the particle number densities are perturbed from their equilibrium values:

(i) $\overline{n}_1 = -0.15$, $\overline{n}_2 = 0.05$, $\overline{n}_3 = 0.151$, $\overline{n}_4 = 0.1$ and $\overline{T} = 0$, which means that initially the mixture is at the equilibrium temperature T_{eq}, the affinity is negative ($\mathcal{A}(0)/kT_{\mathrm{eq}} = -0.351 < 0$) and the direction of the reaction takes place from right to left;

(ii) $\overline{n}_1 = 0.1$, $\overline{n}_2 = -0.05$, $\overline{n}_3 = -0.186$, $\overline{n}_4 = 0.05$ and $\overline{T} = 0$, which also means that the initial temperature of the mixture is the equilibrium one, but the affinity is positive ($\mathcal{A}(0)/kT_{\mathrm{eq}} = 0.186 > 0$) and the reaction takes place from left to right.

In Figure 9.10, the behaviors of affinity (left frame) and temperature perturbation (right frame) are shown as functions of a dimensionless time $t^\star = t\zeta_R$, where $\zeta_R = 10^8$ Hz is a mean frequency related to the reactive collisions. The dashed lines correspond to a mixture with an equilibrium temperature equal to $T_{\mathrm{eq}} = 600$ K, whereas the straight lines refer to $T_{\mathrm{eq}} = 500$ K. From the left frame of this figure, one infers that the affinity tends to zero for large times where the system reaches another chemical equilibrium state. Furthermore, one concludes that the time decay of the affinity is faster for $T_{\mathrm{eq}} = 600$ K, i.e., the time decays depend on the temperature, being faster for higher temperatures. The right frame of Figure 9.10 represents the behavior of the temperature perturbation with respect to time, and one infers

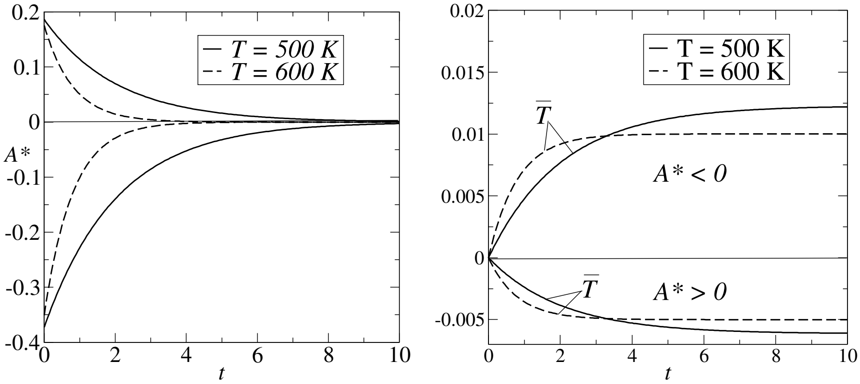

Fig. 9.10 Left frame: Affinity versus time; right frame: temperature's perturbation versus time. Dashed lines $T_{\mathrm{eq}} = 600$ K and solid lines $T_{\mathrm{eq}} = 500$ K.

from this figure that for negative affinities, the temperature of the mixture increases and an exothermic reaction happens, while for positive affinities, an endothermic reaction follows, since the temperature of the mixture decreases. Furthermore, the temperature perturbation tends to a constant value more rapidly when the equilibrium temperature of the mixture is higher, since it is connected with the trend to equilibrium of the affinity.

Table 9.4 Particle number and temperature perturbations for $t^\star = 100$, and the new equilibrium temperatures

Temperature	$\overline{n}_1(100)$	$\overline{n}_2(100)$	$\overline{n}_3(100)$	$\overline{n}_4(100)$	$\overline{T}(100)$	$T_{\mathrm{eq}}(100)$
(i) 500 K	-0.100	0.100	0.036	-0.036	0.012	504 K
(i) 600 K	-0.100	0.100	0.025	-0.025	0.010	606 K
(ii) 500 K	0.075	-0.0751	-0.118	0.118	-0.006	496 K
(ii) 600 K	0.075	-0.075	-0.113	0.113	-0.005	595 K

In Table 9.4, the values of the particle number and temperature perturbations for large times ($t^\star = 100$, say) are shown. From the values of the particle number and temperature perturbations, one may obtain the new equilibrium temperatures by using the condition of chemical equilibrium (9.121). These equilibrium temperatures, which are given in the seventh row of the table, are very close to the ones which follows from (9.129). Note that for negative affinity (case **(i)**), the temperature increases, while for positive affinity (case **(ii)**), the temperature decreases.

For the solution of the coupled system of linearized differential equations (9.132), two sets of initial conditions are imposed for $T = 500$ K. In the first case, $\overline{u}_1 = 0.1$, $\overline{u}_3 = \overline{u}_4 = 0$, whereas $\overline{u}_2$ is calculated from the constraint $(9.128)_2$, which represents a diffusion of the constituents H_2 and Cl, the former in the positive x-direction, the latter in the negative one, with the constituents HCl and H at rest. In the second case, $\overline{u}_1 = \overline{u}_2 = 0$, $\overline{u}_3 = 0.1$, while the value of $\overline{u}_4$ is calculated from the constraint $(9.128)_2$, which represents a diffusion of the constituents HCl and H, the former in the positive x-direction, the latter in the negative one, with now the constituents H_2 and Cl at rest. The trend to equilibrium of the diffusion fluxes, $J_\alpha = m_\alpha n_\alpha^{\mathrm{eq}} \overline{u}_\alpha$, is plotted in Figure 9.11, where now the dimensionless time is given by $t^\star = t\zeta_E$, with $\zeta_E = 4 \times 10^9$ Hz representing a mean collision frequency related to the elastic collisions. The left frame refers to the first case and one can infer that the diffusion of the constituents HCl and H happens in the positive x-direction. Moreover, the diffusion flux of the constituent H is very small due to its small mass, and the decay of the lighter components H and H_2 occurs more rapidly with time than those of the heavier components Cl and HCl. The right frame of Figure 9.11 represents the time evolution of the diffusion fluxes for the second case, and shows that the diffusion of the constituents H_2 and Cl happens in the negative x-direction. The same conclusion as the former case about the trend to equilibrium of the lighter components H and H_2 can be drawn here, i.e., the decay with time is more pronounced than the one of the heavier components Cl and HCl.

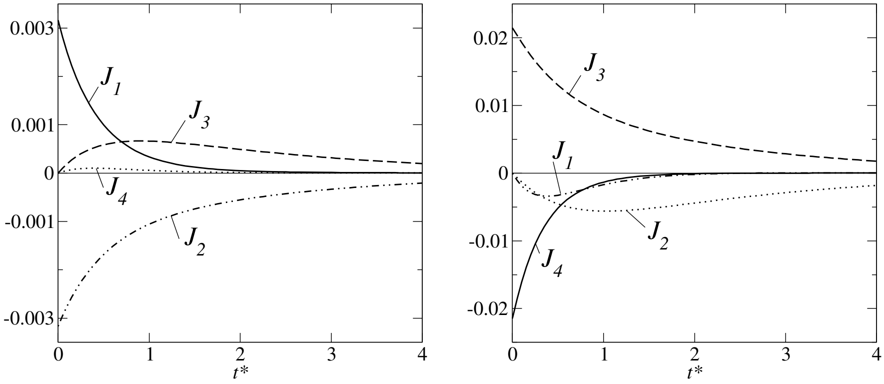

Fig. 9.11 Constituents at same temperature. Diffusion fluxes versus time for $T_{\mathrm{eq}} = 500$ K. Left frame: products initially at rest; right frame: reactants initially at rest.

Exercises

9.21 Obtain the expression for the affinity (9.130).

9.22 Show that the balance equation for the energy of the mixture reduces to the linearized equation (9.133).

9.8 The $\mathcal{H}$-Theorem and the Tendency to Equilibrium

The objective of this section—which is based on the work[12]—is to analyze the tendency to equilibrium of a chemically reacting gas mixture.

Assume that the distribution function is uniform in the space coordinates and introduce a generalized $\mathfrak{H}$-function, which is proportional to the entropy density of the system defined by (9.63), namely,

$$\mathfrak{H} = -\frac{\varrho s}{k} = \sum_{\alpha=1}^{4} \int f_\alpha \ln\left(\frac{\mathsf{b}_\alpha f_\alpha}{m_\alpha^3}\right) d\mathbf{c}_\alpha. \tag{9.136}$$

From the balance of the entropy density of the mixture (9.62), it follows that

$$\frac{d\mathfrak{H}}{dt} = -\frac{1}{k}\frac{d\varrho s}{dt} \leqslant 0, \quad \forall t \in [0, +\infty[\,, \tag{9.137}$$

which assures that the $\mathfrak{H}$-function decreases in time. The following lemma shows that the $\mathfrak{H}$-function is bounded from below by its equilibrium value $\mathfrak{H}_E$.

