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# Macromolecules in Solution and Brownian Relativity

Stefano A. Mezzasalma

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# Macromolecules in Solution and Brownian Relativity

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# FOREWORD

The central purpose of this book is to propound that macromolecules in solution can be investigated by combining the theoretical structures of relativity and Brownian motion. “Brownian relativity” suggests that time and space in a Brownian system can be envisaged similar to the spacetime of Einstein’s relativity. Average size and characteristic time of a macromolecule fluctuating in a liquid are so explained by a Lorentz–FitzGerald length contraction and a time dilation rule, if the system is short-range correlated (or uncorrelated), and by an equivalence criterion for geometry and statistics whenever correlations are long-ranged. We have mainly focused on the universal scaling behavior and the conformational statistics exhibited by linear, flexible and homogeneous polymer chains, planning to look into further cases in the near future.

Since, disciplinarily, relativistic theories are quite distant from polymer science, the first chapter introduces the basic concepts and tools required to understand the following. Several contents are also reported throughout the book as priority subjects for research. Reference and bibliographic sources were mostly limited to those founding the physics and chemistry from which Brownian relativity needs to restart.

After some remarks on Brownian motion, chapter two formulates the special theory of Brownian relativity, and employs it to get the basic universal laws (in the molecular weight) of single polymer chains.

Chapter three enters the general version of the theory, devoted to the analysis of stronger correlations and finite polymer volume fractions. Geodesic and Einstein’s field equations allow geometrical interpretation of the effect of concentration fluctuations and entanglement points.

In chapter four, the attention turns from the universal scaling in physical quantities to the scaling of probability distributions. We worked out in the third section some consequences that this point would have on the longstanding issue of turbulence in liquids.

The fifth chapter presents, in the form of fundamental ideas and a couple of examples about liquids and macromolecules, further Brownian relativity implications. We started out to state the basic concepts of a statistical–mechanical problem by means of geometry alone. This “shape mechanics” would deal with the shape of objects, as an independent physical observable, putting forward that (Brownian) statistical phenomena, likewise polymers in solution, may represent a particular case of a far-reaching “geometrical scaling” of forms and shapes.

In summary, this book is addressed to any polymer scientist, but can certainly be significant to anybody with interests in either theoretical physics and chemistry (i.e., field theory and statistical mechanics) or any $n$-molecular system seen from another perspective.

Trieste, X/2007
Stefano A. Mezzasalma

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## CHAPTER ONE

# CLASSICAL AND RELATIVISTIC MECHANICS

## Contents

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## 1. HISTORICAL SUMMARY

Mechanics is part of field theory (i.e., gravitation and electromagnetism) and generally concerned with the statics and dynamics of any material body or medium. Its classical formulation relies on the existence of frames of reference, named inertial, where Isaac Newton's three laws of motion (1687) hold. The concept of inertial frame is one of the most important of all sciences, and can be found in Newton's first law (or Principle of Inertia), resuming and improving the concept of inertia earlier discussed by Galileo Galilei (1632). It states that there is a family of reference frames in which any isolated particle moves with uniform motion along a straight line. Once compelled by some external interaction, its dynamic state varies, obeying the second law of motion: moving force equals (a constant) mass times acceleration, $\mathbf{F} = m\mathbf{a}$.

Classical mechanics was developed into two complementary views, vectorial and analytical. The first isolates the particles, modelled as they were individual, and makes direct use of Newton's second law of motion. Accordingly, one should be able to separate each resultant particle force, and proceed with solving the associated differential equations. In his principle, Jean B. d'Alembert (1743) stated an equivalence of any accelerating body with the system which is rendered static upon adding the force and torque of inertia. Despite some shortcomings, such as missing the "polygenic" character of inertia that, unlike monogenic (or analytic) forces, is unable to follow from differentiation, this description could fit both statics and dynamics but it can fail to model any particle system which is complicated enough. Additional postulates were next to no use to complete the unknown information on the specific interactions met in concrete experiments, as Newton hoped to supply by his third law, action equals reaction. This spurred Joseph L. Lagrange (1788) to seek a more general assessment of d'Alembert's Principle, attaining a generalization of the virtual work theorem for reversible displacements. The latter was the first variational condition of mechanics, argued by Guidobaldo del Monte (1590 ca) and developed by Galileo Galilei (1638) for the inclined plane and simple machines.

The d'Alembert–Lagrange Principle provides an equilibrium criterion, for forces and motion set in opposition, to understand whether a virtual motion may or may not become actual.

In his 1788 book on analytical mechanics, Lagrange published the famous equations, also known as the Euler–Lagrange equations, allowing a unified treatment of forces. Armed with the concept of total energy, in place of the motion law, one could finally tackle any mechanical system as a whole. His work lay clearly at the basis of other relevant contributions at that age, as the five volumes on celestial mechanics by Pierre–S. Laplace (1798–1825), complementing the geometrical approach initiated by the Principia into (differential) calculus. Successively, William R. Hamilton (1843) interpreted the principles by d'Alembert and Lagrange into a variational problem for a definite time integral, called the functional action, the variation of which is equal to the virtual work time integral. Such as the virtual work theorem states that, at mechanical equilibrium, this variation vanishes at any time, d'Alembert–Lagrange's and Hamilton's views become equivalent whenever the action is stationary. This statement is usually, but mistakenly, named as Principle of Least Action, since the functional needs only to be stationary (i.e., either at a maximum, minimum or saddle points). Hamilton's action integrand identifies Lagrange's function (Lagrangian or, in Mie's language, "world function"), depending on all degrees of freedom, positions and velocities. Requiring the functional to be stationary yields finally the Euler–Lagrange equations, unequivocally defining the laws of motion, regardless of the reference frame. A dually equivalent picture can be promptly derived in terms of Hamilton's function (or Hamiltonian), switching from Lagrangian to Hamiltonian mechanics.

Hamilton thus consolidated a tradition, for which it is not entirely clear to whom the credit should be given, whether it should be to Pierre de Fermat (1662), with his Principle of Least Time for light pathways, or to Pierre L. Maupertuis (1744), who is commonly acknowledged to be the pioneer, or even to Leonhard Euler (1744) and Gottfried Leibniz (1707). In line with d'Alembert's and Lagrange's statements, remember the Principles of Least Constraint, Least Curvature, and stationary action formulated respectively by Carl F. Gauss (1829), Heinrich R. Hertz (1894), and Carl G.J. Jacobi (1842–1843). Last two milestones of variational calculus in mechanics that we would like to recall came from the general theory of relativity (see the Einstein–Hilbert action in the last two section) and the work by Marston Morse (1920–1930), achieving a neat mathematical assessment.

In the mechanics built upon the laws by Galilei (1632–1938) and Newton (1684–1687), time and space are considered to be absolute properties. The expression "inertial frame" denotes therein any reference system, at rest in the absolute space or uniform motion, where time is flowing uniformely, independently of the observer. We must wait for the special relativity by Albert Einstein (1905) to unveil the mistakes behind this physical conception. Special relativity belonged to a wide forward-looking plan which, in the same (1905's "wonder") year, produced the three epoch-making theories of relativity, Brownian movement, and photoelectricity. Researching on the nature of light, heart of Einstein's scientific program, led him to work on the role of some crucial dualities in physics and chemistry: continuity–discreteness, fields–particles, determinacy–undeterminacy.

The theory of relativity, as the name purports, deems the concept of absolute motion as physically unmeaningful. Its special version appeared immediately as the best candidate for conciliating electromagnetism to gravitation and, in particular, for the unification of electromagnetic phenomena (electricity, magnetism and optics). At Einstein's time, gravitational and electromagnetic forces were believed to be the only governors of all natural phenomena. Furthermore, the use of Newtonian mechanics allowed the notions of absolute time and simultaneity, thus of a uniform metric structure (i.e., Euclidean) that would be common to all observers. In particular, every time that space ($x^p$) and time ($t$) coordinates would change according to a Galilean transformation, with given velocity ($v^p$) along a fixed direction:

$$x^{p'} = x^p - v^p t, \qquad x^{q'} = x^q \quad (q \neq p)$$

the second and third laws of motion would be left invariant. Provided they held at least in one inertial frame, Newton's laws were expected to be valid in all of them, implying that one dynamics experiment alone could never suffice to distinguish among different inertial motions.

With the coming of the equations of electromagnetism by James C. Maxwell (1873), which are not invariant upon Galilean transformations, such conclusions were for the first time contradicted. As the light speed ($c$) seemed to play the role of an absolute constant, that particular frame in which Maxwell's equations would apply had to be unambiguously distinguishable from any other. Albert A. Michelson and Edward Morley (1887) performed thus their famous experiment, aimed at detecting if the earth undergoes a relative motion with respect to a preferred reference system. The earth was believed being at rest relative to a special medium, termed ether (or æther), thought of as to host the propagation of electromagnetic waves. In short, an interferometer was designed to measure the time interval coming from the pattern of interference fringes formed by light on its reunion, after traveling along two different paths. Surprisingly, the two experimentalists obtained a "null result" and, since the earth velocity within the ether could not be zero throughout an orbit, there was necessarily something wrong with the supposed dynamic and/or electromagnetic pictures.

Einstein's answer to this puzzle was courageously not concerned with the validity of Newton's or Maxwell's equations, nor with discussing or making any assumption about matter and molecular forces, optics or the nature of light, but "only" with disowning the hypothesis of absolute space and time. He introduced two postulates, of relativity and constancy of the light speed, questioning the assumption of perfect clocks and rigid rods. In his paper dated June 1905, "On the electrodynamics of moving bodies" (the first of his in the references), the dynamics of bodies and fields was unified through a relativistic invariance of movements. It is also instructive to note that Einstein didn't plunge into the wave-particle duality of light, but limited himself to the concept of light-ray, suiting either aspects.

The central implications of the special theory regard the effect of the relative motion on the measurement of lengths and time intervals. With increasing relative speed, clocks run slower and rods shrink along the direction of movement. George F. FitzGerald (1889) and Hendrik A. Lorentz (1892), on supposing that the interferometer arm could contract in relative motion and compensate the earth contribution, independently proposed an (earlier) explanation of Michelson and Morley's experiment. Presumably, as they did not question the ether existence in depth, the FitzGerald–Lorentz contraction failed to make sense to the majority of the scientific community at that time. Another formulation which was even more unlucky is Henry Poincaré's (1904), who had already perceived in 1895 the ideas that nine years later would take the form of a "Principle of Relative Motion" (one of his six principles of physics). He stated it in the form of a deep symmetry law of nature and, in a study which appeared before the 1905's Einstein paper, wrote the relativistic equations for the charge density and velocity. It was his opinion that the absolute motion of any form of weighable matter could never be unmasked, the only possibility being to detect the relative motion of two material bodies. To explain gravity, Poincaré made use of the symmetry group devised by Lorentz (1899–1904), who published a preliminary version of it in 1895, and this is why the coordinate transformation of special relativity carries the names of both authors. However, again, Einstein's work took deeper root in the contemporary thought, and Poincaré's theory didn't get the consideration it deserved. Two last meritworthy mentions go to Woldemar Voigt (1887) and Joseph Larmor (1897). Voigt, in the elastic theory of light, distinguished a local time for the moving frame, descending from a linear function of the spatial coordinates and measured with an invariant unit of time. It is possible to show that the wave equation conserves its validity also in the moving frame. His coordinate transformations were formally close to those published subsequently by Lorentz, but passed totally unobserved in the literature. Larmor's transformations were equal instead to Lorentz's, also pioneering the influence of motion on the measure of time. However, he refused the heart of Einstein's work, such as special relativity and the curvature of space.

The most important consequence of the Lorentz–Poincaré symmetry remains, however, the "energy inertia" and the celebrated mass–energy equivalence, $E = mc^2$. It was still enunciated by Einstein (1905), in a paper entitled "Does the Inertia of a Body depend upon its Energy Content?" (Einstein's second referenced here), and written almost as an afterthought to the special theory. Before this work appeared, mass and energy were regarded separately, each having their own conservation law. Such an equivalence contradicted this belief, advancing the idea that every form of energy possesses the counterpart of an own inertia.

After his "Annus Mirabilis," Einstein proceeded towards a general theory of gravitation which would be consistent with special relativity and giving a relativistic version of Newtonian mechanics. What rendered the former theory "special" was its strict suitability to systems in uniform motion alone. His main objectives were thus to extend it, i.e., accounting for accelerated motions and understanding how gravitation could be dealt within it. Meanwhile, the mathematician Hermann Minkowski (1907) noticed that the natural geometrical space, where embedding relativity, were to be non-Euclidean. The "pseudo-Euclidean" spacetime carrying his name joins the four coordinates into a continuum, giving Einstein invaluable ideas and a robust background from which to proceed further. Ten years later than special relativity, after many attempts and much laborious work, Einstein (1915) published his general relativity and field equations. It was not the only theory of relativistic gravitation ever presented, but the first agreeing with the experimental tests. He introduced the famous (strong) Principle of Equivalence, for gravitation and acceleration, and abandoned the uniform Euclidean spacetime for a more general Riemannian description. Regions of non-vanishing local curvature identify now the accelerated systems, in contrast with flat reference frames that stand for inertial observers. It should be remembered that, independently of Einstein (five days before), also David Hilbert achieved contemporarily the (general covariant) field equations from a variational principle of stationary action (the "Einstein–Hilbert action"). The reasons why such a formulation had however a less resonance in the physics community lie in its axiomatic approach and its strict suitability to a material system governed by the theory of Gustav Mie (1912–1913).

General relativity was strongly influenced by the ideas of Ernst Mach (1883–1893), of whom Einstein considered himself to be one the followers, particularly on inertia. According to Mach, space is not an absolute and indifferent physical structure, as first René Descartes (1644) and then Newton posited. On proceeding with the line of George Berkeley (1710), who rejected the Newtonian conception of an absolute space, and judged meaningless the motion of any body which would not be relative to other matter, he was persuaded that inertia originates from the mass distributed around. Mach referred the laws of inertia to the earth and, for larger mass distributions, to the fixed stars. The Machian notions of "physical" space and inertial frame change thus significantly. The former identifies the ensemble of all concrete distances among material points, the latter should be defined with respect to the rest frame of the universe. Mach argued that gravitation should be univocely (covariantly) formulated only in terms of matter and energy, and stated that Newton's absolute acceleration was to be replaced by that relative to the universe mass distribution. Also, once the resistence to absolute accelerations would be (relativistically) meaningless, on infinitely spacing out all masses in the universe, he expected inertia to vanish (relativity of inertia). Einstein acknowledged a debt to these brilliant insights by calling his postulate Mach's Principle, but general relativity could solely provide a partial account of his view. The (strong) Principle of Equivalence is itself incompatible to it and, being forced to make a choice, the Einsteinian spacetime is more absolute-Newtonian than physical-Machian.

Finally, Einstein's theory replaces the instantaneous interaction at a distance, ruling Newtonian mechanics, with the concept of field. Fields denote physical agents by which forces establish, their action being no longer at a distance, but bounded to the infinitesimal neighbourhood where interactions take place. In Newtonian mechanics, whatever mass distribution is involved, the second law of dynamics never changes its form, but there is a law for any physical entity and type of force (e.g., Coulomb's force for electric charges). Also from the Einsteinian viewpoint, field and motion equations are separated. Test particles move along the geodesics "traced out" via the background metric, while changing geometry corresponds to altering matter and momentum distributions enclosed inside the spacetime. In a synthetic fashion, mass–energy $\sim$ curvature, which sums up one of the most genial insights ever had in the history of science.

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# 2. Analytical Mechanics

## 2.1 Lagrangian mechanics and Hamilton's Principle

In analytical mechanics, any system is characterized by a given Lagrange's function, $L = L(\mathbf{q}_n, \dot{\mathbf{q}}_n, t)$. It depends on a "super-vector" of generalized coordinates $\mathbf{q}_n \equiv \{q_s\colon\ s = 1, 2, \ldots, n\}$ and velocities $\dot{\mathbf{q}}_n \equiv \{\dot{q}_s = \frac{dq_s}{dt}\colon\ s = 1, 2, \ldots, n\}$ and on (an absolute) time $t$. The minimum integer $n$ necessary to a complete description, clearly amounts to the number of degrees of freedom of the system (i.e., for $N$ unconstrained point particles in $d$ dimensions, $n = Nd$). The time integral of the Lagrangian along a given trajectory (or path), $\mathbf{q}_n = \mathbf{q}_n(t)$, defines the action functional ($S$):

$$S\big[\mathbf{q}_n(t)\big] = \int_{t'}^{t''} L(\mathbf{q}_n, \dot{\mathbf{q}}_n, t)\, dt \tag{1.1}$$

with fixed boundaries, $\mathbf{q}_n(t') = \mathbf{q}'_n$ and $\mathbf{q}_n(t'') = \mathbf{q}''_n$. Hamilton's variational principle hypothesizes the action being stationary, and the path extremizing it yields the desired equations of motion. They are not postulated as basic, and the concept of force is prior to that of potential. Conceptually, it were as if nature had assigned the aim of pursuing the path producing a stationary action (e.g., when a minimum is attained, spending the least energy). Mathematically, one perturbes a reference trajectory at first order in the particle displacement, and imposes that the action does not vary:

$$\delta S \equiv S\big[\mathbf{q}_n(t) + \delta\mathbf{q}_n(t)\big] - S\big[\mathbf{q}_n(t)\big] = 0 \tag{1.2}$$

where $\delta\mathbf{q}_n \equiv \{\delta q_s\colon\ s = 1, 2, \dots, n\}$, the absolute time being the independent variable and, when not otherwise specified, $\delta \equiv \delta^{(1)}$. Let the vector derivative denote the (row) operator $\frac{\partial}{\partial \mathbf{q}_n} \equiv \{\frac{\partial}{\partial q_s}\colon\ s = 1, 2, \dots, n\}$ and $\cdot$ be an Euclidean scalar product (e.g., $\mathbf{q}_n \cdot \dot{\mathbf{q}}_n = q_1\dot{q}_1 + \cdots + q_n\dot{q}_n$), it turns out:

$$\delta S = \delta\mathbf{q}_n \cdot \left(\frac{\partial L}{\partial \dot{\mathbf{q}}_n}\right)\bigg|_{t'}^{t''} + \int_{t'}^{t''} \delta\mathbf{q}_n \cdot \left[\left(\frac{\partial L}{\partial \mathbf{q}_n}\right) - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\mathbf{q}}_n}\right) dt\right] \tag{1.3}$$

With fixed boundaries, $\delta\mathbf{q}_n(t') = \delta\mathbf{q}_n(t'') = 0$, the first contribution dies off. The functional is thus stationary if and only if, for every $s = 1, 2, \dots, n$, the “Euler–Lagrange functional derivative” vanishes, i.e.,

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\mathbf{q}}_n}\right) - \left(\frac{\partial L}{\partial \mathbf{q}_n}\right) = \mathbf{0} \tag{1.4}$$

yielding the Euler–Lagrange equations of motion, i.e., the accelerations ($\ddot{\mathbf{q}}_n$) as a function of velocities ($\dot{\mathbf{q}}_n$) and positions ($\mathbf{q}_n$), whose integration returns the trajectory $\mathbf{q}_n = \mathbf{q}_n(t)$. For a dissipative system, they can be rewritten as before, provided the Lagrangian ($L'$) separates the “conservative” forces (when they stem from some potential function) from those “non-conservative” ($\bar{\mathbf{f}}_i$):

$$\frac{d}{dt}\left(\frac{\partial L'}{\partial \dot{\mathbf{q}}_n}\right) - \left(\frac{\partial L'}{\partial \mathbf{q}_n}\right) = \bar{\mathbf{F}}_n \tag{1.5}$$

where, for a discrete system:

$$\bar{\mathbf{F}}_n = \sum_i \bar{\mathbf{f}}_i \cdot \left(\frac{\partial \mathbf{r}_i}{\partial \mathbf{q}_n}\right) \tag{1.6}$$

vectors $\mathbf{r}_i$ now indicating the actual positions, and $(\frac{\partial \mathbf{r}_i}{\partial \mathbf{q}_n})$ representing the vector of its first derivatives with respect to $q_s$ ($s = 1, 2, \dots, n$). Also, when first orders no longer suffice, the Euler–Lagrange functional derivative is to be extended to the next terms in $\frac{d^i \mathbf{q}_n}{dt^i}$, i.e.:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\mathbf{q}}_n}\right) - \left(\frac{\partial L}{\partial \mathbf{q}_n}\right) = \frac{d^2}{dt^2}\left(\frac{\partial L}{\partial \dddot{\mathbf{q}}_n}\right) + \cdots \tag{1.7}$$

The Lagrangian function can be very complicated, and normally requires a discussion of the involved constraints (i.e., the mechanical limitations to the motion). We cannot address their classification properties here in detail (i.e., holonomy or anholonomy, scleronomy or rheonomy, and so on) but should remember, for example, that the former variational calculation strictly applies to “ideal” constraints (basically, when their resultant force obeys the virtual work theorem for reversible displacements) and “holonomous” systems (i.e., if each constraint is expressible as an integrable relation, for the only generalized coordinates and time). Otherwise, the coordinate variations in the action functional of a system of $m$ (ideal) anholonomous constraints are not independent, $\delta\mathbf{q}_n\mathbf{C} = \mathbf{0}$, with $\mathbf{C}$ being a (known) matrix of rank $n \times m$. Hence, the Euler–Lagrange equations to be generally solved take the form:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\mathbf{q}}_n}\right) - \left(\frac{\partial L}{\partial \mathbf{q}_n}\right) = \mathbf{C}\mathbf{l}_m \tag{1.8}$$

where $\mathbf{l}_m = (l_1, l_2, \ldots, l_m)$ is a (column) vector of Lagrange's multipliers.