Lemma 2. *Let $\mathfrak{H}_E$ denote the $\mathfrak{H}$-function referred to the equilibrium Maxwellian distributions $f_\alpha^{(0)}$ given by (9.72). Then*

$$\mathfrak{H} - \mathfrak{H}_E \geqslant 0, \quad \forall t \in [0, +\infty[\,. \tag{9.138}$$

Proof. The substitution of $x = f_\alpha / f_\alpha^{(0)}$ into the well-known convexity inequality $x \ln(x) \geqslant x - 1$, yields

$$f_\alpha \left[\ln f_\alpha - \ln f_\alpha^{(0)}\right] \geqslant f_\alpha - f_\alpha^{(0)}$$

and after some rather simple calculations, one obtains

$$f_\alpha \ln\left(\frac{\mathsf{b}_\alpha f_\alpha}{m_\alpha^3}\right) - f_\alpha^{(0)} \ln\left(\frac{\mathsf{b}_\alpha f_\alpha^{(0)}}{m_\alpha^3}\right) \geqslant \left(f_\alpha - f_\alpha^{(0)}\right)\left[1 + \ln\left(\frac{\mathsf{b}_\alpha f_\alpha^{(0)}}{m_\alpha^3}\right)\right]. \tag{9.139}$$

By integrating the inequality (9.139) over all velocities $\mathbf{c}_\alpha$ and summing over all constituents, one obtains

$$\mathfrak{H} - \mathfrak{H}_E \geqslant \sum_{\alpha=1}^{4} \int \left(f_\alpha - f_\alpha^{(0)}\right)\left[1 + \ln\left(\frac{\mathsf{b}_\alpha f_\alpha^{(0)}}{m_\alpha^3}\right)\right] d\mathbf{c}_\alpha, \tag{9.140}$$

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[12] G.M. Kremer, F. Oliveira & A.J. Soares, "$\mathcal{H}$-theorem and trend to equilibrium of chemically reacting mixtures of gases", *Kinetic and Related Models*, **2**, 333-343 (2009).

thanks to the definition (9.136) of the $\mathfrak{H}$-function. Since $\ln\left(\mathsf{b}_\alpha f_\alpha^{(0)}/m_\alpha^3\right)$ is a collisional invariant, one has from (8.43) that the above expression can be written as

$$\mathfrak{H}-\mathfrak{H}_E \geqslant \sum_{\alpha=1}^{4}\int\left(f_\alpha-f_\alpha^{(0)}\right)\left[1+A_\alpha+m_\alpha B_i c_i^\alpha+D\left(\frac{1}{2}m_\alpha c_\alpha^2+\epsilon_\alpha\right)\right]d\mathbf{c}_\alpha. \tag{9.141}$$

The right-hand-side of the inequality (9.141) vanishes due to the supposition that the Maxwellian distribution functions $f_\alpha^{(0)}$ have the same local macroscopic properties as the solution f_α of the Boltzmann equations (9.31), i.e.,

$$\int f_\alpha d\mathbf{c}_\alpha=\int f_\alpha^{(0)}d\mathbf{c}_\alpha, \tag{9.142}$$

$$\sum_{\alpha=1}^{4}\int m_\alpha c_i^\alpha f_\alpha d\mathbf{c}_\alpha=\sum_{\alpha=1}^{4}\int m_\alpha c_i^\alpha f_\alpha^{(0)}d\mathbf{c}_\alpha, \tag{9.143}$$

$$\sum_{\alpha=1}^{4}\int\left(\frac{1}{2}m_\alpha c_\alpha^2+\epsilon_\alpha\right)f_\alpha d\mathbf{c}_\alpha=\sum_{\alpha=1}^{4}\int\left(\frac{1}{2}m_\alpha c_\alpha^2+\epsilon_\alpha\right)f_\alpha^{(0)}d\mathbf{c}_\alpha. \tag{9.144}$$

Finally, one gets $\mathfrak{H}\geqslant\mathfrak{H}_E$, and the proof is complete.

The next theorem shows that the Boltzmann equations (9.31) describe a reacting mixture which for very large times evolves toward an equilibrium state.

Theorem 3. *By assuming that $\mathfrak{H}$ is a continuously differentiable function, $\mathfrak{H}\in\mathcal{C}^1([0;+\infty[)$, and that every f_α is uniformly bounded and equicontinuous in t, then*

$$\lim_{t\to+\infty}\mathfrak{H}(t)=\mathfrak{H}_E.$$

Proof. By taking into account the decreasing behavior of $\mathfrak{H}$—see the inequality (9.137)—and the lower bound of $\mathfrak{H}$ stated in Lemma 2, the Lagrange's theorem assures the existence of $t_n\in\,]n,n+1[$, such that

$$\frac{d\mathfrak{H}}{dt}(t_n)=\frac{\mathfrak{H}(n+1)-\mathfrak{H}(n)}{(n+1)-n}\,. \tag{9.145}$$

Therefore,

$$\lim_{n\to\infty}t_n=+\infty\qquad\text{and}\qquad\lim_{n\to\infty}\frac{d}{dt}\mathfrak{H}(t_n)=\ell-\ell=0,$$

where $\ell=\lim_{t\to\infty}\mathfrak{H}(t)$, whose existence results from the boundedness and decreasing behavior of $\mathfrak{H}$.

Furthermore, the Ascoli-Arzelás theorem assures the existence of a convergent subsequence of

$$f_n^{(\alpha)} \overset{\text{def}}{=} f_\alpha(t_n),$$

which will be still denoted by $f_n^{(\alpha)}$, such that $\lim_{n\to\infty} f_n^{(\alpha)} = f_\alpha^\infty$. Moreover, the convergence is uniform in $\mathbf{c}_\alpha$ in any compact set $\mathcal{S} \subset \mathbb{R}^3$.

The proof proceeds by showing that the identities

$$f'^{\infty}_\alpha \, f'^{\infty}_\beta = f_\alpha^\infty \, f_\beta^\infty, \quad \text{for all} \quad \alpha, \beta \in \{1, \ldots, 4\}, \tag{9.146}$$

$$f_3^\infty \, f_4^\infty = \left(\frac{m_{34}}{m_{12}}\right)^3 f_1^\infty \, f_2^\infty, \tag{9.147}$$

hold. Otherwise, one can find a compact set of positive measure in $\mathbb{R}^3$, say $\mathcal{C}$, and constants $N \geqslant 0$ and $M_{\alpha\beta} \geqslant 0$ for some $\alpha, \beta \in \{1, \ldots, 4\}$, such that

$$\left| f'^{\infty}_\alpha \, f'^{\infty}_\beta - f_\alpha^\infty \, f_\beta^\infty \right| \geqslant M_{\alpha\beta}, \quad \forall \mathbf{c}_\alpha, \mathbf{c}_\beta, \mathbf{c}'_\alpha, \mathbf{c}'_\beta \in \mathcal{C},$$

$$\left| f_3^\infty \, f_4^\infty - \left(\frac{m_{34}}{m_{12}}\right)^3 f_1^\infty \, f_2^\infty \right| \geqslant N, \quad \forall \mathbf{c}_1, \mathbf{c}_2, \mathbf{c}_3, \mathbf{c}_4 \in \mathcal{C},$$

where $N > 0$ or $M_{\alpha\beta} > 0$.

Due to the uniform convergence of $f_n^{(\alpha)}$ to f_α^∞, for n_0 large enough and $n \geqslant n_0$, one has

$$\left| f'^{(\alpha)}_n \, f'^{(\beta)}_n - f_n^{(\alpha)} \, f_n^{(\beta)} \right| \geqslant \frac{M_{\alpha\beta}}{2}, \quad \forall \mathbf{c}_\alpha, \mathbf{c}_\beta, \mathbf{c}'_\alpha, \mathbf{c}'_\beta \in \mathcal{C}, \tag{9.148}$$

$$\left| f_n^{(3)} \, f_n^{(4)} - \left(\frac{m_{34}}{m_{12}}\right)^3 f_n^{(1)} \, f_n^{2)} \right| \geqslant \frac{N}{2}, \quad \forall \mathbf{c}_1, \mathbf{c}_2, \mathbf{c}_3, \mathbf{c}_4 \in \mathcal{C}. \tag{9.149}$$

Moreover, since $f^{(\alpha)}$ is bounded, say by a positive constant F_α, one obtains

$$\left| \ln\left(\frac{f_n^{(\alpha)} \, f_n^{(\beta)}}{f'^{(\alpha)}_n f'^{(\beta)}_n} \right) \right| = \left| \ln\left(1 + \frac{f_n^{(\alpha)} f_n^{(\beta)} - f'^{(\alpha)}_n f'^{(\beta)}_n}{f'^{(\alpha)}_n f'^{(\beta)}_n} \right) \right|$$

$$\geqslant \ln\left(1 + \left| \frac{f_n^{(\alpha)} f_n^{(\beta)} - f'^{(\alpha)}_n f'^{(\beta)}_n}{f'^{(\alpha)}_n f'^{(\beta)}_n} \right| \right) \geqslant \ln\left(1 + \frac{M_{\alpha\beta}}{2F_\alpha^2} \right), \tag{9.150}$$

and

$$\left| \ln\left[\left(\frac{m_{34}}{m_{12}}\right)^3 \frac{f_n^{(1)} f_n^{(2)}}{f_n^{(3)} f_n^{(4)}} \right] \right| \geqslant \ln\left(1 + \frac{N}{2F_3 F_4} \right). \tag{9.151}$$

Now, from (9.148)–(9.151), it follows that

$$\left| f'^{(\alpha)}_n \, f'^{(\beta)}_n - f_n^{(\alpha)} \, f_n^{(\beta)} \right| \left| \ln\left(\frac{f_n^{(\alpha)} \, f_n^{(\beta)}}{f'^{(\alpha)}_n f'^{(\beta)}_n} \right) \right| > \frac{M_{\alpha\beta}}{2} \ln\left(1 + \frac{M_{\alpha\beta}}{2F_\alpha^2} \right), \tag{9.152}$$

$$\left| f_n^{(3)}\, f_n^{(4)} - \left(\frac{m_{34}}{m_{12}}\right)^3 f_n^{(1)}\, f_n^{2)} \right| \left| \ln\left[\left(\frac{m_{34}}{m_{12}}\right)^3 \frac{f_n^{(1)} f_n^{(2)}}{f_n^{(3)} f_n^{(4)}} \right] \right| \\ > \frac{N}{2} \ln\left(1 + \frac{N}{2F_3F_4}\right). \qquad (9.153)$$

Therefore, for $n \geqslant n_0$, one obtains

$$-\frac{d}{dt}\mathfrak{H}(t_n) > \frac{1}{4} \sum_{\alpha=1}^{4} \sum_{\beta=1}^{4} \frac{M_{\alpha\beta}}{2} \ln\left(1 + \frac{M_{\alpha\beta}}{2F_\alpha^2}\right) \int_{\mathcal{C}\times\mathcal{C}} g_{\beta\alpha}\sigma_{\beta\alpha} d\Omega\, d\mathbf{c}_\beta d\mathbf{c}_\alpha \\ + \frac{N}{2} \ln\left(1 + \frac{N}{2F_3F_4}\right) \int_{\mathcal{C}\times\mathcal{C}} \sigma_{12}^\star g_{21} d\Omega^\star d\mathbf{c}_1 d\mathbf{c}_2, \qquad (9.154)$$

by multiplying the inequalities (9.152) and (9.153) by $g_{\beta\alpha}\sigma_{\beta\alpha} d\Omega\, d\mathbf{c}_\beta d\mathbf{c}_\alpha$ and $\sigma_{12}^\star g_{21} d\Omega^\star d\mathbf{c}_1 d\mathbf{c}_2$, respectively, then integrating over all velocities and, finally, by taking the sum of the latter resulting inequality together with the former one, previously summed over all constituents α and β.