If a system is "scleronomous" (say, the physical analogue of "autonomous" function, as used in mathematics), $L$ does not depend explicitly on time (i.e., the independent variable). This is the case of all isolated systems, or embedding a constant (external) field, contrarily to those "rheonomous," for which $L = L(t)$ (e.g., a moving constraint). Hence, the condition $(\frac{\partial L}{\partial t}) = 0$ implies:

$$\left(\frac{dL}{dt}\right) = \dot{\mathbf{q}}_n \cdot \left(\frac{\partial L}{\partial \mathbf{q}_n}\right) + \ddot{\mathbf{q}}_n \cdot \left(\frac{\partial L}{\partial \dot{\mathbf{q}}_n}\right) \tag{1.9}$$

and, from the Euler–Lagrange equations, the following quantity:

$$E = \dot{\mathbf{q}}_n \cdot \left(\frac{\partial L}{\partial \dot{\mathbf{q}}_n}\right) - L \tag{1.10}$$

does not change, $(\frac{dE}{dt}) = 0$. The function $E$ defines the energy of the system, and homogeneity with respect to time imposes it to be invariant during the motion (i.e., an "integral of motion"). Scleronomy implies the kinetic energy ($K$) to be expressible as a quadratic form of the generalized velocities (while rheonomy would bring in addition linear velocity terms):

$$K(\mathbf{q}_n, \dot{\mathbf{q}}_n) = \frac{1}{2}\dot{\mathbf{q}}_n^{\mathrm{T}} \cdot \mathbf{M}(\mathbf{q}_n)\dot{\mathbf{q}}_n \tag{1.11}$$

where $\mathbf{M}$ is a matrix of rank $n$ and $^{\mathrm{T}}$ denotes the transpose operation. If the system is conservative, the potential energy depends as $U = U(\mathbf{q}_n)$, and the Lagrangian quantifies the kinetic energy excess over it:

$$L(\mathbf{q}_n, \dot{\mathbf{q}}_n) = K(\mathbf{q}_n, \dot{\mathbf{q}}_n) - U(\mathbf{q}_n) \tag{1.12}$$

After applying Euler's theorem for homogeneous functions, $K = \frac{1}{2}\dot{\mathbf{q}}_n \cdot (\frac{\partial L}{\partial \dot{\mathbf{q}}_n})$, the energy takes the form:

$$E(\mathbf{q}_n, \dot{\mathbf{q}}_n) = K(\mathbf{q}_n, \dot{\mathbf{q}}_n) + U(\mathbf{q}_n) \tag{1.13}$$

and, when $\mathbf{M} = \mathbf{m} \neq \mathbf{m}(\mathbf{q}_n)$ is a constant "mass tensor," Newton's second law is recovered as:

$$\mathbf{F}_n = \mathbf{m}\mathbf{a}_n \tag{1.14}$$

where $\mathbf{F}_n = -(\frac{\partial U}{\partial \mathbf{q}_n})$ identifies the conservative force and $\mathbf{a}_n = \ddot{\mathbf{q}}_n$.

Lagrangians can also be explicitly independent of the $s$th degree of freedom, $(\frac{\partial L}{\partial q_s}) = 0$, and in this case $(\frac{\partial L}{\partial \dot{q}_s}) =$ constant. The latter is the $s$th element of a super-vector $\mathbf{p}_n \equiv \{p_s\colon\ s = 1, 2, \ldots, n\}$ of "conjugate momenta" ($p_s$), defined by:

$$\left(\frac{\partial L}{\partial \dot{\mathbf{q}}_n}\right) = \mathbf{p}_n \tag{1.15}$$

and the generalized coordinate $q_i$ in which the conjugate momentum $p_i$ is conserved bears the name of "cyclic."

Finally, it is instructive to note the rewriting $K = \frac{1}{2}\dot{s}_n^2$, in terms of the squared "distance" metric induced by $d\mathbf{q}_n^{\mathrm{T}} \cdot \mathbf{M}\, d\mathbf{q}_n = ds_n^2$. In the absence of external forces ($U$ = constant), the principle of stationary action thus reduces to a length minimization of the form:

$$\delta \int_{\mathbf{q}'}^{\mathbf{q}''} ds_n = 0 \tag{1.16}$$

tantamount to requiring Hertz's principle of Least Curvature (with unlike masses). In the fourth section, a formally close variational problem will be worked out.

## 2.2 Hamiltonian mechanics

The action functional can also be seen as a function of quantities defined along the (actual) trajectory of motion. When the generalized coordinate at the upper extremum ($t''$) is varied, the only displacement which survives is $\delta S = \mathbf{p}_n \cdot \delta \mathbf{q}_n$:

$$\mathbf{p}_n = \left(\frac{\partial S}{\partial \mathbf{q}_n}\right) \tag{1.17}$$

while, by definition, the Lagrangian follows from conceiving the action as an explicit function of time:

$$L = \left(\frac{dS}{dt}\right) \tag{1.18}$$

Therefore, applying to $S$ the total time (or "Lagrangian") derivative $\frac{d}{dt} = \frac{\partial}{\partial t} + \dot{\mathbf{q}}_n \cdot \frac{\partial}{\partial \mathbf{q}_n}$, the Hamilton–Jacobi equation is obtained:

$$H(\mathbf{q}_n, \mathbf{p}_n, t) = -\left(\frac{\partial S}{\partial t}\right) \tag{1.19}$$

where $H$ equals the previous expression for $E$, giving the energy of the system at any time, and is called the Hamilton's function (or Hamiltonian):

$$H(\mathbf{q}_n, \mathbf{p}_n, t) = \dot{\mathbf{q}}_n \cdot \mathbf{p}_n - L \tag{1.20}$$

It provides the starting point for an alternative, on some occasions more convenient, description of mechanics. To briefly convince ourselves of this, note that the Hamiltonian is nothing but a Legendre-transformed Lagrangian, i.e., $H = x(\frac{dL}{dx}) - L$, with $x = \dot{q}_s$. From the theory of Legendre's transformations, the conjugate momentum is the natural variable to work with, $p_s = (\frac{dL}{d\mathbf{x}})$, replacing the generalized velocity and suggesting the "phase space" $\{\mathbf{q}_n, \mathbf{p}_n\} \equiv \{(q_s, p_s)\colon\ s = 1, 2, \ldots, n\}$ to be the natural environment for the Hamilton's mechanics. In this representation, the action easily rewrites as:

$$S = S_0 - \int H\, dt \tag{1.21}$$

where:

$$S_0 = \int \mathbf{p}_n \cdot d\mathbf{q}_n \tag{1.22}$$

is termed the abbreviated action. Again, when scleronomy applies, both Lagrangian and Hamiltonian do not explicitly depend upon time, and energy does not vary throughout the motion:

$$H(\mathbf{q}_n, \mathbf{p}_n) = E \tag{1.23}$$

The variational principle for this case is thus the Maupertuis's (or Maupertuis–Euler principle):

$$\delta S_0 = 0 \tag{1.24}$$

limited to a determination of the "shape of motion," that is, in the generalized coordinates alone. Here, the speed with which any path is traveled, and thus any time parametrization, is clearly not influential.

Hamilton's principle comprises instead two independent variations:

$$\begin{aligned} \delta S = \mathbf{p}_n \cdot \delta \mathbf{q}_n \Big|_{t'}^{t''} &+ \int_{t'}^{t''} \delta \mathbf{p}_n \cdot \left[ d\mathbf{q}_n - \left( \frac{dH}{d\mathbf{p}_n} \right) dt \right] \\ &+ \int_{t'}^{t''} \delta \mathbf{q}_n \cdot \left[ d\mathbf{p}_n + \left( \frac{dH}{d\mathbf{p}_n} \right) dt \right] \end{aligned} \tag{1.25}$$

their annullments making the functional stationary and giving the so-called "canonical" equations of Hamiltonian mechanics:

$$\dot{\mathbf{q}}_n = \left( \frac{\partial H}{\partial \mathbf{p}_n} \right), \qquad \dot{\mathbf{p}}_n = -\left( \frac{\partial H}{\partial \mathbf{q}_n} \right) \tag{1.26}$$

In summary, each state of a mechanical system corresponds to a phase space point, called "representative," and evolving in $2n$ dimensions by the trajectory described by Hamilton's equations. They are first-order differential equations, against those of second-order met in the Newtonian and Lagrangian theories. Finally, remember that Hamilton's language is generally less appropriate than Lagrange's in the presence of dissipation, in quantum and the so-called "path integral" descriptions, but also in general relativity, where the trajectory is fixed by the (ten) components of a (metric) tensor, as will be seen in three sections.

## 2.3 Poisson's brackets and canonical transformations

The Hamiltonian formulation of mechanics leads to a simple representation of any arbitrary dynamic quantity (or observable), varying along a phase space path. In fact, since:

$$\left(\frac{df}{dt}\right) = \left(\frac{\partial f}{\partial t}\right) + \dot{\mathbf{q}}_n \cdot \left(\frac{\partial f}{\partial \mathbf{q}_n}\right) + \dot{\mathbf{p}}_n \cdot \left(\frac{\partial f}{\partial \mathbf{p}_n}\right) \tag{1.27}$$

from the Hamilton's equations, one has:

$$\left(\frac{df}{dt}\right) = \{f, H\} + \left(\frac{\partial f}{\partial t}\right) \tag{1.28}$$

where the operator written as:

$$\{h, g\} = \left(\frac{\partial h}{\partial \mathbf{q}_n}\right) \cdot \left(\frac{\partial g}{\partial \mathbf{p}_n}\right) - \left(\frac{\partial h}{\partial \mathbf{p}_n}\right) \cdot \left(\frac{\partial g}{\partial \mathbf{q}_n}\right) \tag{1.29}$$

defines Poisson's brackets for any couple of dynamic observables, $g = g(\mathbf{q}_n, \mathbf{p}_n, t)$ and $h = h(\mathbf{q}_n, \mathbf{p}_n, t)$. By construction, the only elementary combination returning non-null brackets is given evidently by any canonically conjugate pair of coordinates:

$$\{q_s, q_{s'}\} = 0, \qquad \{p_s, q_{s'}\} = \delta_{ss'}, \qquad \{p_s, p_{s'}\} = 0 \tag{1.30}$$

where:

$$\delta_{ss'} = \begin{cases} 1 & (s = s') \\ 0 & (s \neq s') \end{cases} \tag{1.31}$$

is Krönecker's symbol. Furthermore, the following rules, of anticommutativity:

$$\{h, g\} = -\{g, h\} \tag{1.32}$$

additivity:

$$\{h + f, g\} = \{h, g\} + \{f, g\} \tag{1.33}$$

and Jacobi's identity:

$$\big\{f, \{g, h\}\big\} + \big\{g, \{h, f\}\big\} + \big\{h, \{f, g\}\big\} = 0 \tag{1.34}$$

are evidently fulfilled. Other relevant properties are:

$$\{h, q_s\} = \left(\frac{\partial h}{\partial p_s}\right), \qquad \{h, p_s\} = -\left(\frac{\partial h}{\partial q_s}\right) \tag{1.35}$$

and:

$$D_t\{h, g\} = \{D_t h, g\} + \{h, D_t g\} \tag{1.36}$$

the operator on the right being either $D_t = \frac{\partial}{\partial t}, \frac{d}{dt}$. Hamilton's equations rewrites thus as:

$$\dot{q}_i = \{q_i, H\}, \qquad \dot{p}_i = \{p_i, H\} \tag{1.37}$$

whereupon, expliciting the Lagrangian derivative of the Hamilton's function:

$$\left(\frac{\partial H}{\partial t}\right) = \left(\frac{dH}{dt}\right) \tag{1.38}$$

Every time Poisson's bracket is zero, as in the elementary cases $\{h, h\} = 0$ and $\{h, \alpha\} = 0$, with $\alpha = \text{const}$, the two observables are said to commute. In particular, $H'$ is an "integral of motion" whenever it does not change along the trajectory, being left invariant by the moving frame of the Hamiltonian flow, $(\frac{dH'}{dt}) = 0$. When $H'$ is autonomous, it will be an integral of motion provided it commutes with Hamilton's function:

$$\{H', H\} = 0 \tag{1.39}$$

This is the case, of course, of the Hamiltonian of any scleronomous and conservative system ($H' = H$), as well as of any function of it ($H' = h(H)$).

Euler–Lagrange's equations are invariant under any local variation of the reference system, but the Hamilton's mechanics generally is not. That particular class of coordinate transformations preserving Hamilton's equations and Poisson's brackets are named canonical (or contact's). Transformations like $\mathbf{q}_n \to \mathbf{Q}_n(\mathbf{q}_n, \mathbf{p}_n, t)$ and $\mathbf{p}_n \to \mathbf{P}_n(\mathbf{q}_n, \mathbf{p}_n, t)$ are thus canonical when:

$$\dot{\mathbf{Q}}_n = \left(\frac{\partial H^*}{\partial \mathbf{P}_n}\right), \qquad \dot{\mathbf{P}}_n = -\left(\frac{\partial H^*}{\partial \mathbf{Q}_n}\right) \tag{1.40}$$

for some new Hamiltonian $H^* = H^*(\mathbf{Q}_n, \mathbf{P}_n, t)$ of the absolute time. From Hamilton's principle, applied to the starting ($L$) and the transformed ($L^*$) Lagrangians, the above equations hold if a function ($\Phi$) such as $(\frac{d\Phi}{dt}) = L - L^*$ exists. It is called the generating function of the canonical transformation, and can be represented by an exact differential:

$$d\Phi = \left(H^* - H\right) dt + \mathbf{p}_n \cdot d\mathbf{q}_n - \mathbf{P}_n \cdot d\mathbf{Q}_n \tag{1.41}$$

Poisson's brackets are clearly canonically invariant, i.e., for any couple of observables $f$ and $g$:

$$\{h, g\}_{\{\mathbf{q}_n, \mathbf{p}_n\}} = \{h, g\}_{\{\mathbf{Q}_n, \mathbf{P}_n\}} \tag{1.42}$$

still with:

$$\{Q_s, Q_{s'}\} = 0, \qquad \{P_s, Q_{s'}\} = \delta_{ss'}, \qquad \{P_s, Q_{s'}\} = 0 \tag{1.43}$$

## 2.4 Liouville's theorem

Liouville's mechanics is generally concerned with the evolution of probability distribution functions in the phase space. In (classical) Hamiltonian mechanics, it is related to Liouville's theorem, asserting that any phase space portion evolves at constant volume, i.e.:

$$\int \cdots \int dq_n dp_n = \int \cdots \int dQ_n \, dP_n = \text{const} \tag{1.44}$$

with $dq_n^2 = d\mathbf{q}_n^{\mathrm{T}} \cdot d\mathbf{q}_n$, and similarly for each of the other integration measures here employed. Mathematically, this means that the associated Jacobian transformation is unitary:

$$\left\| \frac{\partial(\mathbf{Q}_n, \mathbf{P}_n)}{\partial(\mathbf{q}_n, \mathbf{p}_n)} \right\| = 1 \tag{1.45}$$

Physically, the distribution function $\rho_n = \rho_n(\mathbf{q}_n, \mathbf{p}_n, t)$, counting the number of representative points per unit volume of the phase space, will be an integral of motion:

$$\left( \frac{\partial \rho_n}{\partial t} \right) = \mathcal{L}(\rho_n) \tag{1.46}$$

The latter is (classical) Liouville's equation and $\mathcal{L}(\ldots) \equiv \{\ldots, f\}$ is said to be the Liouvillian operator. A typical equilibrium situation it depicts at once is when the distribution function only depends on a set of integrals of motion, $(i_1, \ldots, i_q) \equiv \mathbf{i}_q$. If $\rho_n = \rho_n(\mathbf{i}_q)$, then for any $q_s$ $(s = 1, 2, \ldots, n)$:

$$\left( \frac{\partial \rho_n}{\partial q_s} \right) = \left( \frac{\partial \rho_n}{\partial \mathbf{i}_q} \right) \cdot \left( \frac{\partial \mathbf{i}_q}{\partial q_s} \right) = 0 \tag{1.47}$$

and identically for any conjugate momentum, getting $(\frac{\partial \rho_n}{\partial t}) = 0$.

# 3. SPECIAL RELATIVITY

## 3.1 Einstein's postulates

The theory of special relativity made its appearance in the 1905's Einstein paper on "the electrodynamics of moving bodies." As mentioned in the historical introduction, the central aim was to demonstrate that, under the Lorentz–Poincaré symmetry of motion, electric and magnetic forces transform so as to preserve Maxwell's equations. We will not be concerned here with electromagnetism (e.g., the Maxwell–Hertz equations for empty space, Doppler's shift and the aberration theory), but will concentrate for now on the kinematic part.

Special relativity could be defined in fact as the (first modern) theory of inertial (or non-accelerated) frames, and is consequence of Einstein's two postulates, normally the first said of relativity and the second of constancy of the light speed:

1. The laws of physics are the same in all inertial frames of reference.
2. The light speed in vacuum ($c$) has the same constant value in all inertial frames, irrespective of the velocities of its source and the observer.

The first postulate asserts that any law of nature (or any measurement) detected in non-accelerated frames is never affected by relative translational movements. It can be interpreted as a principle of metric uniformity, on account of which space and time appear isotropic and homogeneous from whatever inertial observer. Furthermore, it portrays the symmetry among a triply infinite set of frames that move rectilinearly and uniformely with respect to each other, witnessing an "absolute" accord about any experiment and law of nature. For example, should a new physical equation be unveiled, it would immediately reveal the roles of space and time in all inertial systems. All the aforesaid crystallizes into a popular notion, that of covariance, pointing to the feature of being invariant under a change of coordinate system.

While the first postulate settles a symmetry of nature for an entire class of observers, the second gives the light speed the privileged status to be an uppermost limit of nature. Einstein posited the constancy of $c$ in a single frame, deriving its invariance for any other inertial system. Recall that, on imposing the form-invariance (or covariance) of Maxwell's equations, the simple requirement of linear and invertible coordinate changes would suffice to dispense the derivation of the Lorentz–Poincaré transformation with the second postulate. This, nevertheless, would fade from the Einsteinian kinematic view of motion. Despite the numerous criticisms received, some of which certainly deserve consideration, Einstein's two postulates drew together a robust conception of the kinematics of inertial systems, paving the way for the general theory of accelerated frames.

## 3.2 Lorentz–Poincaré transformation

Consider two inertial frames, $O = \{t, \mathbf{r} = (x, y, z)\}$ and $O' = \{t', \mathbf{r}' = (x', y', z')\}$, both expressing time ($t$) and space ($\mathbf{r}$) in Cartesian coordinates. Each point in $O$ and $O'$ defines a spatio-temporal "event," and the path depicted as time goes in the 4-dimensional spacetime continuum is called "worldline." Assume now that $O'$ moves along the positive direction of the axis $x$ in common to both observers, with constant velocity $\mathbf{v} = (v, 0, 0)$ relative to $O$, and consider a pointwise source set at the origin of $O$, emitting a light pulse traveling in every direction with speed $c$. At any time $t$, the spherically symmetric representation of the wavefront of radius $ct$, centered at the origin in $O$, is:

$$c^2t^2 - \mathbf{r}^2 = 0 \tag{1.48}$$

while, consistently with Einstein's postulates, $O'$ will detect:

$$c^2t'^2 - \mathbf{r}'^2 = 0 \tag{1.49}$$

meaning $\mathbf{r}^2 = \mathbf{r} \cdot \mathbf{r}$ in both cases. Imposing the transformation relating $O$ and $O'$ to be linear, one may write:

$$c^2t^2 - \mathbf{r}^2 = f\big(O', O; \mathbf{v}\big)\big(c^2t'^2 - \mathbf{r}'^2\big) \tag{1.50}$$

where, in a homogeneous and isotropic spacetime, the function on the right can only depend on the absolute value of the relative velocity, $f(O, O'; |\mathbf{v}|) = f(v)$. If the direction of any movement along $x$ does not change with changing coordinates, it turns out:

$$t' = f(v)\gamma_L(t - \beta x/c), \qquad x' = f(v)\gamma_L(x - vt) \tag{1.51}$$

with:

$$\frac{y'}{y} = \frac{z'}{z} = f(v) \tag{1.52}$$

where $\gamma_L = (1 - \beta^2)^{-1/2}$ is the so-called Lorentz's factor, taking the effect of the relative motion into account by the square velocity ratio $\beta = \frac{v}{c}$. It brings a singularity in $v = c$ that was clearly expected from the second postulate. Conversely, since $O$ is moving relative to $O'$ with velocity $-\mathbf{v}$:

$$f\big(O, O'; -\mathbf{v}\big)\big(c^2t^2 - \mathbf{r}^2\big) = c^2t'^2 - \mathbf{r}'^2 \tag{1.53}$$

then:

$$f(-v) = f^{-1}(v) \tag{1.54}$$

Isotropy requires the above transformation not to be affected by changing the direction of motion, that is, $f^2(v) = 1$. The negative solution, when $v = 0$ and $t = 0$, yields $\mathbf{r}'^2 = -\mathbf{r}^2$ and is therefore rejected. We are left thus with $f(v) = 1$, setting definitely the Lorentz–Poincaré transformation to:

$$t' = \gamma_L(t - \beta x/c), \quad x' = \gamma_L(x - vt), \quad y' = y, \quad z' = z \tag{1.55}$$

As expected, the Galilean transformation restores upon $c \to \infty$, when signals can proceed with arbitrary speed and an absolute time establishes again ($t' = t$).

In terms of infinitesimal displacements, the spacetime interval becomes:

$$ds^2 = c^2\,dt^2 - d\mathbf{r}^2 \tag{1.56}$$

and takes the same value in any inertial system:

$$ds^2 = ds'^2 \tag{1.57}$$

It translates the notion of Galilean frame used in the Newtonian theory, and the picture of motion it affords corresponds to the Newton's law, where a 4-dimensional light path is traveling along a straight line. Its invariance encompasses $\infty^{10}$ linear transformations, identifying the Lorentz–Poincaré group. Mathematically speaking, special relativity may be defined as the theory of the invariants of the Lorentz–Poincaré group, assessed beautifully by Minkowski some years later. He replaced time with the imaginary coordinate $ict$, and rewrote the former interval in an Euclidean 4-dimensional space, i.e.,

$$ds^2 = -\eta_{\alpha\beta}\,dx^\alpha\,dx^\beta \tag{1.58}$$

the metric structure of which being specified by the Minkowskian pseudometric $(\eta_{\alpha\beta})$. In Cartesian coordinates, it is evidently $\eta_{\alpha\beta} = \mathrm{diag}(-1, 1, 1, 1)$, and said to have signature $-2$. Lorentz–Poincaré transformations thereby connect Minkowskian frames, just as Galilean transformations connect Galilean observers. In principle, another option could be for an interval where all coordinates are totally equivalent:

$$ds^2 = c^2\,dt^2 + d\mathbf{r}^2 \tag{1.59}$$

For example, rotating the plane $(t, x)$ about an angle $\theta$ would stand for $\mathbf{v} = (\tan\theta, 0, 0)$, space and time getting interchangeable when $\alpha \to \frac{\pi}{2}$ $(v \to \infty)$:

$$t \leftrightarrow -x', \qquad x \leftrightarrow t', \qquad y \leftrightarrow y', \qquad z \leftrightarrow z' \tag{1.60}$$

Nobody was able compelling logical reasons to disown this symmetry, but common sense would be so plainly contradicted that it was always ignored, leaving to Minkowski's spacetime the role of the only possible candidate.

## 3.3 Rules of length contraction and time dilation

Consider a measuring-rod at rest in $O'$, parallel to the $x$-axis, with fixed end-point coordinates and size $\Delta l_0 = x_2 - x_1$. It is a "proper" length, seen from any observer in "its" reference frame. The Lorentz–Poincaré transformation for the spatial positions of both points implies $(i = 1, 2)$:

$$x'_i = \gamma_L\big(x_i(t) - vt\big), \qquad i = 1, 2 \tag{1.61}$$

$x_i(t)$ denoting the motions of the rod extremities in $O$. Accordingly, let $x_2(t) - x_1(t) = \Delta l$, it turns out:

$$\frac{\Delta l_0}{\Delta l} = \gamma_L \tag{1.62}$$

This rule, said of length contraction, had already been noticed by FitzGerald and Lorentz for the dimension of a body that is parallel to the motion direction. Lorentz gave an electrodynamic explanation for it, but Einstein succeeded to demonstrate that length contractions (and the next time dilation) represent a more fundamental phenomenon, characterizing the relative motion. Of course, the contraction formula for (proper) volumes reads equally, $\Delta V_0 = \gamma_L \Delta V$.

To get the corresponding rule in the temporal coordinate, consider the "proper" time $\Delta t_0 = t'_2 - t'_1$, of a clock resting in $O'$, and the interval $\Delta t = t_2 - t_1$, of another one located in $O$, still proceeding with speed $v$ relative to $O'$. Now, since $c\Delta t' = \gamma_L(c\Delta t - \beta \Delta x)$ and $\Delta x = v\Delta t$, the result is:

$$\frac{\Delta t}{\Delta t_0} = \gamma_L \tag{1.63}$$

The above rules of length contraction and time dilation lie among the most important implications of special relativity. If $v \ll c$, proper and relativistic intervals tend to get indistinguishable. With increasing relative velocity, clocks run slower and lengths contract in the direction of motion. When $\gamma_L$ is not constant, such rules are to be integrated along the worldline. Note that a time-dependence in the Lorentz's factor would make the observer age more slowly with increasing velocity.

## 3.4 Classification of events

The invariant interval is written by an indefinite quadratic form, and lends itself to a useful classification of events according to the sign it takes. As the light speed is posited as an upper bound to every velocity, spacetime splits into three regions, delimited by a "light cone." Upper-half ($t > 0$) and lower-half ($t < 0$) cones determine respectively the future and past, and any worldline directed from the past to the future will stay inside or outside the cone on the basis of the following scheme. Let $\Delta r$ indicate the spatial distance between events and $\Delta r_c \equiv c\Delta t$, one has:

$$\begin{aligned} &\Delta r < \Delta r_c \quad \text{(time-like)} \\ &\Delta r = \Delta r_c \quad \text{(light-like)} \\ &\Delta r > \Delta r_c \quad \text{(space-like)} \end{aligned} \tag{1.64}$$

In the time-like case, intervals take real values ($\Delta s^2 > 0$) and there is a reference system where the two events are located at the same spatial point but are separated in time. The difference $\Delta s$ is known as the proper time interval, and can be used to parametrize the worldline. If events are space-like, their interval is imaginary ($\Delta s^2 < 0$). In this case, a Lorentz–Poincaré transformation can make them simultaneous, lying at the same time at different space points. Finally, when their separation is zero ($\Delta s = 0$), one gets back to the second postulate. Any reference system that moves at the light speed relative to some observer will be light-like in any inertial frame.

The light cone gives thus a simple criterion to pick up if events can be causally connected or not. In fact, any point in the space-like region ("the elsewhere") can never be reached by, or come from, any event located outside it. Naturally, as the above classification is Lorentz–Poincaré invariant, two events which are displaced by a space-like separation in one reference system will not be causally related in all reference systems. No signal can propagate faster than light, and an event may stand in a causal relation only to events separated from it by a time-like interval.

The limitation imposed by Einstein's causality to natural phenomena reduces essentially to forbid any propagation faster than light, giving rise to interesting relations among causality, geometry and topology. More generally, geometry entails events, their order being shaped by causal structures, expressible as partial ordering operations among events. For instance, several analysis addressing the Minkowski's spacetime concluded that causality would be characterized by linear coordinate transformations. In a discrete spacetime, the relation between causality and Lorentz–Poincaré covariance needs to be discussed. The central issue is understanding if, on passing from a continuous to a discrete manifold, the Lorentz–Poincaré symmetry is invalidated or not. Though sounding intuitive, it is not always clear what a discrete Lorentz–Poincaré covariance actually stands for, and the literature seems to report conflicting answers on it. Some authors circumvented the problem by imposing a priori this symmetry property (by causal sets, named "causets"). They consist of locally bounded sets, partially ordered and endowed with a binary application between events, getting back in the continuum limit to the ordinary causal description.

Another classification is suggested by the sign of the square root of the quadratic form:

$$ds = \pm\sqrt{-\eta_{\alpha\beta}\, dx^\alpha\, dx^\beta} \tag{1.65}$$

which, for two events instantaneously at rest at the same spatial coordinate, clearly reduces the proper time to $ds = \pm c\,dt$. We have just learnt that it is the sum of all positive displacements, the "proper age" the particle experiences along the worldline. However, negative solutions $ds = -c\,dt$ would imply that proper time and time coordinate evolve in opposite directions or, otherwise said, the order of two events would be systematically "time-reversed." By close arguments, one may parallel a "space-reversal" (or inversion) transformation, showing an equally unacceptable "chirality" for right-type and left-type spatial measurements. Again, these symmetries are surely at odds with our daily experience but, at least when concerned with kinematics alone, no logical reasoning may be able ultimately to produce a criterion discriminating them.

## 3.5 Notes on tensor analysis

In the Lorentz–Poincaré covariance, a quadratic form is preserved in the four space-time coordinates. Thus, the most natural theory of the invariants of this symmetry group comes from an extension of tensor calculus to a four-dimensional space (or "variety"). An account of the main notions and calculation rules met in special relativity are so going to be given, then to be enlarged to the transformation rules of the general theory.

Tensor calculus deals with objects of the form:

$$A^{\alpha\beta\gamma\ldots}{}_{\omega\sigma\tau\ldots} \tag{1.66}$$

where each index can take, independently of each other, the values $1, 2, \ldots, d$ (the space dimensionality), and is named "contravariant" when it is upper, or "covariant" when is lower. Tensors like the former, with both kinds of indices, are said "mixed." Quantities and equations are used to being represented by "Einstein's convention," summing over repeated indices, e.g.:

$$A^{\alpha\beta}{}_{\gamma} B^{\omega}{}_{\alpha} C^{\alpha}_{\zeta} = A^{1\beta}{}_{\gamma} B^{\omega}{}_{1} C^{1}{}_{\zeta} + A^{2\beta}{}_{\gamma} B^{\omega}{}_{2} C^{2}{}_{\zeta} + \cdots + A^{d\beta}{}_{\gamma} B^{\omega}{}_{d} C^{d}{}_{\zeta} \tag{1.67}$$

Tensors generally depend on coordinates, $x^{\alpha} \equiv \{x^1, x^2, \ldots, x^d\}$, changing in turn by a given transformation rule $o^{\mu}{}_{\nu}$ (sometimes called affine):

$$x'^{\mu} = o^{\mu}{}_{\nu} x^{\nu} \tag{1.68}$$

with inverse $\bar{o}^{\nu}{}_{\mu}$. On this basis, when the above object transforms as:

$$A'^{\alpha\beta\gamma\ldots}{}_{\omega\sigma\tau\ldots} = o^{\alpha}{}_{\kappa} o^{\beta}{}_{\chi} o^{\gamma}{}_{\zeta} \ldots \bar{o}^{\rho}{}_{\omega} \bar{o}^{\delta}{}_{\sigma} \bar{o}^{\lambda}{}_{\tau} \ldots A^{\kappa\chi\zeta\ldots}{}_{\rho\delta\lambda\ldots} \tag{1.69}$$

it is said to be a tensor with contravariant components in the indices $\alpha, \beta, \gamma, \ldots$ and covariant components in $\omega, \sigma, \tau$, and so on. The number of indices specifies the tensor order (or rank).

Among the main properties which all tensors fulfill, remember:

$$\begin{aligned} &H^{\mu}{}_{\nu} = f F^{\mu}{}_{\nu} + g G^{\mu}{}_{\nu} \quad \text{(linear combination)} \\ &H^{\mu\tau}{}_{\nu} = F^{\mu}{}_{\nu} G^{\tau} \quad \text{(direct product)} \\ &H^{\mu\tau} = F^{\mu\gamma\tau}{}_{\gamma} \quad \text{(contraction)} \\ &H^{\mu\tau}{}_{\nu} = G^{\mu\tau}{}_{,\nu} \quad \text{(differentiation)} \end{aligned} \tag{1.70}$$

where $f$, $g$ are arbitrary scalar quantities and, for brevity, any partial derivative as $\frac{\partial \ldots}{\partial x^\nu} \equiv \ldots_{,\nu}$ is denoted heretofore by the "comma operator." These equations mean that, whenever $F$ and $G$ are tensors, the expressions on the right are also obeying the tensor transformation rule. Nevertheless, not every index operation gives the components of a tensor. For instance, let the mixed tensor $H^{\mu\tau}{}_\nu$, those obtained upon contraction on two upper indices, $H^{\mu\mu}{}_\nu$, are not.

## 3.6 Covariant and contravariant vector components

The simplest first-order tensor is a $d$-dimensional contravariant vector ($V^\mu$), transforming as:

$$V'^\mu = o^\mu{}_\nu V^\nu \tag{1.71}$$

while:

$$V'_\mu = \bar{o}^\nu{}_\mu V_\nu \tag{1.72}$$

Evidently, the distinct ways in which contravariant and covariant components transform under a continuous coordinate change are those of the coordinates themselves (the differentials, $dx^\mu$):

$$o^\mu{}_\nu = \left(\frac{\partial x'^\mu}{\partial x^\nu}\right) \tag{1.73}$$

and of the gradient operator (the derivatives, $\frac{\partial}{\partial x^\mu}$):

$$\left(\frac{\partial}{\partial x'^\mu}\right) = \bar{o}^\alpha{}_\mu \left(\frac{\partial}{\partial x^\alpha}\right) \tag{1.74}$$

being, obviously:

$$\bar{o}^\nu{}_\mu = \left(o^\mu{}_\nu\right)^{-1} = \left(\frac{\partial x^\nu}{\partial x'^\mu}\right) \tag{1.75}$$

In more abstract treatises, contravariant and covariant vectors substitute another couple of terms, vectors and "linear forms," the letters forming a "dual space" in which vectors are mapped into scalars. However, this classification does not refer to different coordinate systems, but is a convention for any single frame.

Let it denote by a unit vector basis, $\{\mathbf{e}_\alpha\}$, and consider a scalar product defined in it. For any pair of vectors, $\mathbf{u}$ and $\mathbf{v}$:

$$\mathbf{u} \cdot \mathbf{v} = \left(U^\mu \mathbf{e}_\mu\right) \cdot \left(V^\alpha \mathbf{e}_\alpha\right) = g_{\mu\alpha} U^\mu V^\alpha \tag{1.76}$$

their contravariant components following from parallel projections onto each axis, and:

$$g_{\mu\alpha} = g_{\alpha\mu} \equiv \mathbf{e}_\mu \cdot \mathbf{e}_\alpha \tag{1.77}$$

Consider now a "reciprocal" (or "dual") vector basis, $\{\bar{\mathbf{e}}_\alpha\}$, defined by the orthogonality condition, $\bar{\mathbf{e}}_\alpha \cdot \mathbf{e}_\mu = \delta^\alpha_\mu$, the latter being a "mixed" Krönecker symbol. If

$\mathbf{u} = U_\mu \bar{\mathbf{e}}_\mu$, it is simple to show:

$$U_\mu = g_{\mu\alpha} U^\alpha \tag{1.78}$$

that is, covariant components ($U_\mu$) are the parallel projections onto the reciprocal axes. They can also be intended as the perpendicular projections onto each contravariant axis, i.e., $\mathbf{u} \perp \mathbf{e}_\mu = U_\mu / |\mathbf{e}_\mu|$, with $|\mathbf{e}_\mu| = \sqrt{\mathbf{e}_\mu \cdot \mathbf{e}_\mu} = \sqrt{g_{\mu\mu}}$ (at fixed $\mu$). Furthermore:

$$U^\mu = g^{\mu\alpha} U_\alpha \tag{1.79}$$

where:

$$g^{\mu\alpha} = g^{\alpha\mu} = \bar{\mathbf{e}}_\mu \cdot \bar{\mathbf{e}}_\alpha \tag{1.80}$$

$$g^{\mu\nu} g_{\nu\kappa} = \delta^\mu{}_\kappa \tag{1.81}$$

and:

$$\mathbf{u} \cdot \mathbf{v} = U_\alpha V^\alpha = U^\mu V_\mu = g^{\mu\alpha} U_\mu V_\alpha \tag{1.82}$$

Clearly, from $\mathbf{u} = U'^\mu \mathbf{e}'_\mu = U^\alpha \mathbf{e}_\alpha$, the basis transformation rule is given by:

$$\mathbf{e}_\alpha = o^\mu{}_\alpha \mathbf{e}_\mu, \qquad \mathbf{e}'_\mu = \bar{o}^\alpha{}_\mu \mathbf{e}_\alpha \tag{1.83}$$

In summary, a couple of main points should be retained from the last two paragraphs. Changing representation, contravariant or covariant, corresponds to the raising or lowering of indices, and can be accomplished by multiplying by $g^{\mu\nu}$ or $g_{\mu\nu}$. Changing reference frame requires instead multiplying by $o^\mu{}_\alpha$ and $\bar{o}^\alpha{}_\mu$. In Cartesian systems, $g_{\mu\nu} = \delta_{\mu\nu}$ and $\mathbf{e}_\alpha = \bar{\mathbf{e}}_\alpha$, covariant and contravariant descriptions get coincident, a property of any "orthogonal" vector basis (which does not mean "rectilinear," as will be seen shortly). The quantity $g_{\mu\nu}$ obviously behaves as a tensor, and is familiarly known as the metric tensor. It is of extraordinary importance, and will be extensively used in the following. Note finally that the distinction between contravariant and covariant representations, and thus the notion of metric tensor, are generally deemed unnecessary for any space devoid of curvature. Nevertheless, before proceeding, it is important to introduce their geometrical meaning.