Now, from the positivity of the measure of the compact set $\mathcal{C}$ and the inequality (9.154), in view of $N > 0$ or $M_{\alpha\beta} > 0$, there exists a positive constant, say A, such that

$$-\frac{d}{dt}\mathfrak{H}(t_n) > A > 0. \qquad (9.155)$$

This last conclusion is absurd, since $\lim_{n\to\infty} \frac{d}{dt}\mathfrak{H}(t_n) = 0$. Therefore, (9.146) and (9.147) hold.

Consequently, the $\mathfrak{H}$-function has a critical point for $f_\alpha = f_\alpha^\infty$, as it can be seen from the expression (9.137) for its time derivative. Finally, the convexity of the $\mathfrak{H}$-functional on the manifold defined by the conservation of moments (9.142)–(9.144) implies that this critical point corresponds to the minimum of $\mathfrak{H}$, attained for $f_\alpha = f_\alpha^{(0)}$. Therefore, $f_\alpha^\infty = f_\alpha^{(0)}$, so that

$$\lim_{n\to\infty} f_n^{(\alpha)} = f_\alpha^{(0)} \qquad \text{and} \qquad \lim_{t\to+\infty} \mathfrak{H}(t) = \mathfrak{H}_E. \qquad (9.156)$$

This completes the proof of Theorem 3.

From the proof of the previous theorem, it results, in particular, that $\lim_{t\to+\infty} f_\alpha(t) = f_\alpha^{(0)}(t)$ and the next theorem shows that this convergence is strong in the L^1-norm.

Theorem 4. *Under the assumptions of Theorem 3, f_α converges in strong L^1-sense to $f_\alpha^{(0)}$.*

Proof. The idea is to use a rather sophisticated convexity inequality. In fact, it is not difficult to check the existence of a constant $C > 0$ such that

$$x \ln x + 1 - x \geqslant C|x-1|\, G\big(|x-1|\big), \quad \text{for all } x > 0, \qquad (9.157)$$

where G is the function defined by

$$G\big(|x-1|\big)=\begin{cases}|x-1| & \text{if}\ \ 0\leqslant|x-1|\leqslant 1,\\ 1 & \text{if}\ \ |x-1|>1.\end{cases}\tag{9.158}$$

Now, inserting $x=f_\alpha/f_\alpha^{(0)}$ into the inequality (9.157), one obtains

$$f_\alpha\left(\ln f_\alpha-\ln f_\alpha^{(0)}\right)\geqslant f_\alpha-f_\alpha^{(0)}+C\left|f_\alpha-f_\alpha^{(0)}\right|G\left(\left|\frac{f_\alpha}{f_\alpha^{(0)}}-1\right|\right),$$

and after some rearrangements, it results in

$$\begin{aligned}f_\alpha\ln\left(\frac{\mathsf{b}_\alpha f_\alpha}{m_\alpha^3}\right)-f_\alpha^{(0)}\ln\left(\frac{\mathsf{b}_\alpha f_\alpha^{(0)}}{m_\alpha^3}\right)\geqslant\left(f_\alpha-f_\alpha^{(0)}\right)\left[1+\ln\left(\frac{\mathsf{b}_\alpha f_\alpha^{(0)}}{m_\alpha^3}\right)\right]\\+C\left|f_\alpha-f_\alpha^{(0)}\right|G\left(\left|\frac{f_\alpha}{f_\alpha^{(0)}}-1\right|\right).\end{aligned}\tag{9.159}$$

From the definition (9.136) of the $\mathfrak{H}$-function, one obtains by integrating the inequality (9.159) over all velocities $\mathbf{c}_\alpha$ and summing over all constituents

$$\mathfrak{H}(t)-\mathfrak{H}_E\geqslant\sum_{\alpha=1}^{4}\int C\left|f_\alpha-f_\alpha^{(0)}\right|G\left(\left|\frac{f_\alpha}{f_\alpha^{(0)}}-1\right|\right)d\mathbf{c}_\alpha.\tag{9.160}$$

Above, the constraints (9.142)–(9.144) has been used and the fact that $\ln\left(\mathsf{b}_\alpha f_\alpha^{(0)}/m_\alpha^3\right)$ defines a collisional invariant. Now, by introducing the sets

$$\begin{aligned}D_\alpha^1&=\left\{\mathbf{c}_\alpha\in\mathbb{R}^3:\ \left|f_\alpha-f_\alpha^{(0)}\right|\leqslant f_\alpha^{(0)}\right\},\\ D_\alpha^2&=\left\{\mathbf{c}_\alpha\in\mathbb{R}^3:\ \left|f_\alpha-f_\alpha^{(0)}\right|>f_\alpha^{(0)}\right\},\end{aligned}$$

and by taking into account the definition (9.158) of the function G, one obtains from the inequality (9.160):

$$\mathfrak{H}(t)-\mathfrak{H}_E\geqslant\sum_{\alpha=1}^{4}\int_{D_\alpha^1}\frac{C}{f_\alpha^{(0)}}\left|f_\alpha-f_\alpha^{(0)}\right|^2d\mathbf{c}_\alpha+\sum_{\alpha=1}^{4}\int_{D_\alpha^2}C\left|f_\alpha-f_\alpha^{(0)}\right|d\mathbf{c}_\alpha\geqslant 0.\tag{9.161}$$

Due to the relationship $\lim_{t\to+\infty}\mathfrak{H}(t)=\mathfrak{H}_E$, the passage to the limit $t\longrightarrow+\infty$ in the inequality (9.161) gives

$$\lim_{t\to+\infty}\left[\sum_{\alpha=1}^{4}\int_{D_\alpha^1}\frac{C}{f_\alpha^{(0)}}\left|f_\alpha-f_\alpha^{(0)}\right|^2d\mathbf{c}_\alpha+\sum_{\alpha=1}^{4}\int_{D_\alpha^2}C\left|f_\alpha-f_\alpha^{(0)}\right|d\mathbf{c}_\alpha\right]=0.\tag{9.162}$$

This last limit condition can be verified if and only if

$$\lim_{t\to+\infty}\int_{D^1_\alpha}\frac{1}{f^{(0)}_\alpha}\left|f_\alpha-f^{(0)}_\alpha\right|^2 d\mathbf{c}_\alpha=0 \quad \text{and} \quad \lim_{t\to+\infty}\int_{D^2_\alpha}\left|f_\alpha-f^{(0)}_\alpha\right| d\mathbf{c}_\alpha=0, \tag{9.163}$$

because all contributions to the sums in (9.162) have the same non-negative sign. Now, by recalling the Cauchy–Schwarz inequality, one can write

$$\begin{aligned}\int_{D^1_\alpha}\left|f_\alpha-f^{(0)}_\alpha\right| d\mathbf{c}_\alpha &= \int_{D^1_\alpha}\sqrt{f^{(0)}_\alpha}\,\frac{\left|f_\alpha-f^{(0)}_\alpha\right|}{\sqrt{f^{(0)}_\alpha}}\,d\mathbf{c}_\alpha \\ &\leqslant \left[\int_{D^1_\alpha} f^{(0)}_\alpha d\mathbf{c}_\alpha\right]^{\frac12}\left(\int_{D^1_\alpha}\frac{\left|f_\alpha-f^{(0)}_\alpha\right|^2}{f^{(0)}_\alpha}\,d\mathbf{c}_\alpha\right)^{\frac12}. \end{aligned} \tag{9.164}$$

By combining the inequality (9.164) with the condition $(9.163)_1$, it follows that

$$\lim_{t\to\infty}\int_{D^1_\alpha}\left|f_\alpha-f^{(0)}_\alpha\right| d\mathbf{c}_\alpha=0. \tag{9.165}$$

Finally, since

$$\int_{D^1_\alpha}\left|f_\alpha-f^{(0)}_\alpha\right| d\mathbf{c}_\alpha+\int_{D^2_\alpha}\left|f_\alpha-f^{(0)}_\alpha\right| d\mathbf{c}_\alpha=\int\left|f_\alpha-f^{(0)}_\alpha\right| d\mathbf{c}_\alpha,$$

the conditions $(9.163)_2$ and (9.165) imply that

$$\lim_{t\to\infty}\int\left|f_\alpha-f^{(0)}_\alpha\right| d\mathbf{c}_\alpha=0,$$

which means that f_α converges strongly to $f^{(0)}_\alpha$ in the L^1-sense. The proof is then complete.

Exercises

9.23 Obtain the inequality (9.139).

9.24 Check the inequality (9.157).

9.9 Symmetric Reactions

The symmetric reaction $A+A \rightleftharpoons B+B$ is a particular case of the bimolecular reaction $A_1+A_2 \rightleftharpoons A_3+A_4$ where the constituents A and B have the same masses $m_A = m_B = m$ and the same diameters $\mathsf{d}_A = \mathsf{d}_B = \mathsf{d}$. In Sections 9.6 and 9.7, reacting systems which were nearby the chemical equilibrium state where the frequencies of the reacting collisions were of the same order of magnitude as those of the elastic ones (fast reactions) was studied and the affinity was considered as a small quantity in comparison with the thermal energy of the mixture ($|\mathcal{A}|/kT < 1$). The transport coefficients for the symmetric reactions which are close to the chemical equilibrium follow as particular cases of the results of Section 9.6 and will not be analyzed here.