## 3.7 Tensor formulation of special relativity

The most effective way to deal with special relativity is to benefit from tensor calculus, where coordinates, vectors and tensors are joined by the Lorentz–Poincaré transformation:

$$o^\mu{}_\nu = \Lambda^\mu{}_\nu \tag{1.84}$$

and spacetime is Minkowskian, i.e., in our notation:

$$g_{\alpha\beta} = \eta_{\alpha\beta} \tag{1.85}$$

The 2-rank tensor $\Lambda^\mu{}_\nu$ expresses the Lorentz–Poincaré group:

$$x'^\mu = \Lambda^\mu{}_\nu x^\nu \tag{1.86}$$

where the 4-vector $x^{\mu} \equiv \{x^0 = ct, x^1 = x, x^2 = y, x^3 = z,\}$ is an event in $O$ and $x'^{\mu}$ denotes its transformed coordinates in $O'$. The following aims at pointing out the widest possible transformation class for $\Lambda^{\mu}{}_{\nu}$. We will start to get familiar with the so-called "natural" units, used throughout the present chapter unless specifically indicated otherwise, where light speed is unity ($c = 1$) and all (Cartesian) coordinates are dimensioned to a length. This avoids worrying about keeping track of combinations of $c$ of no avail to a calculation, allowing us to get back to the standard units only at the end of it.

That said, a Lorentz–Poincaré transformation generally writes as:

$$x'^{\mu} = b^{\mu} + \Lambda^{\mu}{}_{\alpha}x^{\alpha} = b^{\mu} + \Lambda^{\mu}{}_{0}x^0 + \Lambda^{\mu}{}_{1}x^1 + \Lambda^{\mu}{}_{2}x^2 + \Lambda^{\mu}{}_{3}x^3 \tag{1.87}$$

for some 4-dimensional vector $b^{\mu}$. It governs Minkowski's tensor transformation:

$$\eta_{\alpha\beta} = \Lambda^{\mu}{}_{\alpha}\Lambda^{\nu}{}_{\beta}\eta_{\mu\nu} \tag{1.88}$$

whereby $(\Lambda^0{}_0)^2 \geqslant 1$ and $\Lambda^2 = 1$ ($\Lambda = \det\Lambda^{\mu}{}_{\alpha}$). The former equations identify the inhomogeneous Lorentz–Poincaré group (or Poincaré's group), becoming homogeneous under $b^{\mu} = 0$. In both cases, to avoid the undesired symmetries of space inversion ($\Lambda^0{}_0 \geqslant 1$, $\Lambda = -1$), time reversal ($\Lambda^0{}_0 \leqslant 1$, $\Lambda = -1$) or their combination, one can deal with their subgroups, termed proper orthochronous (or restricted Lorentz's) groups ($\Lambda^0{}_0 \geqslant 1$, $\Lambda = 1$). They preserve the spatial orientation, leave the direction of time invariant (i.e., past and future), and include the rotation subgroup, $\Lambda^0{}_0 = 1$, $\Lambda^0{}_l = \Lambda^l{}_0 = 0$, $\Lambda^s{}_l = R^s{}_l$, where $R^s{}_l$ is an orthonormal matrix ($\det R = 1$, $R^{\mathrm{T}}R = 1$). Throughout the following, any Lorentz–Poincaré transformation will be supposed to be proper, orthochronous and homogeneous.

Accordingly, an observer ($O'$), seeing an event at rest in $O$, will write:

$$dx'^l = \Lambda^l{}_0\,dt, \qquad dt' = \Lambda^0{}_0\,dt \tag{1.89}$$

being $dx^l = 0$ ($l = 1, 2, 3$). Introducing the relative velocity ($\mathbf{v}$):

$$\Lambda^l{}_0 = v_l\Lambda^0{}_0 \tag{1.90}$$

with:

$$\Lambda^{\alpha}{}_0\Lambda^{\beta}{}_0\eta_{\alpha\beta} = -\left(\Lambda^0{}_0\right)^2 + \sum_l\left(\Lambda^l{}_0\right)^2 = -1 \tag{1.91}$$

and combining the last two equations, give us:

$$\Lambda^0{}_0 = \gamma_L, \qquad \Lambda^l{}_0 = v_l\gamma_L \tag{1.92}$$

All other components are defined unless arbitrary rotations, which cannot alter the operation of bringing an inertial observer in relative motion with arbitrary velocity. Hence, one may set:

$$\Lambda^l{}_s = \delta_{ls} + (\gamma_L - 1)\frac{v_l v_s}{\mathbf{v}^2} \tag{1.93}$$

with:

$$\Lambda^0{}_l = \gamma_L v_l \tag{1.94}$$

We note that Lorentz–Poincaré and Galilean symmetries deal equivalently with translations and rotations. What makes them sensibly different is their symmetry with respect to "boosts," velocity transformations $\mathbf{v} \to \mathbf{v}'$.

In this framework, aside from the zero tensor (with every component equal to zero), any scalar, Kröenecker's symbol ($\delta_{\alpha\beta}$) and Minkowski's metric ($\eta_{\alpha\beta}$), another basic tensor preserving its components in all reference frames is the permutation symbol:

$$\epsilon^{\mu\nu\lambda\kappa} = \begin{cases} 1 & \text{even permutation of } [0123] \\ -1 & \text{odd permutation of } [0123] \\ 0 & \text{otherwise} \end{cases} \tag{1.95}$$

where even and odd refer to the number of 2-component swaps ("transpositions") and are exclusive properties of any sequence of indices (e.g., $\epsilon^{0231} = 1$, $\epsilon^{3120} = -1$ and $\epsilon^{1120} = 0$). This is a special case of Levi-Civita's pseudo-tensor, which is actually a tensor density, i.e.:

$$\Lambda^{\alpha}{}_{\beta}\Lambda^{\gamma}{}_{\omega}\Lambda^{\mu}{}_{\nu}\Lambda^{\tau}{}_{\sigma}\epsilon^{\beta\omega\nu\sigma} = \Lambda\epsilon^{\alpha\gamma\mu\tau} \tag{1.96}$$

However, within Lorentz's restricted transformation group ($\Lambda = 1$), it certainly behaves as a tensor.

## 3.8 Maxwell's equations and gauge symmetry

Though electrodynamics will be marginal for us, it may be important reminding the main ground of the special relativity paper, Maxwell's equations of electromagnetism:

$$\begin{aligned} &\vec{\nabla} \cdot \mathbf{E} = \varepsilon \quad \text{(Coulomb–Gauss law for electricity)} \\ &\vec{\nabla} \wedge \mathbf{B} = \mathbf{J} + \left(\frac{\partial \mathbf{E}}{\partial t}\right) \quad \text{(Ampère–Maxwell circuital law)} \\ &\vec{\nabla} \wedge \mathbf{E} = -\left(\frac{\partial \mathbf{B}}{\partial t}\right) \quad \text{(Faraday's law of induction)} \\ &\vec{\nabla} \cdot \mathbf{B} = 0 \quad \text{(Gauss's law for magnetism)} \end{aligned} \tag{1.97}$$

They describe the electric and magnetic fields ($\mathbf{E}$ and $\mathbf{B}$) originating from given current and charge densities ($\mathbf{J}$ and $\varepsilon$). Symbols $\vec{\nabla}$ and $\wedge$ denote respectively the vector differential "del" operator and the vector product, so that $\vec{\nabla}$, $\vec{\nabla}\cdot$ and $\vec{\nabla}\wedge$ give respectively the gradient, the divergence and the curl of their arguments. All but Faraday's law were inferred from a steady-state analysis and, in particular, the second was written by Ampère without the temporal derivative of the electric field. Maxwell corrected this shortcoming, providing a consistent equation set that was able to envisage new phenomena, unknown at that time. It is curious that Maxwell's equations could be made formally specular in $\mathbf{E}$ and $\mathbf{B}$ by introducing a (non-null) "magnetic charge" density in Gauss's law for magnetism and adding a "magnetic current" in the Faraday's. If it were so, there would be particles with net magnetic charge, the so-called "monopoles," whose existence is still debated in particle physics and grand unified theories. Maxwell's fourth equation, rewritten in integral form (by the Gauss–Ostrogradsky theorem), fixes the net magnetic flux out of any closed surface to zero, clearly refusing the existence of magnetic monopoles.

Electromagnetism is thus described by a coupled system of first-order partial differential equations, depending on given charge and current densities. A more effective way to deal with them is to introduce a pair of potentials, reducing the equation number and raising the differential order up to the second. The idea resembles that exploited in static electromagnetic phenomena, where electric and magnetic fields can be derived from a vector and a scalar potential ($\mathbf{A}$ and $\phi$). From Maxwell's third and fourth equations, $\mathbf{E}$ and $\mathbf{B}$ follow from:

$$\begin{aligned}\mathbf{B} &= \vec{\nabla} \wedge \mathbf{A} \\ \mathbf{E} &= -\vec{\nabla}\phi - \left(\frac{\partial \mathbf{A}}{\partial t}\right)\end{aligned} \tag{1.98}$$

which, let $\psi$ be an arbitrary scalar function, are left invariant by the joint transformation:

$$\begin{aligned}\mathbf{A} &\to \mathbf{A} + \vec{\nabla}\psi \\ \phi &\to \phi - \left(\frac{\partial \psi}{\partial t}\right)\end{aligned} \tag{1.99}$$

The latter is called gauge transformation, and the field symmetry it establishes is said to be gauge invariance. From the viewpoint of analytical mechanics, the equations of motion for a particle of charge $e$ in an electromagnetic field (the famous "Lorentz-force equations") descend from transforming the free Hamiltonian as $H_0(q_i, p_s \to p_s - eA_s)$. This principle of gauge theory is called of "minimal coupling" (i.e., for the electromagnetic and electron fields). Notwithstanding, despite its formal beauty, no universal principle is currently available to a general formulation of electromagnetism. Freeman J. Dyson (1990) reported an unpublished analysis of Richard P. Feynman on this subject, witnessing the great difficulty in superseding the gauge theory. Briefly, during his fundamental studies, he made an attempt to relax Poisson's brackets for the momentum, but the freedom introduced via the canonical commutation rules brought him again, with some surprise, to the electromagnetic interaction.

The occurrence of a gauge makes it necessary to borrow some conventional relationship, specifying the potentials unambiguously. Among all possible options, a special role is played by "Lorentz's gauge":

$$\left(\frac{\partial \phi}{\partial t}\right) + \vec{\nabla} \cdot \mathbf{A} = 0 \tag{1.100}$$

under which the Maxwell's equations can be rewritten into a couple of separate inhomogeneous wave equations, dealing with $\mathbf{A}$ and $\phi$ on equal footings:

$$\begin{aligned}\Box \mathbf{A} &= -\mathbf{J} \\ \Box \phi &= -\epsilon\end{aligned} \tag{1.101}$$

where $\Box = \eta^{\alpha\beta} \frac{\partial}{\partial x^\alpha} \frac{\partial}{\partial x^\beta} = \vec{\nabla}^2 - \frac{\partial^2}{\partial t^2}$ is d'Alembert's operator. Lorentz's gauge matches manifestly special relativity, i.e., it is Lorentz–Poincaré invariant. Moreover, to narrow some of the arbitrariness it leaves, the "restricted gauge transformation":

$$\Box \psi = 0 \tag{1.102}$$

can be used, preserving Lorentz's condition as well as $\mathbf{A}$ and $\phi$. When the problem is sourceless ($\phi = 0$), Coulomb's or "transverse" gauge, $\vec{\nabla} \cdot \mathbf{A} = 0$, may be a convenient choice. Finally, it worth remembering that all the so-called "fundamental" interactions can be described by gauge theories.

## 3.9 Lorentz–Poincaré invariance of electrodynamics

As already said, the existence of a symmetry group for electrodynamics was pioneered by Poincaré and Lorentz. Adopting the Einsteinian kinematic view, one can easily verify that Maxwell's equations admit a covariant writing. Define to this end a matrix $F^{\mu\nu}$ such that:

$$F^{0k} = E_k \quad (k = 1, 2, 3) \tag{1.103}$$

$$F^{12} = B_3, \qquad F^{31} = B_2, \qquad F^{23} = B_1 \tag{1.104}$$

the remainder components being settled by the antisymmetry (bivector) property:

$$F^{\mu\nu} = -F^{\nu\mu} \tag{1.105}$$

By doing so, Maxwell's first and second equations can be united into:

$$F^{\mu\nu}{}_{,\mu} = -j^\nu \tag{1.106}$$

where the charge-current 4-vector $j^\nu = (\varepsilon, \mathbf{J})$ complies with the continuity equation:

$$j^\mu{}_{,\mu} = 0 \tag{1.107}$$

Regarding the third and fourth, they yield:

$$\varepsilon^{\mu\nu\alpha\beta} F_{\alpha\beta,\nu} = 0 \tag{1.108}$$

or ($\mu \neq \nu \neq \lambda$):

$$F_{\nu\lambda,\mu} + F_{\lambda\mu,\nu} + F_{\mu\nu,\lambda} = 0 \tag{1.109}$$

with:

$$F_{\alpha\beta} = \eta_{\alpha\mu} \eta_{\beta\nu} F^{\mu\nu} \tag{1.110}$$

As $J^\nu$ is a 4-vector then $F^{\mu\nu}$ is a tensor, said precisely the field-strength or electromagnetic tensor, and:

$$F'^{\tau\alpha} = \Lambda^\tau{}_\gamma \Lambda^\alpha{}_\lambda F^{\gamma\lambda} \tag{1.111}$$

still satisfies the equations of electromagnetism. Finally, from the last but two equation, $F_{\alpha\beta}$ is expressible as the curl of a 4-vector covariant potential ($A_\alpha$):

$$F_{\alpha\beta} = A_{\beta,\alpha} - A_{\alpha,\beta} \tag{1.112}$$

being $A^{\mu} = (\phi, \mathbf{A})$. Again, mapping $A_{\alpha} \to A_{\alpha} + \psi_{,\alpha}$ preserves the electromagnetic tensor, getting back to Lorentz's gauge condition:

$$A_{\alpha,}{}^{\alpha} = 0 \tag{1.113}$$

and:

$$\Box A_{\alpha} = -j_{\alpha} \tag{1.114}$$

bringing the former inhomogeneous wave equations into a joint covariant form. It should be kept in mind, while $F_{\alpha\beta}$ is physically meaningful, that $A_{\alpha}$ is not directly significant.

## 3.10 Doppler's effect

Doppler's effect is a relevant optics phenomenon for moving bodies and recalling it will be of great utility to pick up the role of the Lorentz–Poincaré symmetry in the (plane) wave propagation. Consider thus a light source $O$, far located from and at rest relative to a reference frame $O'$. Another frame $O''$ (e.g., the "observer") moves uniformely along the positive $x'$ direction, with $\mathbf{v} = (v, 0, 0)$ relative to $O'$. The direction between source and observer is fixed to form in $O'$ an angle $\theta'$ with the axis $x'$, while $z'$ is set perpendicular to these two directions. Doppler's effect arises as the (apparent) shift in frequency (or wavelength) of a signal from the source ($\omega'$) in relative motion with the observer ($\omega''$). It is responsible for the cosmological radiation "red-shift," of receding galaxies, and for the broadening of line spectra, arising in a laboratory source from the thermal motion of emitting atoms or molecules. Its relativistic formulae descend from the wave phase invariance. Linearity ensures that the plane wave, as emitted by $O$ and seen by $O'$, will also appear plane in $O''$. However, for the Lorentz–Poincaré covariance to hold throughout the space-time, the phase factor must not vary from one inertial frame to another. In other words, the wave crest-number counted by any inertial observer will not necessarily affected by the relative motion. This can be formally expressed by the scalar product invariance, $q'_{\alpha}x'^{\alpha} = q''_{\mu}x'^{\mu}$, or explicitly:

$$\omega' t' - \mathbf{q}' \cdot \mathbf{r}' = \omega'' t'' - \mathbf{q}'' \cdot \mathbf{r}'' \tag{1.115}$$

where, for light waves, the 4-vector $q^{\mu} = (\omega, \mathbf{q})$ obeys $q_{\mu}q^{\mu} = 0$. In wavevectors and frequencies, the Lorentz–Poincaré transformation formulae generally rewrite as ($c = 1$, $\beta = v$):

$$\omega'' = \gamma_L\big(\omega' - v q'_x\big), \qquad q''_x = \gamma_L\big(q'_x - v\omega'\big), \qquad q''_y = q'_y, \qquad q''_z = q'_z \tag{1.116}$$

They have to be applied to the above experiment:

$$\omega'\big[t' - (x'\cos\theta' + y'\sin\theta')\big] = \omega''\big[t'' - (x''\cos\theta'' + y''\sin\theta'')\big] \tag{1.117}$$

with $\theta' \equiv \widehat{\mathbf{q}'\mathbf{v}}$ and $\theta'' \equiv \widehat{\mathbf{q}''\mathbf{v}}$, yielding:

$$\frac{\omega''}{\omega'} = (1 - v\cos\theta')\gamma_L \tag{1.118}$$

angles transforming as:

$$\frac{\tan(\theta''/2)}{\tan(\theta'/2)} = (1+v)\gamma_L \tag{1.119}$$

Inverse formulas are promptly derived upon $v \to -v$, written in terms of the angle in $O''$, $\omega' \to \omega''$ and $\theta' \to \theta''$. If $\omega'' \equiv \omega$ and $\omega' \equiv \omega_0$ denote respectively the frequencies of the moving and resting clocks, one arrives at the popular expression ($\theta'' \equiv \theta$):

$$(1 + v\cos\theta)\omega = \gamma_L^{-1}\omega_0 \tag{1.120}$$

Lorentz's modified factors $(1 + v\cos\theta)\gamma_L$ establish the period of reception of wavefronts. It is a feature of special relativity that, when source and observer are perpendicular ($\cos\theta = 0$), it does not vanish, $\omega_0/\omega = \gamma_L$. Doppler's "transverse" effect reduces thus to a pure time dilation redshift, implied by the Lorentz–Poincaré symmetry of motion. In general, a red-shift is observed in the line spectra whenever source and observer are moving away (i.e., a decrease in frequency or an increase in wavelength). Otherwise, for motion towards, a violet- (or blue-) shift takes place. Note finally that relativistic and classical formulas coincide at the lowest order in $v$ ($\beta \ll 1$):

$$\omega \simeq \omega_0(1 + v\cos\theta) \qquad (\theta \neq \pi/2) \tag{1.121}$$

$$\omega \simeq \omega_0\big(1 - v^2/2\big) \qquad (\theta' = \pi/2) \tag{1.122}$$

## 3.11 Criticism of the Einstein's postulates

Einstein's relativity has received several attacks and criticism over the years. Among the major issues, one was due to Dayton Miller (1906–1930) and his "ether drift experiment." In one of the most interesting reviews of special relativity, he questioned the Michelson and Morley's "null result." According to him, a systematic periodic term would alter the interferometer data, regardless of any statistical error, fluctuations or other mechanical effects. Several years later, after his death, his conclusions were reconsidered by Robert S. Shankland (1955), who accepted the systematic patterns in Miller's results, but ascribed them to fluctuations and some other thermal artifact in his measurement technique. The Michelson and Morley's outcome resisted over the years to this controversial, but the reasons for a critical analysis of their experiment seem to have survived until nowadays. For example, the point was made that the fring shift magnitude should be determined by the typical speed of the solar system in our galaxy. Others, referencing recent electromagnetic theories, suggested that a possible light speed anisotropy might cancel in Michelson and Morley's measurement. Nevertheless, in another experiment, Roy J. Kennedy and Edward M. Thorndike (1932) could not only confirm the isotropy of the light spread but that also its speed had to possess the same numerical value for any inertial observer.

From the conceptual viewpoint, special relativity is not fully devoid of conceptual subtleties and ambiguities. Einstein, for example, made use in his original treatation of an intermediate Galilean frame ($x' = x - vt$), constraining any fixed point in $O'$ to take well defined coordinates in $O$. If it is nothing but an expedient to define separate times from $O$, then it could even be avoided. Unfortunately, despite the fact that time is always regarded as a relativistic coordinate, this intermediate observer was explicitly introduced by Einstein as "an auxiliary set of spacetime coordinates whose spatial portion transforms according to a Galilean transformation," and thus some hesitation may remain. It was also noticed that the Lorentz–Poincaré transformation can stem from less severe assumptions on the relative motion. Five years after Einstein's paper, Waldemar von Ignatowsky (1910) could already conclude that to posit an absolute light speed would not be co-essential to the symmetry of nature aimed by special relativity, a thesis taken back by Francesco Severi (1924) and several others until recent times.

Further debates came from the outlook of slightly amending postulates and assumptions of special relativity, such as the light speed constancy, space homogeneity and so on. Einstein's inertial frames, for instance, do not exist in real natural phenomena. The notion of covariance was suspected over the years to be physically unmeaningful, a kind of trick to (or by) which to uniforme natural phenomena at will, and the use of tensor quantities it exploits to be equally fictitious. This doubt was raised, for example, by Charles G. Darwin (1928): "The relativity theory is based on nothing but the idea of invariance, and develops from it the conception of tensors as a matter of necessity; and it is rather disconcerting to find that apparently something has slipped through the net, so that physical quantities exist, which it would be, to say at least, very artificial and inconvenient to express as tensors." Cosmology and high-energy physics, for instance, seem to comprise situations where the Lorentz–Poincaré symmetry is violated, requiring a modification of the second postulate. To attempt a description that is still relativistic but no longer Lorentz–Poincaré covariant, different "varying speed of light" theories were proposed, allowing the light velocity to displace the value of $c$, and it is instructive dwelling for a moment on those by Vladimir A. Fock (1964) and Edward A. Milne (1932).

In Fock's approach, distinct inertial frames are still equivalent, but the light speed is a function of coordinates. He required that reference systems in relative motion no longer transform linearly, and defined a new quadratic form ($\bar{s}$) via:

$$\bar{s} = \gamma_F(t)s \tag{1.123}$$

where $s$ is the invariant interval in special relativity and (in standard units) $\gamma_F = (1 + l_F c^2 t)^{-1}$, the (small) coupling constant $l_F$ carrying the dimension of a time per unit surface. The question was raised as to whether this spacetime would actually be locally isometric to the Minkowski's, but rewritten in non-Cartesian coordinates:

$$\bar{s}^2 = \bar{c}^2\bar{t}^2 - \bar{\mathbf{r}}^2 \tag{1.124}$$

with $\bar{t}/t = \overline{x^k}/x^k = \gamma_F$ and light speed $\bar{c}/c = |\gamma_F(\mathbf{e}_n + l_F c\mathbf{r})|$ ($\mathbf{e}_n$ = unit vector). Alongside, the Fock's spacetime would equal Milne's, $(\bar{\tau}, \bar{\rho})$:

$$d\bar{s}^2 = d\bar{\tau}^2 - \bar{\tau}^2 d\bar{\rho}^2 \tag{1.125}$$

with $\bar{\tau} = \sqrt{\bar{t}^2 - \bar{x}^2}$, $\tanh\bar{\rho} = \bar{x}/\bar{t}$ and "light velocity" $\chi = (d\bar{\rho}/d\bar{\tau}) = \bar{\tau}^{-1}$, decreasing with time.

Another line of criticism, of a certain deepness and not limited to relativity, developed from inquiring the meaning of constancy of any-dimensionally constant quantity. This is a delicate point because, when laws of nature are form-invariant, physical differences are ascribed to variations of the involved numerical terms. On the other hand, any measurement is always a unit ratio. Again, to make the Lorentz–Poincaré symmetry unit invariant, and exclude any meaningless comparison of light velocity values in separate events, one should be available to generally deal with $c = c(x^0)$, varying with some temporal coordinate ($x^0 \neq t$). This, nevertheless, would lead to the existence of a privileged observer for the laws of nature, a sort of "light frame," breaking the symmetry of motion into a multiplicity of "almost inertial" systems.

## 4. RELATIVISTIC MECHANICS

### 4.1 Point particle dynamics

We are now in a position to step back to the principles of mechanics, and look at the consequences of incorporating special relativity in point particle dynamics. The machinery of classical (non-relativistic) mechanics was seen to generate a trajectory ensemble, contemplating the existence of a single time and a single energy. Here, the Lorentz–Poincaré-transformed ensemble of trajectories should always look the same, coordinates detected in a reference frame being used (equivalently) in the motion equation of another observer. Bear in mind that the name of relativistic mechanics normally refers to the mechanics governed by the Lorentz–Poincaré group. It represents the closest translation of mechanics for a non-relativistic theory, endowed with a principle of relativity.

To define a proper reference frame for an accelerated observer, the starting point is (still) the assumption of Newton's second law in a certain system ($O$), in which the material point is instantaneously at rest. As the motion equations may depend on an arbitrary function of the relative velocity, an unambiguous definition of what a force $f^\mu$ is in relativistic mechanics should be given. To remove any indeterminacy, let us start from the following definition of force:

$$f^\mu = m\left(\frac{d^2x^\mu}{ds^2}\right) \tag{1.126}$$

exerted on a mass $m$ along a worldline parametrized by the invariant proper time. It is implicitly assumed that the particle experiences a 4-velocity ($v^\mu$) and a 4-acceleration ($a_\mu$), set to:

$$v^\mu(s) = \left(\frac{dx^\mu}{ds}\right), \qquad a^\mu(s) = \left(\frac{d^2x^\mu}{ds^2}\right) \tag{1.127}$$

For a particle instantaneously at rest, relativistic and non-relativistic forces must be equal, $f^\mu = F^\mu$ and $F^0 = 0$. Furthermore, for a boost transformation $\mathbf{0} \rightarrow \mathbf{v}$, the

Lorentz–Poincaré invariance of the proper time yields:

$$f'^{\mu} = \Lambda^{\mu}{}_{\nu}(\mathbf{v}) f^{\nu} \tag{1.128}$$

hence:

$$f^{\mu} = \Lambda^{\mu}{}_{\nu}(\mathbf{v}) F^{\nu} \tag{1.129}$$

From the expression of $\Lambda^{\mu}{}_{\nu}$, and the annulment of the zero force component, it turns out that the 4-vector $f^{\mu} = (f^0, \mathbf{f})$ is specified by:

$$\begin{aligned} f^0 &= \gamma_L \mathbf{v} \cdot \mathbf{F} = \mathbf{v} \cdot \mathbf{f} \\ \mathbf{f} &= \mathbf{F} + (\gamma_L - 1)\frac{\mathbf{v} \cdot \mathbf{F}}{v^2}\mathbf{v} \end{aligned} \tag{1.130}$$

## 4.2 Energy and momentum

The most natural definition of energy–momentum 4-vector $(p^{\mu})$ descends from rewriting Newton's second law as:

$$f^{\mu} = m\left(\frac{dp^{\mu}}{ds}\right) \tag{1.131}$$

clearly with:

$$p^{\mu} = m\left(\frac{dx^{\mu}}{ds}\right) \tag{1.132}$$

Remind the time dilation rule for proper $(s)$ and relativistic $(t)$ times, $\frac{dt}{ds} = \gamma_L$, thence:

$$\mathbf{p} = m\gamma_L \mathbf{v} \tag{1.133}$$

while the (single) particle energy identifies the time component:

$$p^0 = m\gamma_L \equiv E \tag{1.134}$$

Expanding $\gamma_L$ in power series returns, for small velocities:

$$\begin{aligned} \mathbf{p} &= m\mathbf{v} + \mathrm{O}\left(\mathbf{v}^3\right) \\ E &= m + \frac{1}{2}m\mathbf{v}^2 + \mathrm{O}\left(\mathbf{v}^4\right) \end{aligned} \tag{1.135}$$

the second of which being the celebrated mass–energy equivalence. Before its derivation, mass and energy were believed to have separate conservation laws. Any mass content assigns instead the owner a rest energy, given by (in standard units):

$$E_0 \equiv E(\mathbf{p} = \mathbf{0}) = mc^2 \tag{1.136}$$

It may be interesting to a chemist to recall that Pierre Langevin (1920) proposed to explain all displacements of the atomic weight from integer values by the energy inertia of each chemical element (referred to the hydrogen element $\mathrm{H}(1) = 1$

and with absent isotope effects). The mass–energy equivalence is a universal law, thus it has basic implications in chemistry too. Imagine, for instance, detecting and comparing the weights of all reactant and product molecules, it would be possible to derive the weak (equivalent) energy, developed in a chemical reaction. Note also that, though for several decades it has fallen into disuse, $m\gamma$ has often been popular with the name of "relativistic mass." Remember, however, that (the intrinsic, invariant, proper or rest) mass is a unique feature, and incorporating velocity into mass could illude us to create a 4-momentum from quantities that have not a Lorentz–Poincaré product.

In conclusion, for any finite velocity value, energy and momentum are generally connected by the proper time invariance:

$$-m^2 = p^\alpha p_\alpha = \eta_{\alpha\beta} p^\alpha p^\beta \tag{1.137}$$

where energy, in the Hamilton's representation, reads:

$$E(\mathbf{p}) = \left(\mathbf{p}^2 + m^2\right)^{\frac{1}{2}} \tag{1.138}$$

and the 4-vector which they form transforms manifestly as the coordinates of a spacetime event:

$$E' = \gamma_L(E - vp_x), \qquad p'_x = \gamma_L(p_x - vE), \qquad p'_y = p_y, \qquad p'_z = p_z \tag{1.139}$$

We take this opportunity to express the relativistic limit ($\beta \to 1$) in energy terms. It suffices to insert in the Lorentz's factor the typical value $v^2 = (\frac{Gm}{r})$, where $G \simeq 6.674 \times 10^{-11}$ N m$^2$ Kg$^{-2}$ is Newton's gravitational constant. This rewrites $\beta^2$ as the ratio between gravitational ($E_G = \frac{Gm^2}{r}$) and rest energies, also named gravitational parameter ($\kappa_m(r) \equiv \frac{Gm}{rc^2}$, in standard units), rearranging the relativistic limit into $E_G \to E_0$. Note that, in Newtonian mechanics, kinetic and potential terms are approximately of the same order of magnitude ($v^2 \sim \frac{Gm}{r}$) and $\kappa_m \ll 1$.

## 4.3 Hamilton's principle and mechanics

We refer back in this paragraph to some fundamental notions of Hamiltonian mechanics. Once the formal consequences of the Lorentz–Poincaré symmetry are understood, it is not difficult to rewrite the equations of Hamilton's theory under the relativistic transformation for space and time. The action functional for a free point particle, for example, is easily made invariant under a Lorentz–Poincaré transformation. It will have to be built on the first-order differential of the proper time, the simplest scalar to work with, and a simple discussion settles it to:

$$S = -m \int_{s'}^{s''} ds \tag{1.140}$$

where $ds = \sqrt{-dx_\mu \, dx^\mu}$ and the associated Lagrangian is $L = -m/\gamma_L \simeq -m + \frac{mv^2}{2} = K - E_0$. Since $\delta \int ds = -\int dx_\mu \, \delta \, dx^\mu / ds$, an integration by parts implies:

$$\delta S = mv_\mu \delta x^\mu - m \int_{s'}^{s''} \left( \frac{dv_\mu}{ds} \right) \delta x^\mu \, ds \tag{1.141}$$

where $v_\mu$ is the $\mu$th covariant velocity component. As expected, the motion equation is given evidently by $(\frac{dv_\mu}{ds}) = 0$, or:

$$a_\mu(s) = 0 \tag{1.142}$$

expressing the constancy of each 4-velocity component (integrals of motion).

Otherwise, on seeing the action as a function of coordinates, only the first variation survives, and one is carried again to the (covariant) 4-momentum:

$$p_\mu = S_{,\mu} \tag{1.143}$$

By replacing the action derivatives with the corresponding momentum components, the relativistic Hamilton–Jacobi equation is determined at once:

$$-m^2 = S_{,\mu} S^\mu{}_{,} = \eta^{\alpha\beta} S_{,\alpha} S_{,\beta} \tag{1.144}$$

i.e.:

$$\left( \frac{\partial S}{\partial t} \right)^2 - \left( \frac{\partial S}{\partial x} \right)^2 - \left( \frac{\partial S}{\partial y} \right)^2 - \left( \frac{\partial S}{\partial z} \right)^2 = m^2 \tag{1.145}$$

the non-relativistic limit being recovered thereof upon $c \to \infty$ and the action change $S \to S' = S + E_0 t$, which gets rid of the rest energy. Note that, as the 4-momentum complies with the conservation law, $\partial_\mu p^\mu = 0$, whereby $\Box S = 0$. Both this (wave) equation and Hamilton–Jacobi's are solved by $S = \eta_{\alpha\mu} p^\alpha x^\mu = -Et + \mathbf{p} \cdot \mathbf{x}$, as expected for a scleronomous, free-particle system.

We may also wonder whether the Lorentz–Poincaré symmetry preserves the volume element of the particle phase space, $d\Gamma = d^3\mathbf{r} \, d^3\mathbf{p}$:

$$d\Gamma' = d\Gamma'' \tag{1.146}$$

To check the answer is positive, consider two boost transformations, $\gamma_L'(\mathbf{v}')$ and $\gamma_L''(\mathbf{v}'')$, relative to $O = (t, \mathbf{r})$. Volumes will change as $d^3\mathbf{r} = \gamma_L' \, d^3\mathbf{r}' = \gamma_L'' \, d^3\mathbf{r}''$ and energies (or times) as $\gamma_L''/\gamma_L' = E'/E''$. Each boost preserves evidently the ratio $d^3\mathbf{p}/E$, thereby $d^3\mathbf{r}'/d^3\mathbf{r}'' = \gamma_L''/\gamma_L' = E''/E' = d^3\mathbf{p}'/d^3\mathbf{p}''$, proving the hypothesis. Hereupon, any phase space distribution function ($\rho$), denoting a particle number by $\rho(\mathbf{r}, \mathbf{p}) \, d\Gamma$, is Lorentz–Poincaré invariant as well:

$$\rho'(\mathbf{r}', \mathbf{p}') = \rho''(\mathbf{r}'', \mathbf{p}'') \tag{1.147}$$

## 4.4 Experimental confirmations

The energy–mass equivalence descends from embodying the kinematic laws of special relativity into the classical point particle dynamics. Soon it will be recalled how the presence of mass alters (curves) Minkowski's spacetime, but special relativity, however, can access a first explanation of gravity field effects. One of the most popular examples was the residual perihelion advance of Mercury, to which Simon Newcomb (1882–1898) assigned a centennial excess precession of about $43''$ (arcseconds). According to the theorem by Joseph. L.F. Bertrand (1873), the only power-law central potentials producing (bounded and stable) closed trajectories are that harmonic ($U \sim r^2$) and those giving rise to inverse-square central forces ($U \sim r^{-1}$), such as gravitational and Coulomb's. When these dependences are perturbed, the orbit shape is opened, giving rise to a perihelion advancement or retardation in Kepler's third law. Without resorting to the Einsteinian views of gravity, special relativity combined with Newtonian mechanics can sketch out a solution for this phenomenon, and a preliminary understanding of how Newton's results modify in a general relativistic picture. We should keep in mind that, following Alfred Schild (1960), gravity and Minkowskian descriptions would not be compatible, and great care should be taken when mixing them together.

Briefly, from the mass–energy equivalence, the overall mass which a planet "feels out" does not only comprise the sun's ($M$), but a gravitational contribution too ($\delta M$). This would perturb Newton's potential ($U_G = -GmM/r$) in the energy conservation law ($\delta E \sim \delta U_G$) and a simple dimensional analysis, employing $\delta M \sim \frac{1}{2} M \kappa_M(r)$, would set $\delta E \sim U_G \kappa_M(r)$. Hence, the perihelion advance would be $\sim \delta E / U_G \sim \kappa_M(R)$, evaluated at the radius of the larger mass ($r \equiv R$) and per completed orbit ($2\pi$). This result does not take into consideration numerical prefactors but is in line with general relativity, predicting the same expression multiplied by 3.

Another of Einstein's successes lay in a reinterpretation of Doppler's shift, a well posed experimental effect which is not susceptible to subtleties or ambiguities. Photon redshift, conceived as the climbing of photons in a gravitational field, is accompanied by an energy loss which can be estimated by the variation of Newton's potential at an altitude change equal to the mass radius ($\sim R$). Therefore, the relative frequency redshift equates the gravitational parameter, $(\omega - \omega_0)/\omega_0 \sim -\kappa_M(R)$. Several years later, Herbert E. Ives and G.R. Stilwell (1938) confirmed spectroscopically the relativistic transverse Doppler's shift from emitting atoms in motion.

However, the most popular of Einstein's predictions probably remains the curvature of light rays bending near large masses. Light in fact, being endowed with mass, was expected to interact with large gravitational masses. This effect was first noticed by Arthur S. Eddington, Frank W. Dyson and Charles Davidson (1919), and the sound interpretation it found in relativity had a great impact on the scientific community at that time. We shall see it better in the general relativity section, but may find a first explanation from Kepler's problem, in which the light deflection angle ($\phi$) coincides with the difference between perturbed and unperturbed asymptotes. This returns the Newtonian value, which is half the general relativity result, $\delta\theta/2 \sim \kappa_M(R)$, with $R$ playing the role of the "impact parameter" (here, the distance to the mass gravity field).

## 4.5 Notes on general field theory and Noether's theorem

We conclude this section by some fundamentals of general field theory. Though being limited to a flat spacetime, they will be useful in introducing several notions of the general relativity formalism. The variational criterion set by Hamilton's principle can be reformulated for an action functional of the form:

$$S[\boldsymbol{\phi}_n] = \int_1^2 \mathsf{L}(\boldsymbol{\phi}_n, \boldsymbol{\phi}_{n,\mu})\, d^4x \tag{1.148}$$

where the super-vector $\boldsymbol{\phi}_n \equiv \{\phi^s\colon\ s = 1, 2, \ldots, n\}$ comprises now $n$ quantities (the fields) and, for brevity, $\boldsymbol{\phi}_{n,\mu} \equiv \{\frac{\partial \phi^s}{\partial x^\mu}\colon\ s = 1, 2, \ldots, n\}$ collects their derivatives. The fields determine the state of a (particle) system at all points in some spacetime domain. For example, $\phi(x^\mu)$ specifies at each point an independent degree of freedom, and the field system represents a continuous infinity of degrees of freedom. The function $\mathsf{L}$ denotes a Lagrangian density ($L = \int \mathsf{L}\, d^3x$) that, in principle, might depend explicitly on coordinates ($x^\mu$). We ignore for the moment this possibility, corresponding to a Lagrangian that is form-invariant upon translations, and parallel the Euler–Lagrange equations of classical mechanics.