9.9.1 The Influence of the Heat of Reaction on Slow Reactions

The aim of this section is to analyze the case where the reactions are considered far from the chemical equilibrium (slow reactions), which refers to the initial stage of a chemical reaction. In this case, the frequencies of the elastic collisions are larger than those of the reactive ones and the affinity is much larger than the thermal energy of the mixture, i.e., $|\mathcal{A}|/kT \gg 1$. It will be shown that in this case the heat of reaction has a predominant influence on the Maxwellian distribution function and on the reaction rate coefficient. This section is based on the work.[13]

For symmetric reactions, one obtains from (9.15) and (9.17) that the heat of reaction and the affinity are given by

$$Q = 2(\epsilon_B - \epsilon_A) = \left(\frac{n_A^{\mathrm{eq}}}{n_B^{\mathrm{eq}}}\right)^2, \qquad \mathcal{A}^\star = -Q^\star + \ln\left(\frac{n_A}{n_B}\right)^2, \tag{9.166}$$

respectively. Furthermore, the conservation laws of linear momentum and total energy for the reactive collisions are given by

$$m\mathbf{c}_A + m\mathbf{c}_{A_1} = m\mathbf{c}_B + m\mathbf{c}_{B_1}, \quad \epsilon_A + \frac{m}{4}(\mathbf{c}_A^2 + \mathbf{c}_{A_1}^2) = \epsilon_B + \frac{m}{4}(\mathbf{c}_B^2 + \mathbf{c}_{B_1}^2), \tag{9.167}$$

and the conservation law of total energy $(9.167)_2$ can be rewritten as

$$\frac{1}{4}mg_A^2 = \frac{1}{4}mg_B^2 + Q. \tag{9.168}$$

To begin with, one may rewrite the system of reacting Boltzmann equations (9.31) for the case in study as

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[13] G.M. Kremer & A.J. Soares, "Effect of reaction heat on Maxwellian distribution functions and rate of reactions", *J. Stat. Mech.*, **P12003** (2007).

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = \sum_{\beta=A}^{B} \int \left(f'_\alpha f'_\beta - f_\alpha f_\beta\right) g_{\beta\alpha}\sigma_{\beta\alpha} d\Omega\, d\mathbf{c}_\beta + \mathcal{Q}_\alpha^R, \qquad (9.169)$$

where the reactive collision term is given by

$$\mathcal{Q}_\alpha^R = \int \left[f_\gamma f_{\gamma_1} - f_\alpha f_{\alpha_1}\right] \sigma_\alpha^\star g_\alpha d\Omega^\star d\mathbf{c}_{\alpha_1}, \qquad \alpha = A, B \qquad (9.170)$$

where the index $\alpha = A, B$ corresponds to $\gamma = B, A$, respectively. Furthermore, $(\mathbf{c}_A, \mathbf{c}_{A_1})$ and $(\mathbf{c}_B, \mathbf{c}_{B_1})$ are the velocities of the reactants and products of the forward reaction, respectively, and the sub-index 1 is used to distinguish two identical molecules that participate in the reactive collision. The reactive differential cross section is denoted by $\sigma_\alpha^\star$ and the relative velocity by $\mathbf{g}_\alpha = \mathbf{c}_{\alpha_1} - \mathbf{c}_\alpha$.

As in Section 9.4, it will be considered that the elastic collisions are described by the differential cross sections of hard spheres $\sigma_{\alpha\beta} = \mathsf{d}^2/4$, while the differential cross sections for the reactive collisions are given by the line-of centers model, which for the case of study read

$$\sigma_A^\star = \begin{cases} 0, & \text{for} \quad \frac{mg_A^2}{4} < \epsilon_f, \\ \frac{1}{4}(\mathsf{sd})^2 \left(1 - \frac{4\epsilon_f}{mg_A^2}\right), & \text{for} \quad \frac{mg_A^2}{4} \geqslant \epsilon_f, \end{cases} \qquad (9.171)$$

$$\sigma_B^\star = \begin{cases} 0, & \text{for} \quad \frac{mg_B^2}{4} < \epsilon_r, \\ \frac{1}{4}(\mathsf{sd})^2 \left(1 - \frac{4\epsilon_r}{mg_B^2}\right), & \text{for} \quad \frac{mg_B^2}{4} \geqslant \epsilon_r. \end{cases} \qquad (9.172)$$

In the above equations, s denotes the steric factor, ϵ_f is the forward activation energy and $\epsilon_r = \epsilon_f - Q$ is the reverse activation energy.

In the chemical regime for which the reaction is close to its initial stage (slow process), the reactive interactions are less frequent than the elastic collisions. This means that the reactive relaxation time is larger than the elastic one. In this case, the reactive collision term is of the same order of the material time derivatives, while the gradients of the particle number densities, velocity and temperature of the mixture are of successive order. Under these assumptions, the system of Boltzmann equations (9.169) become

$$\mathcal{D} f_\alpha + \epsilon\, \xi_i^\alpha \frac{\partial f_\alpha}{\partial x_i} - \int \left[f_\gamma f_{\gamma_1} - f_\alpha f_{\alpha_1}\right] \sigma_\alpha^\star g_\alpha d\Omega^\star d\mathbf{c}_{\alpha_1}$$
$$= \frac{1}{\epsilon} \sum_{\beta=A}^{B} \int \left(f'_\alpha f'_\beta - f_\alpha f_\beta\right) g_{\beta\alpha}\sigma_{\beta\alpha} d\Omega\, d\mathbf{c}_\beta, \qquad (9.173)$$

where ϵ is a parameter of order of the Knudsen number (see Section 3.3) and $\mathcal{D} = (\partial/\partial t) + v_i \partial/\partial x_i$ is the material time derivative.

According to Section 3.3, in order to apply the Chapman–Enskog method, one should expand the distribution functions and the material time derivative in series. The series expansion of the material time derivative is the same as that given by (3.70), namely,

$$\mathcal{D} = \mathcal{D}_0 + \epsilon\mathcal{D}_1 + \epsilon^2\mathcal{D}_2 + \dots . \tag{9.174}$$

However, the series expansion of the distribution functions differs from the one presented in (3.64), since it is written as

$$f_\alpha = f_\alpha^M + \epsilon f_\alpha^{(0)} + \epsilon^2 f_\alpha^{(1)} + \dots . \tag{9.175}$$

The above representation will be elucidated in the following.

By inserting the expansions (9.174) and (9.175) into the Boltzmann equations (9.173) and by equating equal powers of ϵ, it follows the system of integral equations, namely,

$$0 = \sum_{\beta=A}^{B} \int \left(f_\alpha^{M\prime} f_\beta^{M\prime} - f_\alpha^M f_\beta^M \right) g_{\beta\alpha}\sigma_{\beta\alpha} d\Omega\, d\mathbf{c}_\beta, \tag{9.176}$$

$$\mathcal{D}_0 f_\alpha^M - \int \left[f_\gamma^M f_{\gamma_1}^M - f_\alpha^M f_{\alpha_1}^M \right] \sigma_\alpha^\star g_\alpha d\Omega^\star d\mathbf{c}_{\alpha_1} = \sum_{\beta=A}^{B} \int \big(f_\alpha^{(0)\prime} f_\beta^{M\prime} + f_\alpha^{M\prime} f_\beta^{(0)\prime}$$

$$- f_\alpha^{(0)} f_\beta^M - f_\alpha^M f_\beta^{(0)} \big) g_{\beta\alpha}\sigma_{\beta\alpha} d\Omega\, d\mathbf{c}_\beta. \tag{9.177}$$

Above, only the two first integral equations were considered.

The solutions of the integral equations (9.176) are Maxwellian distribution functions

$$f_\alpha^M = n_\alpha \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m\xi_\alpha^2}{2kT}}, \tag{9.178}$$

where the particle number densities n_α are not correlated with the chemical equilibrium condition (9.5).

For the solution of the integral equations (9.177), one assumes that the heat of reaction affects the distribution functions and one should expect that their solution is no longer a Maxwellian distribution (see the Chapter 7 on granular gases). Therefore, in order to evaluate the effect of the reaction heat, it is convenient to write $f_\alpha^{(0)}$ in terms of Sonine polynomials and retain, at least, up to the second order terms in the expansion, namely,

$$f_\alpha^{(0)} = f_\alpha^M \left[a_1^\alpha \left(\frac{3}{2} - \frac{m\xi_\alpha^2}{2kT} \right) + a_2^\alpha \left(\frac{15}{8} - \frac{5m\xi_\alpha^2}{4kT} + \frac{m^2\xi_\alpha^4}{8(kT)^2} \right) \right], \tag{9.179}$$

where a_1^α and a_2^α are scalar coefficients to be determined from the integral equations (9.177).

The determination of the coefficients a_1^α and a_2^α from the integral equations (9.177) proceeds as follows. First, one may show that the coefficients a_1^α must vanish. Indeed, by writing the distribution function of the constituent α as

$$f_\alpha = f_\alpha^M \left[1 + a_1^\alpha\left(\frac{3}{2} - \frac{m\xi_\alpha^2}{2kT}\right) + a_2^\alpha\left(\frac{15}{8} - \frac{5m\xi_\alpha^2}{4kT} + \frac{m^2\xi_\alpha^4}{8(kT)^2}\right)\right] \tag{9.180}$$

and by inserting it into the definition of the internal energy density of constituent α associated with the translational degrees of freedom, i.e.,

$$\varrho_\alpha\varepsilon_\alpha = \frac{3}{2}n_\alpha kT = \frac{m}{2}\int C_\alpha^2 f_\alpha d\mathbf{c}_\alpha, \tag{9.181}$$

it follows—from the integration of the resulting equation and by neglecting all non-linear terms in the diffusion velocity—that $a_1^\alpha \equiv 0$. Note that it was considered that both constituents are at the same temperature T, which is the temperature of the mixture.

Next, the integral equation (9.177) for the constituent α is multiplied by an arbitrary function $\psi_\alpha(\mathbf{x}, \mathbf{c}_\alpha, t)$ and integrated over all values of $\mathbf{c}_\alpha$, yielding

$$\begin{aligned}\int \psi_\alpha f_\alpha^M &\left\{\frac{\mathcal{D}_0 n_\alpha}{n_\alpha} - \left(\frac{3}{2} - \frac{m\xi_\alpha^2}{2kT}\right)\frac{\mathcal{D}_0 T}{T} + \frac{m}{kT}\xi_i^\alpha \mathcal{D}_0 v_i\right\} d\mathbf{c}_\alpha \\ &- \int \frac{\psi_\alpha + \psi_{\alpha_1}}{2}\left[f_\gamma^M f_{\gamma_1}^M - f_\alpha^M f_{\alpha_1}^M\right]\sigma_\alpha^\star g_\alpha d\Omega^\star d\mathbf{c}_{\alpha_1} d\mathbf{c}_\alpha \\ = \sum_{\beta=A}^{B} &\int (\psi_\alpha' - \psi_\alpha)\big(f_\alpha^{(0)} f_\beta^M + f_\alpha^M f_\beta^{(0)}\big) g_{\beta\alpha}\sigma_{\beta\alpha} d\Omega\, d\mathbf{c}_\beta d\mathbf{c}_\alpha.\end{aligned} \tag{9.182}$$

If one chooses $\psi_\alpha = m$, mc_i^α, and $mc_\alpha^2/2 + \epsilon_\alpha$ in (9.182), one obtains the balance equations for the mass, momentum and energy densities of a non-viscous, non-heat conducting and non-diffusive reactive mixture of gases, respectively. Furthermore, by considering $\psi_\alpha = [15/8 - 5m\xi_\alpha^2/4kT + m^2\xi_\alpha^4/8(kT)^2]$ (with $\alpha = A, B$), the following system of algebraic equations for the determination of the coefficients a_2^α yields:

$$\left(1 - e^{-\mathcal{A}^\star}\right)\frac{\mathsf{s}^2}{2}\left[1 + 4\epsilon_f^\star(1 - \epsilon_f^\star)\right]e^{-\epsilon_f^\star} = \left[16a_2^A + \frac{n_B}{n_A}(31a_2^A - 15a_2^B)\right], \tag{9.183}$$

$$\left(e^{-\mathcal{A}^\star} - 1\right)\frac{\mathsf{s}^2}{2}\left[1 + 4\epsilon_r^\star(1 - \epsilon_r^\star)\right]e^{-\epsilon_f^\star} = \left[16\frac{n_B^2}{n_A^2}a_2^B + \frac{n_B}{n_A}(31a_2^B - 15a_2^A)\right], \tag{9.184}$$

As previously pointed out, the considered chemical regime refers to an early stage of the reaction, where the concentrations of the products are negligible in comparison to those of the reactants and the affinity is very large, i.e., $n_B/n_A \ll 1$ and $\mathcal{A} \to \infty$.

In order to determine the coefficient a_2^A, one proceeds as follows: the sum of (9.183) and (9.184) leads to

$$(1-e^{-\mathcal{A}^\star})\frac{\mathsf{s}^2}{8}Q^\star\left[1-2\epsilon_f^\star+Q^\star\right]e^{-\epsilon_f^\star}=\left(1+\frac{n_B}{n_A}\right)\left[a_2^A+\frac{n_B}{n_A}a_2^B\right], \quad (9.185)$$

and by considering $n_B/n_A \ll 1$ and $\mathcal{A}\to\infty$, it follows that

$$a_2^A=\frac{\mathsf{s}^2}{8}Q^\star\left[1-2\epsilon_f^\star+Q^\star\right]e^{-\epsilon_f^\star}. \quad (9.186)$$

Hence, the distribution function for the constituent A can be written as

$$f_A=n_A\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}e^{-\frac{m\xi_A^2}{2kT}}\left[1+\frac{\mathsf{s}^2}{8}Q^\star\left[1-2\epsilon_f^\star+Q^\star\right]e^{-\epsilon_f^\star}\right.$$
$$\left.\times\left(\frac{15}{8}-\frac{5m\xi_\alpha^2}{4kT}+\frac{m^2\xi_\alpha^4}{8(kT)^2}\right)\right], \quad (9.187)$$

due to (9.180) and (9.186).

One may observe from (9.187) that the deviation from the Maxwellian distribution function has an explicit dependence on the heat of reaction $Q^\star$ and this deviation vanishes when $Q^\star=0$. In Figure 9.12, the dimensionless distribution function $f_A/\left[n_A\left(m/2\pi kT\right)^{3/2}\right]$ is plotted versus the dimensionless quantity $x=\sqrt{m\xi_A^2/2kT}$, for an exothermic process $Q^\star=-2$, for an endothermic process $Q^\star=2$ and for a vanishing heat of reaction $Q^\star=0$.

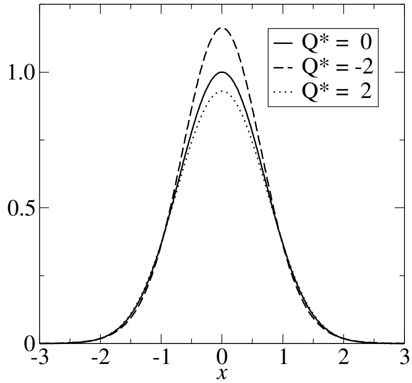

Fig. 9.12 The profile of the dimensionless distribution function $f_A/\left[n_A\left(m/2\pi kT\right)^{3/2}\right]$ as a function of the dimensionless quantity $x=\sqrt{m\xi_A^2/2kT}$, for endothermic process $Q^\star>0$ (dotted line), exothermic process $Q^\star<0$ (dashed line) and $Q^\star=0$ (solid line).

Furthermore, the following values for the forward activation energy and for the steric factor were adopted: $\epsilon_f^\star = 3$ and $\mathsf{s} = 1$. From this figure, one can infer that the heat of reaction modifies the profile of the Maxwellian distribution function and the maximum of the Gaussian curve decreases by increasing the reaction heat, since the maximum of the distribution function is higher for the exothermic process than for the endothermic one.

Once the distribution function (9.187) is known, one may obtain the forward reaction rate coefficient (9.45), which for the symmetric reaction $A + A \rightleftharpoons B + B$ reads

$$\mathsf{k}_f = \frac{1}{n_A^2} \int f_A f_{A_1} \sigma_A^\star g_A d\Omega^\star d\mathbf{c}_A d\mathbf{c}_{A_1}. \tag{9.188}$$

Indeed, from the insertion of the distribution function (9.187) into the above equation, one obtains through the integration of the resulting equation and by neglecting the products of a_2^A:

$$\mathsf{k}_f = 4(\mathsf{sd})^2 \sqrt{\frac{\pi k T}{m}} e^{-\epsilon_f^\star} \left[1 - \underline{\frac{\mathsf{s}^2}{256} Q^\star \left(1 - 2\epsilon_f^\star + Q^\star\right) \left[1 + 4\epsilon_f^\star \left(1 - \epsilon_f^\star\right)\right] e^{-\epsilon_f^\star}} \right]. \tag{9.189}$$

The underlined term represents the contribution of the heat of reaction to the reaction rate coefficient.

In Figure 9.13, the dimensionless reaction rate coefficient $\mathsf{k}_f / \left[(\mathsf{sd})^2 \sqrt{\pi k T / m}\right]$ is plotted as function of the forward activation energy $\epsilon_f^\star$ for $\mathsf{s} = 1$. From this figure, one can conclude that, in comparison with the case $Q^\star = 0$, the reaction rate is larger for an exothermic process and smaller for

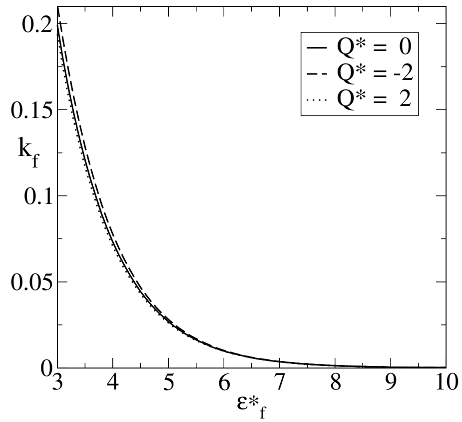

Fig. 9.13 Dimensionless reaction rate coefficient $\mathsf{k}_f / \left[(\mathsf{sd})^2 \sqrt{\pi k T / m}\right]$ as function of the activation energy $\epsilon_f^\star$ for exothermic process (dashed line), endothermic process (dotted line) and $Q^\star = 0$ (solid line).

an endothermic process. This behavior is justified by the contribution of the heat of reaction on the distribution function. One can also observe that by increasing the activation energy, the reaction rate coefficient becomes smaller, since for high values of the activation energy, no chemical reaction occurs, due to the fact that the energy barrier is too high and in this case the reaction rate coefficient tends to zero.

Exercises

9.25 Show from (9.180) and (9.181) that the coefficients a_1^α vanish.

9.26 Obtain the left-hand side of equation (9.185).

9.27 Show that the reaction rate coefficient is given by the expression (9.189).

9.9.2 Chemical Reactions without Activation Energy

In order to treat properly chemical reactions which proceeds without barriers, one should, according to Section 9.6.4, introduce probability coefficients in the elastic and reactive collisional terms, which allow to take into account the contributions from each binary encounter exactly once, namely either as a reactive or elastic contribution. For a symmetric reaction $A+A \rightleftharpoons B+B$, the system of the Boltzmann equation (9.169) should read

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = \sum_{\beta=A}^{B} (1-\chi\delta_{\alpha\beta}) \int \left[f'_\alpha f'_\beta - f_\alpha f_\beta\right] g_{\beta\alpha}\sigma_{\alpha\beta} d\Omega \, d\mathbf{c}_\beta$$
$$+ \chi \int \left[f_\gamma f_{\gamma_1} - f_\alpha f_{\alpha_1}\right] \sigma_\alpha^\star g_\alpha d\Omega^\star d\mathbf{c}_{\alpha_1}, \qquad \alpha = A, B. \tag{9.190}$$

The parameter χ, with $0 \leqslant \chi \leqslant 1$, is a scalar factor, which represents the probability of a reactive binary encounter among identical molecules. In the case $\alpha = \beta$, the term $(1-\chi)$ is a reduced factor for the elastic contributions among identical molecules which avoids a double counting in the sense that each encounter among identical molecules gives only one contribution to (9.190), which can be either of elastic or reactive type.