Varying at first-order with respect to each coordinate, $x^\mu \to x^\mu + \delta x^\mu$, and field, $\boldsymbol{\phi}_n \to \boldsymbol{\phi}_n + \delta\boldsymbol{\phi}_n$, return:

$$\delta S = \int_1^2 \delta\boldsymbol{\phi}_n \cdot \left[\left(\frac{\partial \mathsf{L}}{\partial \boldsymbol{\phi}_n}\right) - \left(\frac{\partial \mathsf{L}}{\partial \boldsymbol{\phi}_{n,\mu}}\right)_{,\mu}\right] d^4x + \delta\Xi \tag{1.149}$$

with $\delta\Xi \equiv \Xi(2) - \Xi(1)$ indicating the difference of hypersurface (or hypervolume) integrals as:

$$\Xi(k) = \int_{v(k)} \left[\delta\boldsymbol{\phi}_n \cdot \left(\frac{\partial \mathsf{L}}{\partial \boldsymbol{\phi}_{n,\mu}}\right) + \mathsf{L}\delta x^\mu\right] dv_\mu \tag{1.150}$$

where the (small) volume elements ($dv_\mu$) over which the integration is performed are not scalar quantities, but denote (covariant) vectors, describing the hypersurface magnitude and orientation. We now state that, as customary, for some field configuration:

$$\delta S = 0 \tag{1.151}$$

where boundaries are kept fixed and each variation over them vanish, $\delta x_\mu = 0$ and $\delta\phi^s = 0$ $(\forall \mu, s)$. In this way, only the first contribution will survive, bringing to the Euler–Lagrange field equations, i.e.:

$$\left(\frac{\partial \mathsf{L}}{\partial \boldsymbol{\phi}_n}\right) - \left(\frac{\partial \mathsf{L}}{\partial \boldsymbol{\phi}_{n,\mu}}\right)_{,\mu} = \mathbf{0} \tag{1.152}$$

This notation indicates a super-vector of $n$ equations (in $\phi^s$), summed over the repeated $\mu$.

They are clearly Lorentz–Poincaré invariant. Any (infinitesimal) coordinate change will tend to act as a small variation of all fields, coming from its rearrangement in the new inertial system:

$$\bar{\delta}\boldsymbol{\phi}_n \equiv \boldsymbol{\phi}'_n\left(x'^{\mu}\right) - \boldsymbol{\phi}_n\left(x^{\mu}\right) \tag{1.153}$$

with $\bar{\delta}\boldsymbol{\phi}_n = (\bar{\delta}\phi^1, \ldots, \bar{\delta}\phi^n)$. Therefore, let $x'^{\mu} = x^{\mu} + \varepsilon^{\mu}$ denote an infinitesimal Lorentz–Poincaré transformation, one has:

$$\int_1^2 \mathsf{L}(\boldsymbol{\phi}_n, \boldsymbol{\phi}_{n,\mu})\, d^4x = \int_1^2 \mathsf{L}\left(\boldsymbol{\phi}'_n, \boldsymbol{\phi}'_{n,\mu}\right) d^4x' \tag{1.154}$$

where, since:

$$\left(\frac{d^4x'}{d^4x}\right) = \left\| \frac{\partial x'}{\partial x} \right\| = 1 + \left(\delta x^{\mu}\right)_{,\mu} \tag{1.155}$$

it turns out $\delta d^4x = (\delta x^{\mu})_{,\mu}$. This means that coordinate and field variations are constrained by:

$$\delta \Xi = 0 \tag{1.156}$$

or, equivalently:

$$\int_1^2 \delta\left(\mathsf{L}\, d^4x\right) = \int_1^2 \left[\delta\boldsymbol{\phi}_n \cdot \left(\frac{\partial \mathsf{L}}{\partial \boldsymbol{\phi}_{n,\mu}}\right) + \mathsf{L}\delta x^{\mu}\right]_{,\mu} d^4x = 0 \tag{1.157}$$

We can verify that these equations yield the energy and linear momentum conservations for an infinitesimal spacetime translation, and the angular momentum conservation for an infinitesimal rotation (i.e., a Lorentz–Poincaré transformation). Such results lie generally in the framework of an important theorem, by Amalie (Emmy) Noether (1918), formalizing a profound insight on the relationship between the notions of symmetry and conservation in a Lagrangian theory. Noether's theorem, in informal terms, proves that every symmetry generates a conservation law (and vice versa), the so-called continuity equation for a conserved quantity and a flux transporting it (Noether's charge and current). According to the global or local character of the symmetry, one may also distinguish between two versions of it (Noether's first and second theorems) and, when locality applies, charges can be expressed by a surface integral.

Technically, the concept of symmetry spells out that of covariance under a given (continuous) transformation group, satisfying certain mathematical recipes. Thus, while symmetry is generally pointed out by any action-preserving operation, continuous symmetries are the counterparts of conservation laws. The simplest interpretation of this dualism probably comes from the commutation relation $[H, q] = 0$. Regarded as the action of the Hamiltonian on a coordinate, it requires $q$ to be conserved. Conversely, $q$ can be conceived as it gives rise to a symmetry group. A memorable application lay in a paper by Ernst Bessel-Hagen (1921), who expressed the conservation laws of $n$ bodies in a gravity field with the 10-parameter Galilean group, comprising rotations, spacetime and velocity translations. The third invariance, under Galilean transformations, obviously fixes how the center of mass is moving (i.e., uniformely).

There is a last wider invariance, worth mentioning, called "conformal." The (15-parameter) special conformal group preserves angles and distances up to a scalar multiple and, in addition to translations and rotations (Poincaré's group), involve spacetime dilations (or magnifications) and inversions (relative to a unit sphere). Observe that conformal transformations do not produce true conservation laws, but invariance identities, and a useful representation of them is set by a rescaling of the metric tensor up to a common "conformal factor" ($\phi$), altering every length from point to point:

$$\eta^{\mu\alpha} \rightarrow \phi\left(x^{\rho}\right)\eta^{\mu\alpha} \tag{1.158}$$

Lorentz–Poincaré's are thus conformal transformations with unitary factor, while the Maxwell's equations have been shown to be conformally invariant since the works of Harry Bateman (1910) and Ebenezer Cunningham (1910).

Details of Noether's original theorem lie somewhat out of the present purposes. However, it is promptly recovered from setting $\delta x^{\mu} = 0$ in the last but one equation, when the Lagrangian varies as $\delta \mathsf{L} = F^{\alpha}{}_{,\alpha}$. The quantity $F^{\alpha} = F^{\alpha}(\boldsymbol{\phi}_n, \boldsymbol{\phi}_{n,\mu})$ dies off over the integration boundaries, and concurs to define Noether's current:

$$J^{\mu} = \delta\boldsymbol{\phi}_n \cdot \left(\frac{\partial \mathsf{L}}{\partial \boldsymbol{\phi}_{n,\mu}}\right) - F^{\mu} \tag{1.159}$$

that obeys the continuity equation:

$$J^{\mu}{}_{,\mu} = 0 \tag{1.160}$$

The constraint $\delta\Xi(\delta x^{\mu} \neq 0) = 0$ extends thus Noether's original result, and can be used to get the general conservation laws produced by translational and rotational symmetries.

In the former case, let the super-vector of components $\delta\phi^{s}$ provide the field variations at a fixed point:

$$\delta\boldsymbol{\phi}_n = \boldsymbol{\phi}_n'\left(x^{\mu}\right) - \boldsymbol{\phi}_n\left(x^{\mu}\right) \tag{1.161}$$

the connection to their total change is given by:

$$\bar{\delta}\boldsymbol{\phi}_n = \delta\boldsymbol{\phi}_n + \boldsymbol{\phi}_{n,\mu}\delta x^{\mu} \tag{1.162}$$

thence the condition $\bar{\delta}\boldsymbol{\phi}_n = \mathbf{0}$ implies:

$$\delta\boldsymbol{\phi}_n = -\boldsymbol{\phi}_{n,\mu}\epsilon^{\mu} \tag{1.163}$$

with $\delta x^{\mu} \equiv \epsilon^{\mu}$. In these terms, one obtains:

$$\Xi(k) = -\epsilon_{\nu}P^{\nu}(k) \tag{1.164}$$

where the 4-vector representative of the total energy and momentum:

$$P^{\nu}(k) \equiv \int\limits_{\upsilon(k)} T^{\mu\nu}\, d\upsilon_{\mu} \tag{1.165}$$

is conserved, $\delta P^{\nu} = 0$, and defines the "canonical energy–momentum" tensor:

$$T^{\mu\nu} = \boldsymbol{\phi}_{n,}{}^{\nu} \cdot \left(\frac{\partial \mathsf{L}}{\partial \boldsymbol{\phi}_{n,\mu}}\right) - \eta^{\mu\nu}\mathsf{L} \tag{1.166}$$

In Noether's language, $P^{\nu}$ denote the conserved charges of the currents $T^{\mu\nu}$, with conservation law $T^{\mu\nu}{}_{,\mu} = 0$. We will readdress this point in the next section.

In the second case, one may seek the conservation law arising from a homogeneous and infinitesimal Lorentz–Poincaré transformation (i.e., the rotational symmetry):

$$\Lambda^{\alpha}{}_{\mu} = \delta^{\alpha}{}_{\mu} + \eta^{\alpha\nu}\omega_{\nu\mu} \tag{1.167}$$

Perturbation terms on the right comply with a couple of prescriptions, $|\omega_{\nu\mu}| \ll 1$ and the antisimmetry property, $\omega_{\nu\mu} = -\omega_{\mu\nu}$, which comes from imposing the Lorentz–Poincaré transformation rule to Minkowski's tensor. Furthermore, it is known that Lorentz–Poincaré transformations ($\{\mathrm{L}_i\}$) form a group, e.g.,

$$\boldsymbol{\phi}'_n = \left[\mathbf{S}(\mathrm{L}_i)\right]_{nm}\boldsymbol{\phi}_m \tag{1.168}$$

here represented by the set of matrices in square parentheses. We will not enter this subject in detail, but may note that the matrix representation of our transformation ($\Omega$) will have to be infinitesimally near the identity operation:

$$\mathbf{S}(\mathrm{I} + \Omega) = \mathrm{I} + \frac{1}{2}\omega^{\alpha\mu} M_{(\alpha\mu)} \tag{1.169}$$

where the set of $n$-dimensional matrices $M_{(\mu\alpha)}$ (e.g., with covariant components $M_{(\mu\alpha)\gamma\kappa}$) can also be chosen antisymmetric, $M_{(\mu\alpha)} = -M_{(\alpha\mu)}$. Now observe that, let $\mathrm{L} \in \mathrm{L}_i$:

$$\mathbf{S}(\mathrm{L})\mathbf{S}(\mathrm{I} + \Omega)\mathbf{S}\left(\mathrm{L}^{-1}\right) = \mathbf{S}\left(\mathrm{I} + \mathrm{L}\Omega\mathrm{L}^{-1}\right) \tag{1.170}$$

implying the first-order constraint:

$$\mathbf{S}(\mathrm{L})M_{(\alpha\mu)}\mathbf{S}\left(\mathrm{L}^{-1}\right) = \Lambda^{\mu'}{}_{\mu}\Lambda^{\alpha'}{}_{\alpha}M_{(\alpha'\mu')} \tag{1.171}$$

and, because $\mathrm{L}^{\pm 1} = \mathrm{I} \pm \Omega$, the sought representation obeys the commutation relation:

$$\begin{aligned}[M_{(\kappa\omega)}, M_{(\mu\nu)}] &\equiv M_{(\kappa\omega)}M_{(\mu\nu)} - M_{(\mu\nu)}M_{(\kappa\omega)} \\ &= \eta_{\mu\omega}M_{(\kappa\nu)} - \eta_{\mu\kappa}M_{(\omega\nu)} + \eta_{\nu\omega}M_{(\mu\kappa)} - \eta_{\nu\kappa}M_{(\mu\omega)}\end{aligned} \tag{1.172}$$

The (six) generators $M_{(\alpha\mu)}$ defines "Lie's algebra" of the infinitesimal homogeneous Lorentz's group, the governor of any coordinate and field variations. In general, a decomposition like:

$$M_{(\alpha\mu)} = P_{(\alpha\mu)} + L_{\alpha\mu} \tag{1.173}$$

may be assumed, being:

$$\delta\boldsymbol{\phi}_n = \frac{1}{2}\omega^{\alpha\mu}P_{(\alpha\mu)}\boldsymbol{\phi}_n - \boldsymbol{\phi}_{n,\mu}\delta x^{\mu} \tag{1.174}$$

From this latter, the (angular momentum) operator:

$$L_{\alpha\mu} = x_{\alpha}P_{\mu} - x_{\mu}P_{\alpha} = -L_{\mu\alpha} \tag{1.175}$$

is identified, with $P_{\mu} \equiv \frac{\partial}{\partial x^{\mu}}$ denoting here the translation generators:

$$x'^{\alpha} = x^{\alpha} + \epsilon^{\mu}P_{\mu}x^{\alpha} \tag{1.176}$$

and characterizing the infinitesimal Lorentz–Poincaré transformation as:

$$\delta x^{\rho} = \frac{1}{2}\omega^{\mu\alpha}L_{\alpha\mu}x^{\rho} \tag{1.177}$$

Hence, it turns out:

$$\Xi(k) = \frac{1}{2}\omega^{\alpha\mu}J_{\alpha\mu}(k) \tag{1.178}$$

where:

$$J^{\alpha\mu}(k) = \int\limits_{\upsilon(k)} \left[S^{\alpha\mu\rho} + L^{\alpha\mu\rho}\right] d\upsilon_{\rho} \tag{1.179}$$

is a conserved quantity, expressed by the integral of the "spin" density of angular momentum, written explicitly as $(q, s = 1, \ldots, n)$:

$$S^{\alpha\mu\rho} = \left(\frac{\partial \mathsf{L}}{\partial \phi^{s}_{,\alpha}}\right)\left[P^{(\mu\rho)}\right]^{s}{}_{q}\phi^{q} = -S^{\alpha\rho\mu} \tag{1.180}$$

and summed to the "orbital" density:

$$L^{\alpha\mu\rho} = x^{\mu}T^{\alpha\rho} - x^{\rho}T^{\alpha\mu} \tag{1.181}$$

It resembles as well an ordinary angular momentum, returning $L^{\alpha\mu} = \int L^{\alpha\mu\rho}\, d\upsilon_{\rho}$. The former algebra, married to the commutation rules $[P_{\alpha}, P_{\mu}] = 0$ and $[M_{(\alpha\mu)}, P_{\rho}] = \eta_{\alpha\rho}P_{\mu} - \eta_{\mu\rho}P_{\alpha}$, form Lie's algebra of the Poincaré group, of the (10) generators $M_{(\alpha\mu)}$ and $P_{\rho}$. It should also be remembered that a complete (quantum) field-theoretical analysis would demand dealing with imaginary-valued operators (e.g., $P_{\rho} \equiv -\mathrm{i}\frac{\partial}{\partial x^{\rho}}$), what is limited here to their real domain.

An interpretation of $T^{\mu\alpha}$ as an energy–momentum tensor can be plainly illustrated by a comparison of spinless particles with single scalar fields, that is, single real numbers representing the physical state at each point regardless of the coordinate system. Keep in mind that spin is a prerogative of multicomponent scalar fields ($n > 1$), while classical particles have no spin. Apart from the orbital properties, the case $n > 1$ does not meet a full parallelism with ordinary particle mechanics. When $n = 1$, for which $P_{(\mu\alpha)} \equiv \mathbf{0}$, no spin must arise and the conservation law for the orbital contribution alone implies the energy–momentum tensor to be symmetrical, $T^{\alpha\mu} = T^{\mu\alpha}$. Conversely, if $T^{\alpha\mu} \neq T^{\mu\alpha}$ then $L^{\alpha\mu}$ is not conserved, and an extra (spin) contribution must be added to $T^{\mu\alpha}$:

$$\Theta^{\alpha\mu} = T^{\alpha\mu} + \theta^{\alpha\mu} \tag{1.182}$$

In short, the new tensor $\Theta^{\alpha\mu}$ (the total angular momentum) will have to be symmetric, so that:

$$J'^{\alpha\mu}(k) = \int\limits_{v(k)} \left(x^{\alpha}\Theta^{\rho\mu} - x^{\mu}\Theta^{\rho\alpha}\right) dv_{\rho} \tag{1.183}$$

is conserved. After working on the spin contribution, expressed by another (partially) antisymmetric quantity, $\psi^{\mu\alpha\rho} = -\psi^{\alpha\mu\rho}$:

$$S^{\mu\alpha\rho} = \psi^{\mu\alpha\rho} - \psi^{\mu\rho\alpha} \tag{1.184}$$

the final result is the so-called Belinfante's tensor:

$$\theta^{\alpha\mu} = \frac{1}{2}\left(S^{\kappa\alpha\mu} + S^{\alpha\mu\kappa} + S^{\mu\alpha\kappa}\right)_{,\kappa} \tag{1.185}$$

As expected, it does not contribute to the total 4-momentum, but the freedom left by $\psi^{\alpha\beta\gamma}$ determines that the energy–momentum distribution cannot be described univocally.

Another particular case is given by a vector field ($V_{\alpha}$), transforming evidently as the gradient of a scalar field ($\phi_{,\alpha}$):

$$\phi'_{,\alpha}\left(x'^{\rho}\right) = \Lambda^{\mu}{}_{\alpha}\phi_{,\mu}\left(x^{\rho}\right) \tag{1.186}$$

for which the generators can be set to:

$$\left[P^{(\alpha\mu)}\right]^{\rho}{}_{\varphi} = \eta^{\alpha\rho}\delta^{\mu}_{\varphi} - \eta^{\mu\rho}\delta^{\alpha}_{\varphi} \tag{1.187}$$

and:

$$\phi'_{,\alpha}\left(x'^{\rho}\right) - \phi_{,\alpha}\left(x^{\rho}\right) = \omega_{\alpha\mu}\phi_{,}{}^{\mu}\left(x^{\rho}\right) \tag{1.188}$$

## 5. GENERAL RELATIVITY

### 5.1 The principle of equivalence

The principle of equivalence, of gravitation and inertia, is the founding postulate of Einstein's general relativity. According to it, one can always find a "locally inertial" (or "locally geodesic") coordinate frame, within a sufficiently small neighbourhood of every spacetime point in a gravitational field, where all physical laws are taking the same form as in unaccelerated Cartesian systems, where gravity is absent.

In other words, providing it remains inside small spatio-temporal regions, a gravitational field at rest is tantamount to a reference frame that moves with constant acceleration in a spacetime devoid of gravitation. Furthermore, there would be no possibility discriminating experimentally between such two situations.

This principle of Einstein's is known as of "strong equivalence." Another statement, concurring to the previous and known as of weak equivalence, regards the local equality of inertial and gravitational masses. In brief, consider Newton's law for the gravitational attraction between two bodies at a distance $r$:

$$m'a = -G\frac{mM}{r^2} \tag{1.189}$$

The three mass values stand in principle for different quantities: that on the left is the "inertial" mass ($m'$), while its counterpart on the righthand side ($m$) refers to a "passive" body, undergoing the gravitational field produced by the larger, "active" mass ($M$). Trusting their equivalence, which is not at all obvious and does not descend from any law of mechanics, required an intensive experimental investigation, as witnessed by the work of Lloyd B. Kreuzer (1966–1968), who demonstrated the equality of active and passive mass values with a relative uncertainty bound equal approximately to $\simeq 5 \times 10^{-5}$.

The weak equivalence principle, for inertial and gravitational (passive) masses, has instead a longer history. It goes back to Galileo's first experiments, and its invalidation would have great consequences on the laws of nature. Thus, two bodies with equal mass but different chemistry would fall differently, the chemical specificity of their constituents weighting significantly in their dynamics. Fortunately, the experimental work by Loránd von Eötvös (1885–1889; 1906–1909) assigned the ratio of inertial and gravitational masses the uncertainty of $10^{-(8\div 9)}$ for all substances. This value was refined to $10^{-11}$, by a critical analysis of Robert H. Dicke (1961), and to $10^{-(17\div 20)}$ by Paul W. Worden and C.W. Francis Everitt (1973).

Einstein was able to conclude that, in a freely falling elevator for example, no external static and homogeneous gravitational field could be measured. This can be seen from Newton's second law:

$$m_i\left(\frac{d^2\mathbf{x}_i}{dt^2}\right) = m_i\mathbf{g} + \sum_j \mathbf{F}(\mathbf{x}_i - \mathbf{x}_j) \tag{1.190}$$

where, under validity of the weak equivalence principle, the free falling coordinate transformation, $\mathbf{x}' = \mathbf{x} - \frac{1}{2}\mathbf{g}t^2$ and $t' = t$, cancels the effect of the external gravitational field ($\mathbf{g}$). An elevator, for example, points out a "local" inertial frame, where gravitation is not felt and each massive body behaves as it were free. Einstein defined in this way a class of observers retaining the special picture of relativity, proceeding thereof toward the general formulation. Also, the existence of a scale where spacetime is reasonably homogeneous took in this respect a favourable role.

As an aside, strong and weak principles differ by two (strong) assumptions, on the independence of the spacetime position and velocity. The former addresses all laws of nature, irrespective of the laboratory features, while the latter limits itself to making all laws of motion equivalent. It is instructive emphasizing that, independently of the reasons behind it, reducing such an ample class of laws might seem, at first sight, to be tantamount to naivety and scientifically unsound. Notwithstanding, given the unlimited number of possible options, the Einsteinian assumptions were certainly plausible a priori, even if not necessary. This did not prevent ample, and on some occasions controversial, discussions on their validity. For instance, a further classification between very strong and "medium-strong" principles was introduced to discriminate between the equivalence of all phenomena indistinctly, with the sole exception of gravity. Einstein's field equations rely in any case on the very strong equivalence principle, which will be assumed throughout the following.

## 5.2 Curved and accelerated reference frames

Bernard Riemann (1854) foresaw a long time ago that "geometry is not a rigid, homogeneous something, susceptible to no change or conditions, but takes part in physical events and may have a direct physical meaning in its own right." Geometry is not only a formal entity, giving a passive background to phenomena, but itself contains the physical phenomenology. In relativity, while the arena of the special theory is the flat spacetime, with Minkowski's pseudo-metric and straight inertial motions, the general theory takes place in curved 4-dimensional spaces. Thus, before entering (some) non-Euclidean geometry, it may be useful to provide the reader with some preliminary arguments. Consider the famous example of two clocks, fixed at different heights inside a rocket moving with constant acceleration, clearly directed from the lower clock (L) to the uppermost (U). Imagine that U emits one light ray per second, which another observer compares downstairs with the ticking of L. It is not difficult to convince ourselves that U will seem to run faster than L, experiencing a delay produced by the acceleration. In accordance to the principle of equivalence, this picture will not change in a rocket at rest in a gravity field, and the ticking of a motionless clock will run faster with increasing height. We may expect that light cones and spacetime metric modify consequently, but the constancy of Minkowski's tensor components forbids any time and space unit change. Intuitively, this picture will become feasible once spacetime is allowed to curve.

To arrive at the equivalence of accelerated and curved frames of reference, the previous experiment can be rearranged into the following, sketching out Einstein's two central insights: time has to run slower with increasing gravity and, as a consequence, spacetime has to be curved. Consider thus the worldlines portraited in a rectangle $AA'BB'$, with equal heights $\overline{AA'} = \overline{BB'}$. Wishing to go in uniform motion from $A$ to $B$ and from $A'$ to $B'$, whenever $\overline{AB} = \overline{A'B'}$ the two times would also be equal, $t(\overline{AB}) = t'(\overline{A'B'})$. In a gravity field, with intensity decreasing with increasing height, the upper clock will proceed faster. This means that "closing" the worldlines by traveling uniformely along $AB$ and $A'B'$ for equal time intervals will no longer be possible. In trying to do so, a deficit length (or angle) will be left along the upper path length $(A'B')$ proportionally to the difference, $t'(\overline{A'B'}) - t(\overline{AB})$. These "deficit" quantities are a key point in bringing our kinematic considerations into non-Euclidean geometry. Einstein's standpoint focuses on the above time difference as an invalidation of Pythagora's theorem applied to a pair of systems in uniform motion, extending the equivalence of flat and inertial frames into one other, for curved and accelerated frames.

In conclusion, the Einsteinian gravity view is based essentially on (i) the strong equivalence of gravitational and inertial masses, and (ii) the "relativization" of time, the reference frames partecipating in (i) and (ii) generally sharing a non-Euclidean spacetime.

## 5.3 Curvatures, geodesic curves and parallel transport

General relativity is formulated in the framework of non-Euclidean (or Riemannian) geometry and tensor analysis. Einstein, in particular, made use of the "absolute differential" (or tensor) calculus, invented by Gregorio Ricci-Curbastro (~1890) and his student Tullio Levi-Civita (1900). Understanding his work would therefore demand handling such languages in the deepest detail possible. We, however, do not have room to do so here, and will limit ourselves to facing case-by-case each tensor quantity. In this respect, it is helpful to illustrate again some intuitive ideas, beginning from the very central notions of curvature and geodesics.

The simplest examples of non-Euclidean calculations are probably the arc length ($C_S$) and surface area ($A_S$) of a circle of radius $r$, lying on a sphere of radius $L$. Without doubt everybody knows their Euclidean expressions, but those for finite $L$ values are probably less popular:

$$\begin{aligned} C_S &= 2\pi L \sin\frac{r}{L} = 2\pi r\left[1 - \frac{1}{6}\left(\frac{r}{L}\right)^2 + \frac{1}{120}\left(\frac{r}{L}\right)^4 - \cdots\right] \\ A_S &= 2\pi L^2\left(1 - \cos\frac{r}{L}\right) = \pi r^2\left[1 - \frac{1}{12}\left(\frac{r}{L}\right)^2 + \frac{1}{360}\left(\frac{r}{L}\right)^4 - \cdots\right] \end{aligned} \tag{1.191}$$

returning evidently $C_S = 2\pi r$ (the circumference) and $A_S = \pi r^2$ on a flat surface ($L \to \infty$). Another simple, yet instructive, operation is drawing a geodesic polygon on it. The intuitive meaning of "geodesics" (or "orthodromic curve") is the generalization of Euclidean "straight lines," particularly after some work by Eugenio Beltrami (1868), where straight lines were conceived as geodesics on a surface (of constant negative curvature). We have already seen that the shortest sides on this "rectangle" substituted the geodesic lines of special relativity, but result in a wordline which can no longer be closed. One is used to saying that summing the angles in a geodesic spherical polygon of $n$ sides always exceeds $(n-2)\pi$. This defect angle, by which the Euclidean value is exceeded (or lowered), is the "total curvature" of the polygonal region.

Essentially, there are three different geometries, according to the "curvature" sign. Curvature is a central concept of non-Euclidean geometry, and is related to the turning rate of the direction vector evolving along the geometrical entity. It will therefore be zero on straightaways, and taking large values on sharp curves. Thus, spherical (or elliptic) geometries will have (conventionally) positive curvatures (pointing inward a center). Their counterparts, with negative curvature values (pointing outward), are called hyperbolic. Standing in between, as a transitional case, is the flat Euclidean (or parabolic) geometry.

Spaces of constant curvature have a wide spectrum of interesting properties and, historically, covered an inescapable role in the formulation of non-Euclidean and Riemannian differential geometries. Their roots may date back to the pioneering work by Gerolamo Saccheri (1733), who inquired into the consequences of renouncing Euclide's V parallels postulate, and bringing over the years to a concrete self-consistent geometrical view, specially by the important contributions of Johan H. Lambert (1786), Adrien-Marie Legendre (1794), Gauss (1792–1844), János Bolyai (1820–1823; 1832), Nikolaj I. Lobačevskij (1823–1826; 1829–1830), and Franz A. Taurinus (1824–1826). The latter formulated a log-spherical geometry, (formally) equivalent to Lobačevskij's imaginary (hyperbolic) "pangeometry." Passing from elliptic to hyperbolic formulas, simple transformations are required. Relations can be mapped onto spheres of imaginary radius ($R \to iR$), bringing them from standing in a spherical to a hyperbolic set of trigonometric equations. The previous formulas, for example, become:

$$\begin{aligned} C_H &= 2\pi L \sinh\frac{r}{L} = 2\pi r\left[1 + \frac{1}{6}\left(\frac{r}{L}\right)^2 + \frac{1}{120}\left(\frac{r}{L}\right)^4 + \cdots\right] \\ A_H &= 2\pi L^2\left(\cosh\frac{r}{L} - 1\right) = \pi r^2\left[1 + \frac{1}{12}\left(\frac{r}{L}\right)^2 + \frac{1}{360}\left(\frac{r}{L}\right)^4 + \cdots\right] \end{aligned} \tag{1.192}$$

and, correspondingly, the sum of all angles in a geodesic hyperbolic polygon of $n$ sides will always be lower than $(n-2)\pi$.

The constant (length) $L$ characterizes at once the curvature surface properties, as will be shortly seen better in more detail. Furthermore, it appears in a famous equation, revealed independently by Lobačevskij and Bolyai for the angle of parallelism ($\alpha_L$) of a hyperbolic space:

$$\tan\frac{\alpha_L(r)}{2} = \mathrm{e}^{-\frac{r}{L}} \tag{1.193}$$

with Euclidean limit $\alpha_{L\to\infty}(r) = \frac{\pi}{2}$. These authors began to suspect that natural phenomena could take place in non-Euclidean geometries. Gauss argued that $L$ may be detectable by measurements of extremely large distances, and Lobačevskij used his relation to estimate it from the earth orbit diameter ($r_O$) and the maximum parallax assigned to the star Sirius ($p \simeq 1''.24$). The result, with such assumptions, would be $\frac{L}{r_O} > (\tan p)^{-1} = 1.66 \times 10^5$.

To understand how curvature is defined in all generality, consider now a surface $\Sigma$ at a given point $P \in \Sigma$, and the (tangent) space formed by all vectors tangent to $\Sigma$ at $P$. To fix the ideas, imagine a quadratic osculating surface. Indicate by $\mathbf{n}$ a unit normal to $\Sigma$ at $P$, and "slice" $\Sigma$ by planes $S$, enclosing $\mathbf{n}$. We will regard the curvature vector, $\mathbf{k}_\rho$, for each of the resulting curves. Remember that, for a parametrized curve $\mathbf{x}(t)$ (generally $\in \mathfrak{R}^n$), $\mathbf{k}_\rho$ is defined as the rate of change of the unit tangent, $\mathbf{t}_u = \dot{\mathbf{x}}/|\dot{\mathbf{x}}|$. Therefore, $\mathbf{k}_\rho = \dot{\mathbf{t}}_u/|\dot{\mathbf{x}}|$, pointing the direction in which it turns, while the turning rate is quantified by the scalar curvature, $\kappa = |\mathbf{k}_\rho|$. If the curve is parametrized by the arc length, $\mathbf{k}_\rho = \frac{d^2\mathbf{x}}{ds^2}$, while for a planar curve, $\kappa = |\frac{d\mathbf{n}}{ds}|$ (for a circle, $\kappa = \frac{1}{\text{radius}}$, directed to the center).

Stepping back to the surface curvature, $\mathbf{k}_\rho = \kappa \mathbf{n}$, and varying $S$ will obviously change the outcome. It turns out however that the so-called "principal curvatures," the maximum and minimum (normal) curvatures, $\kappa_{\min}$ and $\kappa_{\max}$, of all the curves on the surface passing through $P$, give a well-posed description. When their sign is the same, the surface is said to be "synclastic" at $P$, otherwise it is called "anticlastic" (and $P$ is saddle-shaped). Their directions instead are always perpendicular and called "principal directions." Letting $\Sigma_2$ be represented by a local 2-dimensional function, $f = f(x, y)$, the curvature along the direction of a unit vector $\mathbf{u}$ can be defined as:

$$K(P) = f_{ss'} U^s U^{s'} \tag{1.194}$$

with $f_{ss'} \equiv (\frac{\partial^2 f}{\partial x^s \partial x^{s'}})_P$, and the matrix pointed out by $\Pi = \| f_{ss'} \|$ is termed the second fundamental form of $\Sigma$ at $P$. What can be demonstrated is that $K$ has two invariants, coming from the eigenvalue problem for $\Pi$, and identifying the mean curvature:

$$k_H = \frac{1}{2} \operatorname{Tr} \Pi = \frac{1}{2}(\kappa_{\min} + \kappa_{\max}) \tag{1.195}$$

and the Gaussian curvature:

$$k_G = \det \Pi = \kappa_{\min} \kappa_{\max} \tag{1.196}$$

Regardless of the chosen tangent vector, this couple of quantities unambiguously characterize the surface. At the south pole of a unit sphere, for example, it suffices to know $\kappa_{\min} = \kappa_{\max} = 1$, so that $k_H = 2$, $k_G = 1$. In $n$ dimensions, the diagonal entries of $\Pi$ provide the ($n$) principal curvatures of a hypersurface $\Sigma_n$ at $P$. Again, they are the sectional 1-dimensional curvatures in $n$ orthogonal directions, obtained by a rotation of all tangent axes about $\mathbf{n}$ (i.e., by diagonalizing $\Pi$).

Evidently, principal curvatures are "extrinsic" properties. They could never be calculated by measurements confined to the surface. What is rather surprising is that the Gaussian curvature is instead "intrinsic." It is a property "in se," and can always be measured by "staying inside" the surface. This follows from Gauss's Theorema Egregium, and will be of the upmost importance to Einstein's general relativity, whose spacetime is of intrinsic nature. The mean curvature reflects on the contrary the (larger) geometrical structure which can host the surface from outside, and lies unfortunately far beyond our observational experience and interpretational possibilities. Any cylindrical surface, for instance, can be built by rolling a piece of plane and, though having a non-null mean curvature, it remains intrinsically flat ($0 \leqslant k_H \leqslant \frac{1}{\text{radius}}$, $k_G = 0$).

The relevance of the intrinsic curvature can be understood by a clever 2-dimensional experiment, reported by Feynman (1963–1966) in his lectures on physics, and sometimes acknowledged to Poincaré. There, a temperature gradient is applied in a given direction, generating a curvature which invalidates Pythagoras's theorem. In this world, where the longest units of length locate in the hottest regions, he asked himself whether and how its inhabitants could unveil such an effect. From Gauss's theorem, we know that the answer is certainly positive. In the same way, it would not necessitate traveling all around the world to verify the positive sign of the curvature of the surface of the earth. By the above criteria, we have learnt now that drawing a geodesic polygon and summing its angles will suffice, provided it be large enough.

Generally, when a 2-dimensional surface embeds a space of arbitrary dimensionality ($d$), all the orientational degrees of freedom determine a number of distinct curvatures. This description gets more and more complicated as $d$ increases, but there is an object by which a terse summary of the overall features may be given. Consider thus two vectors **u** and **v**, defined at a point $P$, and the surface filled out by the geodesics departing from $P$ (and tangent to the plane identified by the vectors). In this case, the 4-rank tensor appearing in the expression for the intrinsic ("sectional") curvature:

$$k_G(P) = \frac{R_{\alpha\mu\beta\nu} U^\alpha V^\mu U^\beta V^\nu}{(g_{\alpha\nu} g_{\mu\beta} - g_{\alpha\beta} g_{\mu\nu}) U^\alpha V^\mu U^\beta V^\nu} \tag{1.197}$$

is named the Riemann–Christoffel curvature tensor ($R_{\alpha\mu\beta\nu}$). It has $n_d = \frac{d^2}{12}(d^2 - 1)$ independent components, pointing out at once that a curved line has zero curvature ($n_1 = 0$). This was clearly expected, since $R_{\alpha\mu\beta\nu}$ only describes the intrinsic space features. In two dimensions, the number of independent components is $n_2 = 1$ (essentially, the Gaussian curvature), while $n_3 = 6$ and $n_4 = 20$. We will take a look at its main formal properties in the next paragraph. Bear in mind however that, unless the surface be locally flat (at a point $P$), there is no reference frame which can cancel out all curvatures. Precisely, a necessary and sufficient flatness condition requires $R_{\alpha\mu\beta\nu}(P) = 0$.

A last peculiarity of non-Euclidean geometry which is worth remembering is the parallel transport of tangent vectors along curved paths. Consider again for simplicity a spherical polygon, and a tangent vector at some of its points (e.g., a vertex). It will be clear that, when transported along all geodesic edges, back to the initial point, the vector will exhibit a different orientation, characterized by a defect angle equal to the polygon total curvature. This does not happen, of course, when the transport is dragged along a "straight line" (e.g., a geodesic circle) nor in the Euclidean space, where the orientation is never affected by the intermediate path. But, in general, parallel-transporting a vector along a closed curve will result in a new vector. To pick up what this operation means, formally, the notions of affine connection and covariant differentiation are needed. Nevertheless, an instructive definition of the curvature tensor can be given by it.

Let $x^\rho(u, v)$ denote a family of curves, catalogued by $u$ and $w$, and consider a vector $V^\rho$, transported from a point $P(u, w)$ to $P'(u + \Delta u, w)$, $P''(u + \Delta u, w + \Delta w)$, $P'''(u, w + \Delta w)$, back to $P(u, w)$. The difference, $\delta V^\rho$, will be of the order of $\Delta u \Delta w$, and becoming zero when one of the two parameter variations vanishes. Thus, one can take both limits, Lim $\equiv \Delta u$, $\Delta w \to 0$, and obtain, at the point $P(u, w)$:

$$\mathrm{Lim}\left(\frac{\delta V^\rho}{\Delta u \Delta w}\right) = R^\rho_{\alpha\mu\nu} V^\alpha \left(\frac{dx^\mu}{du}\right)\left(\frac{dx^\nu}{dw}\right) \tag{1.198}$$

from which, it turns out for an arbitrary small curve that:

$$\delta V^{\alpha} = \frac{1}{2} R^{\alpha}_{\rho\mu\nu} V^{\rho} \oint x^{\mu}\, dx^{\nu} \tag{1.199}$$

the line integral being generally different from zero. For a parallelogram, with edges $\delta y^{\mu}$ and $\delta z^{\nu}$, this would give the following antisymmetric surface tensor:

$$\oint x^{\mu}\, dx^{\nu} = \delta y^{\mu} \delta z^{\nu} - \delta y^{\nu} \delta z^{\mu} = - \oint x^{\nu}\, dx^{\mu} \tag{1.200}$$

Again, a necessary and sufficient condition not to observe any twist in the vector orientation is having a zero curvature tensor (at $P$).