In this section, it will be considered that the elastic and the reactive collisions are described by the differential cross sections of rigid spheres, i.e.,

$$\sigma_{\alpha\beta} = \frac{\mathsf{d}^2}{4}, \qquad \sigma_\alpha^\star = \frac{(\mathsf{sd})^2}{4}. \tag{9.191}$$

The reactive differential cross section $(9.191)_2$ follows from the representation (9.71) when $n = 1/2$ and by considering the reactive diameter equal to sd with s being the steric factor.

The law of mass action (9.15) for this case reads

$$Q^\star = 2\ln\left[\frac{\mathsf{x}_A^{\mathrm{eq}}}{(1-\mathsf{x}_A^{\mathrm{eq}})}\right], \tag{9.192}$$

where in this section $\mathsf{x}_\alpha = n_\alpha^{\mathrm{eq}}/n_{\mathrm{eq}}$ is the molar fraction of constituent α with $n_{\mathrm{eq}} = n_A^{\mathrm{eq}} + n_B^{\mathrm{eq}}$. One may infer from the law of mass action (9.192) that:

(i) an exothermic chemical reaction ($Q^\star < 0$) corresponds to $\mathsf{x}_A^{\mathrm{eq}} < 0.5$ and
(ii) an endothermic chemical reaction ($Q^\star > 0$) corresponds to $\mathsf{x}_A^{\mathrm{eq}} > 0.5$.

An interesting problem which can be analyzed is the trend to equilibrium of a spatially homogeneous symmetric reaction when it is described by the basic fields of particle number density n_α, diffusion velocity u_i^α and temperature T_α of each constituent. In this case, these fields depend only on time and can be represented as small perturbations of the corresponding constant values, which characterizes a reference equilibrium state of a non-diffusive mixture with particle number density n_α^{eq} and temperature T_{eq}, i.e.,

$$n_\alpha(t) = n_\alpha^{\mathrm{eq}}[1+\overline{n}_\alpha(t)], \qquad u_i^A(t) = \overline{u}_i^A(t), \qquad T_\alpha(t) = T_{\mathrm{eq}}[1+\varDelta_\alpha(t)]. \tag{9.193}$$

Note that due to the constraint

$$\overline{u}_i^B = -\frac{\mathsf{x}_A}{(1-\mathsf{x}_A)}\overline{u}_i^A, \tag{9.194}$$

there exists only one linearly independent diffusion velocity. Furthermore, the affinity (9.17) is given by

$$\mathcal{A}^\star(t) \equiv \frac{\mathcal{A}(t)}{kT_{\mathrm{eq}}} = 2[\overline{n}_A(t) - \overline{n}_B(t)]. \tag{9.195}$$

The linearized spatially homogeneous equations for the basic fields are obtained from (9.43), (9.47) and (9.50) once the production terms (9.44), (9.49) and (9.52) are determined from the distribution function (9.123). The resulting equations are

$$\frac{d\overline{n}_A}{d\mathtt{t}} = -\frac{\chi\mathsf{s}^2}{4}\mathsf{x}_A\left[8(\overline{n}_A-\overline{n}_B)+\varDelta_A-(1-2Q^\star)\varDelta_B\right], \tag{9.196}$$

$$\frac{d\overline{n}_B}{d\mathtt{t}} = \frac{\chi\mathsf{s}^2}{4}\frac{\mathsf{x}_A^2}{1-\mathsf{x}_A}\left[8(\overline{n}_A-\overline{n}_B)+\varDelta_A-(1-2Q^\star)\varDelta_B\right], \tag{9.197}$$

$$\frac{d\overline{n}_A}{d\mathtt{t}} + \frac{d\varDelta_A}{d\mathtt{t}} = \frac{2}{3}(1-\mathsf{x}_A)(\varDelta_B-\varDelta_A) - \frac{\chi\mathsf{s}^2}{6}\mathsf{x}_A\Bigg[14(\overline{n}_A-\overline{n}_B)+\frac{21}{4}\varDelta_A - \left(\frac{21}{4}-\frac{7}{2}Q^\star\right)\varDelta_B\Bigg], \tag{9.198}$$

$$\frac{d\overline{n}_B}{d\mathtt{t}} + \frac{d\Delta_B}{d\mathtt{t}} = \frac{2}{3}x_A(\Delta_A - \Delta_B) + \frac{\chi \mathsf{s}^2}{6}\frac{\mathsf{x}_A^2}{1-\mathsf{x}_A}\Bigg[2(7-2Q^\star)(\overline{n}_A - \overline{n}_B) + \left(\frac{21}{4} - \frac{1}{2}Q^\star\right)\Delta_A - \left(\frac{21}{4} - 4Q^\star + Q^{\star 2}\right)\Delta_B\Bigg], \tag{9.199}$$

$$\frac{d\overline{u}_i^A}{d\mathtt{t}} = -\overline{u}_i^A\left[\frac{2}{3} + \frac{\chi\mathsf{s}^2}{2}\frac{\mathsf{x}_A}{1-\mathsf{x}_A}\right]. \tag{9.200}$$

The above equations are written in a dimensionless form in terms of the dimensionless time $\mathtt{t}$, defined by

$$\mathtt{t} = \frac{t}{t_c}, \qquad \text{with} \qquad t_c = \frac{1}{4n_{\mathrm{eq}}\mathsf{d}^2}\sqrt{\frac{m}{\pi k T_{\mathrm{eq}}}} \tag{9.201}$$

denoting the mean free time of the elastic collisions.

The differential equation (9.200) is independent of (9.196)–(9.199) and can be solved exactly. Its solution can be written in the form

$$\overline{u}_i^A(t) = \overline{u}_i^A(0)\exp\left\{-\mathtt{t}\left[\frac{2}{3} + \frac{\chi\mathsf{s}^2}{2}\,\frac{\mathsf{x}_A}{1-\mathsf{x}_A}\right]\right\}. \tag{9.202}$$

Due to the constraint (9.194), a perturbation on the diffusion velocity of one constituent will induce an opposite perturbation on the diffusion velocity of the other constituent. Furthermore, from (9.202), one infers that the diffusion velocity perturbation decays with time, being more pronounced when the chemical reactions are present.

The system of differential equations (9.196)–(9.199) shows that the effects of the chemical reactions on the macroscopic fields strongly depend on the thermodynamical forces related to the affinity and temperature differences.

In order to investigate the maximum effects induced by the chemical reactions, the system of differential equations (9.196)–(9.199) was solved numerically for a closed system where energy exchanges were allowed. It was assumed that the reactive diameter is equal to the diameter of the molecules, i.e., $\mathsf{s} = 1$ and that the number of reactive collisions was equal to the elastic ones, i.e., the probability coefficient was taken equal to $\chi = 0.5$. Furthermore, the initial conditions were chosen in such a manner that at the end of the reactive process the perturbations of the number densities $\overline{n}_A$, $\overline{n}_B$ and the perturbation on the mixture's temperature $\Delta = \mathsf{x}_A\Delta_A + \mathsf{x}_B\Delta_B$ vanish. Two cases were analyzed, one corresponding to an exothermic reaction ($Q^\star < 0$) where $\mathsf{x}_A = 0.4$ and the other to an endothermic reaction ($Q^\star > 0$) where $\mathsf{x}_A = 0.6$. Moreover, two sets of conditions were considered by fixing the dimensionless time as $\mathtt{t} = 10$:

(a) $\overline{n}_A(10) = 0,\ \overline{n}_B(10) = 0,\ \Delta_A(10) = 10^{-6},\ \Delta_B(10) = -10^{-6}\mathsf{x}_A/\mathsf{x}_B$ and
(b) $\overline{n}_A(10) = 0,\ \overline{n}_B(10) = 0,\ \Delta_A(10) = -10^{-6},\ \Delta_B(10) = 10^{-6}\mathsf{x}_A/\mathsf{x}_B$.

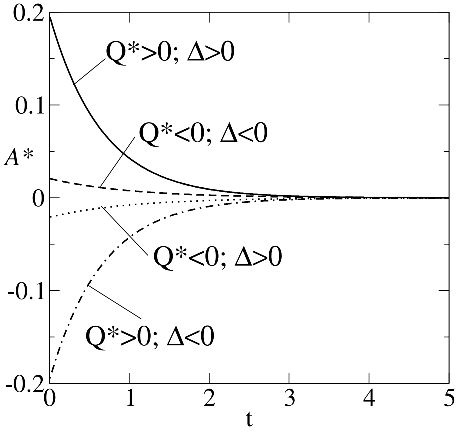

Fig. 9.14 Affinity $\mathcal{A}^\star$ as function of dimensionless time `t`.

Instead of analyzing the perturbations of the number densities and of the temperatures, it is worthwhile to discuss the behavior of the affinity $\mathcal{A}^\star$ as function of the dimensionless time `t` and its relationship with the perturbation of mixtures temperature Δ. The affinity as function of time is represented in Figure 9.14, and the discussion of the results is on the basis of Le Châtelier's principle:

(i) if the system is at equilibrium and the temperature is decreased ($\Delta < 0$) in an exothermic reaction ($Q^\star < 0$), energy must be released in order to oppose the temperature's decrease, the products are favored ($\mathcal{A}^\star > 0$) and the reaction proceeds from left to right, i.e., $A + A \rightharpoonup B + B$;

(ii) if the system is at equilibrium and the temperature is increased ($\Delta > 0$) in an endothermic reaction ($Q^\star > 0$), energy must be absorbed in order to oppose the temperature's increase, the products are favored ($\mathcal{A}^\star > 0$) and the reaction proceeds from left to right, i.e., $A + A \rightharpoonup B + B$;

(iii) if the system is at equilibrium and the temperature is increased ($\Delta > 0$) in an exothermic reaction ($Q^\star < 0$), energy must be absorbed in order to oppose the temperature's increase, the reactants are favored ($\mathcal{A}^\star < 0$) and the reaction proceeds from right to left, i.e., $A + A \leftharpoondown B + B$ and

(iv) if the system is at equilibrium and the temperature is decreased ($\Delta < 0$) in an endothermic reaction ($Q^\star > 0$), energy must be released in order to oppose the temperature's decrease, the reactants are favored ($\mathcal{A}^\star < 0$) and the reaction proceeds from right to left, i.e., $A + A \leftharpoondown B + B$.

Exercises

9.28 Obtain the balance equation (9.196).

9.29 Show that the solution of the differential equation (9.200) is given by (9.202).

9.9.3 Remarks on the Geometry of the Collisions

It is well known in chemistry that the relative orientation of the molecules at the instant of collision is very important for the occurrence of a chemical reaction, i.e., one has to take into account the geometry of the collision for chemically reacting systems. If the orientation of the molecules is not appropriate, the chemical reaction will not occur as is schematically represented in Figure 9.15, which could represent the chemical reaction $H_2 + I_2 \rightharpoonup 2HI$.

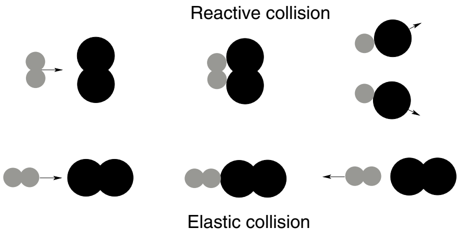

Fig. 9.15 Geometry of a collision–the role of the relative orientation of the molecules.

In order to take into account the relative orientation of the molecules, the reactive cross section for the line-of-centers model (9.171)—in the case of the symmetric reaction $A + A \rightleftharpoons B + B$—is written as

$$\sigma_A^\star = \begin{cases} 0, & \text{for} \quad \frac{m(\mathbf{g}_A \cdot \mathbf{k}_A)^2}{4} < \epsilon_f, \\ \frac{(\mathsf{sd})^2}{4}\left(1 - \frac{4\epsilon_f}{m(\mathbf{g}_A \cdot \mathbf{k}_A)^2}\right), & \text{for} \quad \frac{m(\mathbf{g}_A \cdot \mathbf{k}_A)^2}{4} \geqslant \epsilon_f, \end{cases} \tag{9.203}$$

where $\mathbf{k}_A$ is the unit collision vector which joins the centers of the two colliding spheres pointing from the center of the molecule denoted by A_1 to the center of the particle denoted by A. The quantity $m(\mathbf{g}_A \cdot \mathbf{k}_A)^2/4$ is the relative translational energy of constituent A in the direction of the line, which joins the centers of the molecules during the reactive collision. Note that in the expression for the reactive cross section (9.171), it was considered that a reaction occurs whenever the energy of the relative velocity $mg_A^2/4$ is larger than the activation energy. By considering the expression (9.203), a reaction occurs only when the energy of the relative velocity in the direction of the line which joins the centers of the molecules is larger than the activation energy, and in this sense, the geometry of the collision is taken into account.

It is important to call attention that according to the expression for the reactive cross section (9.203), the square of the normal relative velocity has a lower bound that corresponds to the activation energy of the chemical reaction, i.e., $m(\mathbf{g}_A\cdot\mathbf{k}_A)^2/4=\epsilon_f$. This condition implies that the integrals of the reactive collision terms become more involved. Indeed, whereas the angle for the non-reactive collisions may range from 0 to $\pi/2$, the angle θ_A for the reactive collisions may range only from $0\leqslant\theta_A\leqslant\theta_A^{\max}$, where

$$\theta_A^{\max}=\arccos\sqrt{\frac{4\epsilon_f}{mg_A^2}}. \tag{9.204}$$

From the above equation, one infers that for a vanishing activation energy, $\theta_A^{\max}=\pi/2$.

In order to determine the influence of the reactive cross section (9.203) on the equilibrium value of the forward reaction rate coefficient (9.191), it is expressed as

$$\mathsf{k}_f=\frac{4}{n_A^2}\int f_A\,f_{A_1}\,\sigma_A^\star\,g_A\,\sin\theta_A\,\cos\theta_A\,d\theta_A\,d\mathbf{c}_A\,d\mathbf{c}_{A_1}, \tag{9.205}$$

since $d\Omega^\star=4\sin\theta_A\cos\theta_A d\theta_A d\varepsilon$. The insertion of the Maxwellian distribution function (9.72) into the above equation leads to

$$\mathsf{k}_f^{(0)}=(4\pi\mathsf{sd})^2\left(\frac{m}{2\pi kT}\right)^3\int\exp\left[-\frac{m}{kT}\left(G_A^2+\frac{g_A^2}{4}\right)\right]\left(1-\frac{4\epsilon_f}{mg_A^2\cos^2\theta}\right)$$
$$\times\,G_A^2\,g_A^3\,\sin\theta_A\,\cos\theta_A\,d\theta_A\,d\varepsilon\,dg_A\,dG_A, \tag{9.206}$$

where $\mathbf{G}=(\mathbf{c}_A+\mathbf{c}_{A_1})/2$ and $\mathbf{g}_A=\mathbf{c}_{A_1}-\mathbf{c}_A$ denote the center of mass velocity and relative velocity, respectively. The range of the integrals read: $0\leqslant\varepsilon\leqslant2\pi$, $0\leqslant\theta_A\leqslant\theta_A^{\max}$, $0\leqslant G_A<\infty$, $\sqrt{4\epsilon_f/m}\leqslant g_A<\infty$.

By performing all the integrals, one obtains that the reaction rate coefficient (9.206) becomes

$$\mathsf{k}_f^{(0)}=4\sqrt{\frac{\pi kT}{m}}(\mathsf{sd})^2\,e^{-\epsilon_f^\star}\left(1-\underline{\epsilon_f^\star\,\mathrm{Ei}(\epsilon_f^\star)\,e^{\epsilon_f^\star}}\right), \tag{9.207}$$

where $\mathrm{Ei}(\epsilon_f^\star)$ represents the exponential function $\mathrm{Ei}(\epsilon_f^\star)=\int_{\epsilon_f^\star}^\infty\frac{e^{-y}}{y}\,dy$.

One may infer from (9.207) that the underlined term is a new contribution to the Arrhenius equation which takes into account that a chemical reaction happens only when the energy of the relative velocity in the direction of the line which joins the centers of the molecules is larger than the

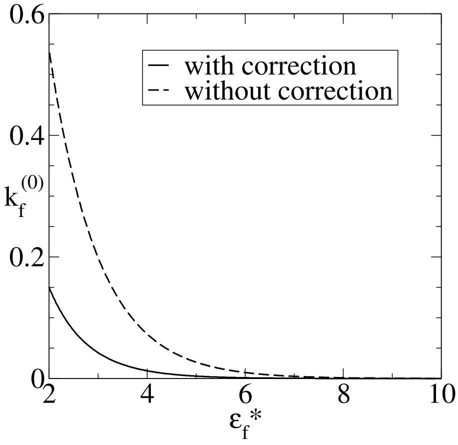

Fig. 9.16 Reaction rates coefficients with the correction due to the geometry (solid line) and without it (dashed line).

activation energy. This contribution indicates that the reaction rate coefficient becomes smaller and this result can be observed by looking at the two curves in Figure 9.16, which shows that the correction diminishes significantly the value of the reaction rate coefficient.

Exercise

9.30 Obtain the expression (9.207) for the reaction rate coefficient.

9.9.4 Remarks on Inelastic Reactive Collisions

As was previously discussed, for small values of the reaction heat, the relationship between the reactive differential cross sections is given by (9.33). In the case where this condition is not fulfilled, one has to consider the reactive collisions as inelastic ones, which will be analyzed in the following.

The inelastic collision associated with the reaction $A + A \rightharpoonup B + B$ is characterized by the relationship $(\mathbf{g}_B \cdot \mathbf{k}_A) = -\mathsf{e}_B(\mathbf{g}_A \cdot \mathbf{k}_A)$, which relates the pre-collisional $\mathbf{g}_A$ and post-collisional $\mathbf{g}_B$ relative velocities at collision. The parameter e_B denotes a normal restitution coefficient, and $\mathbf{k}_A$ is the unit collision vector which joins the centers of the two colliding spheres pointing from the center of the particle denoted by A_1 to the center of the particle denoted by A. In terms of the collision vector, the momentum conservation laws can be written as

$$\mathbf{c}_B = \mathbf{c}_A + \frac{1+\mathsf{e}_B}{2}(\mathbf{g}_A \cdot \mathbf{k}_A)\mathbf{k}_A, \qquad \mathbf{c}_{B_1} = \mathbf{c}_{A_1} - \frac{1+\mathsf{e}_B}{2}(\mathbf{g}_A \cdot \mathbf{k}_A)\mathbf{k}_A, \tag{9.208}$$

and from the above equations, one may obtain that

$$g_B^2 = g_A^2 + (\mathsf{e}_B^2 - 1)(\mathbf{g}_A \cdot \mathbf{k}_A)^2. \tag{9.209}$$

The comparison of (9.168) and (9.209) leads to the determination of the normal restitution coefficients in terms of the reaction heat Q, namely,

$$\mathsf{e}_B = \sqrt{1 - \frac{4Q}{m(\mathbf{g}_A \cdot \mathbf{k}_A)^2}} \approx 1 - \frac{2Q}{m(\mathbf{g}_A \cdot \mathbf{k}_A)^2}, \tag{9.210}$$

where the approximation in the above equation is valid only for small values of the reaction heat. Note that the normal restitution coefficients—like the one for granular gases of viscoelastic particles (see the book by Brilliantov and Pöschel)—depend on the normal component of the relative velocities $(\mathbf{g}_A \cdot \mathbf{k}_A)^2$. One infers from (9.210) that the restitution coefficient for exothermic reactions $Q < 0$ is larger than one ($\mathsf{e}_B > 1$), while for endothermic reactions, $Q > 0$ is smaller than one ($\mathsf{e}_B < 1$). Note that the classification endothermic and exothermic refers to the direct reaction $A + A \rightharpoonup B + B$.

The inelastic restitution collision which corresponds to the reaction $A + A \leftharpoondown B + B$ is characterized by the relationship $(\mathbf{g}_A \cdot \mathbf{k}_B^*) = -\mathsf{e}_A(\mathbf{g}_B^* \cdot \mathbf{k}_B^*)$. It relates the pre-collisional $\mathbf{g}_B^*$ and post-collisional $\mathbf{g}_A$ relative velocities at collision where $\mathbf{k}_B^* = -\mathbf{k}_A$. The relationships of the pre- and post-collisional velocities can be written—thanks to (9.208)—as

$$\mathbf{c}_B^* = \mathbf{c}_A + \frac{1+\mathsf{e}_A}{2\mathsf{e}_A}(\mathbf{g}_A \cdot \mathbf{k}_A)\mathbf{k}_A, \qquad \mathbf{c}_{B_1}^* = \mathbf{c}_{A_1} - \frac{1+\mathsf{e}_A}{2\mathsf{e}_A}(\mathbf{g}_A \cdot \mathbf{k}_A)\mathbf{k}_A. \tag{9.211}$$

By following the same methodology above, the restitution coefficient e_A becomes

$$\mathsf{e}_A = \sqrt{1 + \frac{4Q}{m(\mathbf{g}_B^* \cdot \mathbf{k}_B^*)^2}} = \frac{1}{\sqrt{1 - \frac{4Q}{m(\mathbf{g}_A \cdot \mathbf{k}_A)^2}}}, \tag{9.212}$$

so that the relationship $\mathsf{e}_A \mathsf{e}_B = 1$ holds.

The collision processes are also characterized by differential cross sections and here, it is considered that the elastic cross sections $\sigma_{\alpha\beta}$ $(\alpha, \beta = A, B)$ correspond to a potential of hard spheres of diameter $\mathsf{d}_A = \mathsf{d}_B = \mathsf{d}$ so that $\sigma_{AA} = \sigma_{AB} = \sigma_{BB} = \mathsf{d}^2$. Furthermore, the reactive differential cross sections $\sigma_A^\star$ and $\sigma_B^\star$ refer to the line-of-centers model which takes into account the activation energy (see (9.203)), namely

$$\sigma_A^\star = \begin{cases} 0, & \text{for} \quad \frac{m(\mathbf{g}_A\cdot\mathbf{k}_A)^2}{4} < \epsilon_f, \\ (\mathsf{sd})^2\left(1 - \frac{4\epsilon_f}{m(\mathbf{g}_A\cdot\mathbf{k}_A)^2}\right), & \text{for} \quad \frac{m(\mathbf{g}_A\cdot\mathbf{k}_A)^2}{4} \geqslant \epsilon_f, \end{cases} \tag{9.213}$$

$$\sigma_B^\star = \begin{cases} 0, & \text{for} \quad \frac{m(\mathbf{g}_B^*\cdot\mathbf{k}_B^*)^2}{4} < \epsilon_r, \\ (\mathsf{sd})^2\left(1 - \frac{4\epsilon_r}{m(\mathbf{g}_B^*\cdot\mathbf{k}_B^*)^2}\right), & \text{for} \quad \frac{m(\mathbf{g}_B^*\cdot\mathbf{k}_B^*)^2}{4} \geqslant \epsilon_r, \end{cases} \tag{9.214}$$

The quantities $m(\mathbf{g}_A \cdot \mathbf{k}_A)^2/4$ and $m(\mathbf{g}_B^* \cdot \mathbf{k}_B^*)^2/4$ are relative translational energies in the direction of the line which joins the centers of the molecules during an inelastic collision. As in the previous section, the geometry of the reactive collision is also considered here.[14]

The reactive differential cross sections $\sigma_A^\star$ and $\sigma_B^\star$ are related to each other, since

$$\begin{aligned} \sigma_B^\star &= (\mathsf{sd})^2\left[1 - \frac{4(\varepsilon - Q)}{m(\mathbf{g}_B^* \cdot \mathbf{k}_B^*)^2}\right] = (\mathsf{sd})^2\left[\mathsf{e}_A^2 - \frac{4\varepsilon}{m(\mathbf{g}_B^* \cdot \mathbf{k}_B^*)^2}\right] \\ &= (\mathsf{sd})^2\mathsf{e}_A^2\left[1 - \frac{4\varepsilon}{m(\mathbf{g}_A \cdot \mathbf{k}_A)^2}\right] = \mathsf{e}_A^2\sigma_A^\star, \end{aligned} \tag{9.215}$$

thanks to (9.212) and the relationship $\mathsf{e}_A^2(\mathbf{g}_B^* \cdot \mathbf{k}_B^*)^2 = (\mathbf{g}_A \cdot \mathbf{k}_A)^2$.

One should note that for the direct reaction $A + A \rightharpoonup B + B$, the condition $Q < 0$ implies that $\mathsf{e}_A < 1$ and $\mathsf{e}_B > 1$ so that $\sigma_A^\star > \sigma_B^\star$, while $Q > 0$ implies that $\mathsf{e}_A > 1$ and $\mathsf{e}_B < 1$ so that $\sigma_A^\star < \sigma_B^\star$.

As usual, the distribution functions f_α must satisfy a coupled system of Boltzmann equations, which in the absence of external forces, reads

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = \sum_{\beta=A}^{B} \int \left(f_\alpha' f_\beta' - f_\alpha f_\beta)\right]\mathsf{d}^2(\mathbf{g}_{\beta\alpha} \cdot \mathbf{k}_{\beta\alpha}) d\mathbf{k}\, d\mathbf{c}_\beta + \mathcal{Q}_\alpha^R, \tag{9.216}$$

where $\mathcal{Q}_\alpha^R$ is the collision operator of inelastic interactions.

The collision operator of inelastic interactions for the constituent A is obtained as follows. The number of inelastic collisions for the forward reaction $A + A \rightharpoonup B + B$ in the volume element $d\mathbf{x}$ and time interval Δt is given by

$$(f_A d\mathbf{x} d\mathbf{c}_A)[f_{A_1}(\mathbf{g}_A \cdot \mathbf{k}_A)\Delta t\, \sigma_A^\star d\mathbf{k}\, d\mathbf{c}_{A_1}], \tag{9.217}$$

while the one for the reverse reaction $A + A \leftharpoondown B + B$ reads

$$(f_B^* d\mathbf{x} d\mathbf{c}_B^*)[f_{B_1}^*(\mathbf{g}_B^* \cdot \mathbf{k}_B^*)\Delta t\, \sigma_B^\star d\mathbf{k}\, d\mathbf{c}_{B_1}^*]. \tag{9.218}$$

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[14] Note that the differential cross section (9.213) differ from (9.203) by a factor 4. The reason is that in this section the integration will be performed in the angle θ instead in the angle $\chi = \pi - 2\theta$ and in this case; $\sin\chi\, d\chi = 4\sin\theta\, \cos\theta\, d\theta$.

Above, $d\mathbf{k}$ represents an element of solid angle that characterizes the reactive scattering processes, while $\sigma_\alpha^\star$ denote differential reactive cross sections.

From (9.211), one may obtain

$$d\mathbf{c}_B^* \, d\mathbf{c}_{B_1}^* = \mathsf{e}_A d\mathbf{c}_A \, d\mathbf{c}_{A_1}. \tag{9.219}$$

Note that the modulus of the Jacobian of the transformation is $|J| = \mathsf{e}_A$, due to the fact that e_A depend, on the relative velocity. It differs from the Jacobian of granular gases of constant normal restitution coefficient, since its Jacobian is inversely proportional to the normal restitution coefficient (see exercise 7.2). Hence, from the relationship $(\mathbf{g}_A \cdot \mathbf{k}_A) = \mathsf{e}_A(\mathbf{g}_B^* \cdot \mathbf{k}_B^*)$ together with (9.219) yields

$$(\mathbf{g}_B^* \cdot \mathbf{k}_B^*) d\mathbf{c}_B^* \, d\mathbf{c}_{B_1}^* = (\mathbf{g}_A \cdot \mathbf{k}_A) d\mathbf{c}_A \, d\mathbf{c}_{A_1}. \tag{9.220}$$

The collision operator of inelastic interactions for the constituent A is obtained from the combination of (9.217), (9.218) and (9.220), yielding

$$\mathcal{Q}_A^R = \int \left[f_B^* f_{B_1}^* \sigma_B^\star - f_A f_{A_1} \sigma_A^\star \right] (\mathbf{g}_A \cdot \mathbf{k}_A) d\mathbf{k} \, d\mathbf{c}_{A_1}. \tag{9.221}$$

If one takes into account (9.215) together with $\mathsf{e}_A \mathsf{e}_B = 1$, the above equation can be written as

$$\mathcal{Q}_A^R = \int \left[\frac{1}{\mathsf{e}_B^2} f_B^* f_{B_1}^* - f_A f_{A_1} \right] \sigma_A^\star (\mathbf{g}_A \cdot \mathbf{k}_A) d\mathbf{k} \, d\mathbf{c}_{A_1}, \tag{9.222}$$

which is alike to the expression for granular gases (see (7.8)).

By following analogous arguments, the collision operator of inelastic interactions for the constituent B reads

$$\mathcal{Q}_B^R = \int \left[f_A f_{A_1} \sigma_A^\star - f_B^* f_{B_1}^* \sigma_B^\star \right] (\mathbf{g}_B^* \cdot \mathbf{k}_B^*) d\mathbf{k} \, d\mathbf{c}_{B_1}^*. \tag{9.223}$$

From the knowledge of the collision operators (9.221) and (9.223), the Boltzmann equation (9.216) for the constituent A can be written as

$$\begin{aligned} \frac{\partial f_A}{\partial t} + c_i^A \frac{\partial f_A}{\partial x_i} = \sum_{\beta=A}^{B} \int \left[f_A' f_\beta' - f_A f_\beta \right] \mathsf{d}^2 (\mathbf{g}_{\beta A} \cdot \mathbf{k}_{\beta A}) d\mathbf{k} \, d\mathbf{c}_\beta \\ + \int \left[f_B^* f_{B_1}^* \sigma_B^\star - f_A f_{A_1} \sigma_A^\star \right] (\mathbf{g}_A \cdot \mathbf{k}_A) d\mathbf{k} \, d\mathbf{c}_{A_1}, \end{aligned} \tag{9.224}$$

with a similar equation for the constituent B.

Exercise

9.31 Show that the relationship $d\mathbf{c}_B^* \, d\mathbf{c}_{B_1}^* = \mathsf{e}_A d\mathbf{c}_A \, d\mathbf{c}_{A_1}$ holds.

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