## 5.4 Metric tensor, affine connection and curvature tensor

In a non-Euclidean space, the metric tensor ($g_{\mu\nu}$) indicates how Pythagoras's theorem is amended by the effect of curvature, and provides us with the transformation rules among curved frames. With the former notations, the simplest second-order perturbation to the Euclidean metric tensor ($\delta_{ss'}$) takes the form:

$$g_{ss'} = \delta_{ss'} + f_{sk} f_{s'k'} x^{k} x^{k'} \tag{1.201}$$

Under $f_{ss'} = 0$, Pythagoras's law for the distance ($s$) between two points, infinitesimally close to each other in a Cartesian system ($X^{k}$), is recovered:

$$ds^{2} = \delta_{ss'}\, dX^{s}\, dX^{s'} = dX^{2} + dY^{2} + \cdots \tag{1.202}$$

Note that any coordinate dependence, $g_{ss'} = g_{ss'}(x^{i})$, is not necessarily indicative of non-vanishing intrinsic curvatures (as for a cylindrical surface, for example). Otherwise, another reference frame ($x^{k}$) must be generally introduced to cover any finite part of a curved space. In this case, Gauss's assumption for the infinitesimal distance between $(x, y, \ldots)$ and $(x + dx, y + dy, \ldots)$ becomes:

$$ds^{2} = g_{ss'}\, dx^{s}\, dx^{s'} = g_{xx}\, dx^{2} + 2 g_{xy}\, dx\, dy + g_{yy}\, dy^{2} + \cdots \tag{1.203}$$

the two coordinate systems joining through:

$$g_{ss'} = \left( \frac{\partial X^{k}}{\partial x^{s}} \right) \left( \frac{\partial X^{k'}}{\partial x^{s'}} \right) \delta_{kk'} \tag{1.204}$$

This picture can be promptly rearranged into a 4-dimensional spacetime, provided Minkowski's pseudo-metric replaces the Euclidean tensor, $\delta_{\mu\nu} \rightarrow -\eta_{\mu\nu}$. Therefore, in all generality:

$$ds^{2} = -g_{\mu\nu}\, dx^{\mu}\, dx^{\nu} \tag{1.205}$$

all indices taking the values $\mu, \nu = 0, 1, 2, 3$, and the minus sign being (conventionally) related to the signature of $\eta_{\mu\nu} = (-1, 1, 1, 1)$. The metric tensor is clearly symmetric, $g_{\mu\nu} = g_{\nu\mu}$, now with $d(d + 1)/2 = 10$ independent components. Formally, this extension changes none of the previous relations, either for a curved

3-dimensional or Minkowskian 4-dimensional spaces. For instance, changing coordinate system ($x^\alpha \rightarrow x'^\alpha$) will transform the metric tensor as:

$$g'_{\mu\nu} = \left(\frac{\partial x^\varepsilon}{\partial x'^\mu}\right)\left(\frac{\partial x^\sigma}{\partial x'^\nu}\right) g_{\varepsilon\sigma} \tag{1.206}$$

and, since the inverse of $g_{\mu\nu}$ is a contravariant tensor, $g^{\mu\nu} g_{\mu\alpha} = \delta^\nu_\alpha$:

$$g'^{\mu\nu} = \left(\frac{\partial x'^\mu}{\partial x^\varepsilon}\right)\left(\frac{\partial x'^\nu}{\partial x^\sigma}\right) g^{\varepsilon\sigma} \tag{1.207}$$

As already mentioned, Minkowskian frames generalize the concept of Euclidean system ($X^s$) and define the class of locally inertial reference frames ($\xi^\mu$) postulated by the principle of equivalence:

$$g_{\mu\nu} = \eta_{\alpha\beta}\left(\frac{\partial \xi^\alpha}{\partial x^\mu}\right)\left(\frac{\partial \xi^\beta}{\partial x^\nu}\right) \tag{1.208}$$

The language of general relativity is not therefore very different from the special formalism. Here, rather than having the only class of inertial frames, one deals with a multiplicity of coordinate transformations, where covariant and contravariant representations remain formally unchanged. The raising or lowering of indices again requires multiplication by contravariant or covariant metric tensors:

$$g^{\sigma\nu} g^{\tau\rho} \ldots g_{\beta\omega} g_{\gamma\epsilon} \ldots A^{\omega\epsilon\ldots}{}_{\nu\rho\ldots} = A^{\sigma\tau\ldots}{}_{\beta\gamma\ldots} \tag{1.209}$$

while, on changing reference system, any tensor continues to obey:

$$A'^{\alpha\beta\gamma\ldots}{}_{\ldots\omega\sigma\tau} = \left(\frac{\partial x'^\alpha}{\partial x^\kappa}\right)\left(\frac{\partial x'^\beta}{\partial x^\chi}\right)\left(\frac{\partial x'^\gamma}{\partial x^\zeta}\right)\cdots\left(\frac{\partial x^\rho}{\partial x'^\omega}\right)\left(\frac{\partial x^\delta}{\partial x'^\sigma}\right)\left(\frac{\partial x^\lambda}{\partial x'^\tau}\right) A^{\kappa\chi\zeta\ldots}{}_{\ldots\rho\delta\lambda} \tag{1.210}$$

The metric tensor is the building block of every geometrical quantity of interest. A first example is given by the Levi-Civita affine connection:

$$\Gamma^\tau_{\nu\lambda} = \left(\frac{\partial x^\tau}{\partial X^\mu}\right)\left(\frac{\partial^2 X^\mu}{\partial x^\nu \partial x^\lambda}\right) \tag{1.211}$$

which, however, does not behave as a tensor. Transforming the above equation upon $x^\alpha \rightarrow x'^\alpha$, a coordinate-dependent inhomogeneous term appears on the right (second addendum), making the affine connection a nontensor:

$$\Gamma'^\tau_{\nu\lambda} = \left(\frac{\partial x'^\tau}{\partial x^\rho}\right)\left(\frac{\partial x^\kappa}{\partial x'^\nu}\right)\left(\frac{\partial x^\epsilon}{\partial x'^\lambda}\right)\Gamma^\rho_{\kappa\epsilon} + \left(\frac{\partial x'^\tau}{\partial x^\mu}\right)\left(\frac{\partial^2 x^\mu}{\partial x'^\nu \partial x'^\lambda}\right) \tag{1.212}$$

It also appears in the transformation rule of "Christoffel's symbol" (of the second kind):

$$\left\{ \begin{matrix} \lambda \\ \mu\nu \end{matrix} \right\} \equiv \frac{g^{\lambda\rho}}{2}(g_{\rho\mu,\nu} + g_{\rho\nu,\mu} - g_{\mu\nu,\rho}) \tag{1.213}$$

i.e.:

$$\left(\frac{\partial x'^{\tau}}{\partial x^{\mu}}\right)\left(\frac{\partial^2 x^{\mu}}{\partial x'^{\nu}\partial x'^{\lambda}}\right) = \begin{Bmatrix} \tau \\ \nu\lambda \end{Bmatrix}' - \left(\frac{\partial x'^{\tau}}{\partial x^{\rho}}\right)\left(\frac{\partial x^{\kappa}}{\partial x'^{\nu}}\right)\left(\frac{\partial x^{\epsilon}}{\partial x'^{\lambda}}\right)\begin{Bmatrix} \rho \\ \kappa\epsilon \end{Bmatrix} \tag{1.214}$$

and thus their difference, $\Gamma^{\tau}_{\nu\lambda} - \left\{ {\tau \atop \nu\lambda} \right\}$, is a tensor. As both of them vanish in a flat geometry, the principle of equivalence implies that, in the absence of gravity, their difference will be vanishing in all reference frames, i.e.:

$$\Gamma^{\tau}_{\nu\lambda} = \begin{Bmatrix} \tau \\ \nu\lambda \end{Bmatrix} \tag{1.215}$$

This equality will play a central role in the (geodesic) motion equation, examined in the forthcoming paragraph.

Metric tensor and affine connection give the basis for seeking a tensor out of $g_{\mu\nu}$ and its derivatives. It can be shown that the Riemann–Christoffel curvature tensor is the only one which can be constructed by the metric tensor, up to (a linear part in) the second-order derivatives. The first derivatives can always be made vanishing, under an opportune choice of the reference frame, and would not suffice alone to build a new tensor. The sought expression is from a third-order identity like:

$$\left(\frac{\partial^3 x'^{\tau}}{\partial x^{\kappa}\partial x^{\mu}\partial x^{\nu}}\right) - \left(\frac{\partial^3 x'^{\tau}}{\partial x^{\nu}\partial x^{\mu}\partial x^{\kappa}}\right) = 0 \tag{1.216}$$

each term being evaluated by the transformation rule of the affine connection, and the final result is:

$$\begin{aligned} &\left[\Gamma^{\omega}_{\mu\nu,\kappa} - \Gamma^{\omega}_{\mu\kappa,\nu} + \Gamma^{\alpha}_{\mu\nu}\Gamma^{\omega}_{\kappa\alpha} - \Gamma^{\alpha}_{\mu\kappa}\Gamma^{\omega}_{\nu\alpha}\right]\left(\frac{\partial x'^{\tau}}{\partial x^{\omega}}\right) \\ -&\left[\Gamma'^{\tau}_{\rho\sigma,\alpha} - \Gamma'^{\tau}_{\rho\alpha,\sigma} + \Gamma'^{\tau}_{\omega\alpha}\Gamma'^{\omega}_{\sigma\rho} - \Gamma'^{\tau}_{\omega\sigma}\Gamma'^{\omega}_{\alpha\rho}\right]\left(\frac{\partial x'^{\rho}}{\partial x^{\mu}}\right)\left(\frac{\partial x'^{\sigma}}{\partial x^{\nu}}\right)\left(\frac{\partial x'^{\alpha}}{\partial x^{\kappa}}\right) = 0 \end{aligned} \tag{1.217}$$

where the derivatives (comma operators) of primed quantities ($\Gamma'$) are with respect to primed coordinates ($x'$) and:

$$R^{\omega}{}_{\mu\nu\kappa} \equiv \Gamma^{\omega}_{\mu\nu,\kappa} - \Gamma^{\omega}_{\mu\kappa,\nu} + \Gamma^{\alpha}_{\mu\nu}\Gamma^{\omega}_{\kappa\alpha} - \Gamma^{\alpha}_{\mu\kappa}\Gamma^{\omega}_{\nu\alpha} \tag{1.218}$$

identifies the Riemann–Christoffel curvature tensor:

$$R^{\alpha}{}_{\beta\gamma\omega} = \left(\frac{\partial x'^{\alpha}}{\partial x^{\lambda}}\right)\left(\frac{\partial x^{\mu}}{\partial x'^{\beta}}\right)\left(\frac{\partial x^{\nu}}{\partial x'^{\gamma}}\right)\left(\frac{\partial x^{\kappa}}{\partial x'^{\omega}}\right)R^{\lambda}{}_{\mu\nu\kappa} \tag{1.219}$$

Lowering the upper index returns a fully covariant quantity:

$$R_{\alpha\mu\nu\kappa} = g_{\alpha\lambda}R^{\lambda}{}_{\mu\nu\kappa} \tag{1.220}$$

which is explicitly:

$$\begin{aligned} R_{\omega\mu\nu\kappa} = &\frac{1}{2}(g_{\omega\nu,\kappa\mu} - g_{\mu\nu,\kappa\omega} + g_{\mu\kappa,\nu\omega} - g_{\omega\kappa,\nu\mu}) \\ &+ g_{\alpha\sigma}\left(\Gamma^{\alpha}_{\nu\omega}\Gamma^{\sigma}_{\mu\kappa} - \Gamma^{\alpha}_{\kappa\omega}\Gamma^{\sigma}_{\mu\nu}\right) \end{aligned} \tag{1.221}$$

and has the following algebraic properties:

$$\begin{aligned} &R_{\omega\mu\nu\kappa} = R_{\nu\kappa\omega\mu} \quad \text{(symmetry)} \\ &R_{\omega\mu\nu\kappa} = -R_{\mu\omega\nu\kappa} = -R_{\omega\mu\kappa\nu} = R_{\mu\omega\kappa\nu} \quad \text{(antisymmetry)} \\ &R_{\omega\mu\nu\kappa} + R_{\omega\kappa\mu\nu} + R_{\omega\mu\kappa\nu} = 0 \quad \text{(cyclicity)} \end{aligned} \tag{1.222}$$

By another contraction, it defines the Ricci's tensor:

$$R_{\mu\kappa} \equiv R^{\alpha}{}_{\mu\alpha\kappa} \tag{1.223}$$

whose expression reads in full:

$$R_{\mu\kappa} = \Gamma^{\alpha}_{\mu\alpha,\kappa} - \Gamma^{\alpha}_{\mu\kappa,\alpha} + \Gamma^{\omega}_{\mu\alpha}\Gamma^{\alpha}_{\kappa\omega} - \Gamma^{\omega}_{\mu\kappa}\Gamma^{\alpha}_{\omega\alpha} \tag{1.224}$$

Another quantity to recall is the curvature scalar, set by taking the trace of the Ricci's tensor:

$$R \equiv R^{\mu}{}_{\mu} = g^{\mu\nu} R_{\mu\nu} \tag{1.225}$$

that, in two dimensions, is directly related to the Gaussian curvature (unless a conventional factor, $-\frac{1}{2}$):

$$k_G = -\frac{R}{2} \tag{1.226}$$

## 5.5 Tensor densities

Aside from the affine connection, other non-tensor terms usually arise. The first are the so-called tensor densities, transforming as:

$$D'^{\mu}{}_{\nu} = \left\| \frac{\partial x}{\partial x'} \right\|^{-z} \left( \frac{\partial x'^{\mu}}{\partial x^{\alpha}} \right) \left( \frac{\partial x^{\beta}}{\partial x'^{\nu}} \right) D^{\alpha}{}_{\beta} \tag{1.227}$$

$z$ being the density weight (or rank) and $\| \frac{\partial x}{\partial x'} \|$ denoting again the transformation Jacobian. In particular, the metric tensor determinant, $\mathrm{g} \equiv \det g_{\mu\nu}$, is a (scalar) density with $z = -2$:

$$\mathrm{g}' = \left\| \frac{\partial x}{\partial x'} \right\|^{2} \mathrm{g} \tag{1.228}$$

so that any density with rank $z$ is expressible as a tensor multiplied by $\mathrm{g}^{-\frac{z}{2}}$. This is the case, for instance, of the 4-dimensional infinitesimal volume, $d^4x' = \| \frac{\partial x}{\partial x'} \| \, d^4x$, with invariant element:

$$\sqrt{-\mathrm{g}}\, d^4x = \text{invar} \tag{1.229}$$

Remember that, if $f$, $V^{\mu}$, $A^{\mu\nu}$ are a scalar, a vector and a tensor, the quantities $\sqrt{-\mathrm{g}}\, f$, $\sqrt{-\mathrm{g}}\, V^{\mu}$, $\sqrt{-\mathrm{g}}\, A^{\mu\nu}$ will denote the corresponding scalar, vector and tensor densities. Each of them, multiplied by $d^4x$, will certainly keep their tensor character, but integrals of vectors and tensors, which change from point to point of the integration domain, generally will not. Another relevant case is given by the Levi-Civita tensor density, defined as:

$$\epsilon^{\mu\nu\lambda\kappa} = \begin{cases} 1 & \text{even permutation of } [\mu\nu\lambda\kappa] \\ -1 & \text{even permutation of } [\mu\nu\lambda\kappa] \\ 0 & \text{two or more indices equal} \end{cases} \tag{1.230}$$

where the argument $[\mu\nu\lambda\kappa]$ means a reference sequence. We have already anticipated that $\epsilon^{\mu\nu\lambda\kappa}$ transforms as:

$$\left(\frac{\partial x'^{\alpha}}{\partial x^{\beta}}\right)\left(\frac{\partial x'^{\gamma}}{\partial x^{\omega}}\right)\left(\frac{\partial x'^{\mu}}{\partial x^{\nu}}\right)\left(\frac{\partial x'^{\tau}}{\partial x^{\sigma}}\right)\epsilon^{\beta\omega\nu\sigma} = \left\|\frac{\partial x'}{\partial x}\right\|\epsilon^{\alpha\gamma\mu\tau} \tag{1.231}$$

and, therefore, has weight $-1$. Furthermore, $\epsilon_{\alpha\gamma\mu\tau} = -\mathrm{g}\epsilon^{\alpha\gamma\mu\tau}$ is also a (covariant) density with $z = -1$. Recall that $z$ does not change under raising, lowering and contracting indices, as well as upon linearly combining densities of the same rank, while the direct product of two tensor densities with weights $z_1$ and $z_2$ will give us a density with $z = z_1 + z_2$.

## 5.6 Covariant differentiation and principle of general covariance

In non-Euclidean geometry, linear combinations, direct products and contractions of tensors still produce tensors. An operation breaking the tensor behavior is the differentiation. For instance, the derivative of a contravariant 4-vector:

$$U'^{\mu} = \left(\frac{\partial x'^{\mu}}{\partial x^{\alpha}}\right)U^{\alpha} \tag{1.232}$$

transforms as:

$$U'^{\mu}{}_{,\omega} = \left(\frac{\partial x'^{\mu}}{\partial x^{\alpha}}\right)\left(\frac{\partial x^{\kappa}}{\partial x'^{\omega}}\right)U^{\alpha}{}_{,\kappa} + \left(\frac{\partial^2 x'^{\mu}}{\partial x^{\alpha}\partial x^{\kappa}}\right)\left(\frac{\partial x^{\kappa}}{\partial x'^{\omega}}\right)U^{\alpha} \tag{1.233}$$

whereupon, one succeeds in isolating a inhomogeneous contribution on the right and singles out a quantity transforming as a tensor:

$$U'^{\mu}{}_{;\omega} = \left(\frac{\partial x'^{\mu}}{\partial x^{\alpha}}\right)\left(\frac{\partial x^{\beta}}{\partial x'^{\omega}}\right)U^{\alpha}{}_{;\beta} \tag{1.234}$$

the semicolon operator indicating the covariant derivative:

$$U'^{\mu}{}_{;\omega} = U^{\mu}{}_{,\omega} + \Gamma^{\mu}_{\omega\alpha}U^{\alpha} \tag{1.235}$$

Note that, in any locally inertial frame ($\xi^{\omega}$), the affine connection vanishes, getting back to the ordinary derivative, $U'^{\mu}{}_{;\omega} = U^{\mu}{}_{,\omega}$. This operation finds a natural generalization to tensors and tensor densities. In general, the covariant derivative of a mixed tensor $A::$ in the coordinate $x^{\rho}$ can be represented by:

$$\begin{aligned} A::_{;\rho} = A::_{,\rho} &+ \text{terms } \Gamma^{\mu}_{\nu\rho}A:: \ (\mu \text{ replaced by } \nu) \text{ any contravariant index} \\ &- \text{terms } \Gamma^{\alpha}_{\beta\rho}A:: \ (\beta \text{ replaced by } \alpha) \text{ any covariant index} \end{aligned} \tag{1.236}$$

and, for a tensor density ($Q$) of weight assigned ($z$):

$$Q{::}_{;\rho} = \mathrm{g}^{-\frac{z}{2}}\left(\mathrm{g}^{\frac{z}{2}} Q{::}\right)_{;\rho} \tag{1.237}$$

e.g.:

$$Q^{\nu}{}_{\alpha;\beta} = Q^{\nu}{}_{\alpha,\beta} + \Gamma^{\nu}_{\beta\mu} Q^{\mu}{}_{\alpha} - \Gamma^{\epsilon}_{\alpha\beta} Q^{\nu}{}_{\epsilon} + z\left(\ln\sqrt{-\mathrm{g}}\right)_{,\beta} Q^{\nu}{}_{\alpha} \tag{1.238}$$

The object (in parenthesis) in the last but one definition is clearly a tensor, and the extra term in the last example derives from the supposed non-tensor behavior of $Q$.

The covariant differentiation obviously fulfills the property of linearity, i.e.:

$$\left(\sum_{k} a_k [T{::}]_k\right)_{;\rho} = \sum_{k} a_k [T{::}]_{k;\rho} \tag{1.239}$$

Leibniz's rule, for the direct tensor product, i.e.:

$$\left(\prod_{k} [T{::}]_k\right)_{;\rho} = \sum_{j}\left([T{::}]_{j;\rho} \prod_{k \neq j} [T{::}]_k\right) \tag{1.240}$$

and:

$$A^{\kappa\alpha}{}_{\alpha;\mu} = A^{\kappa\alpha}{}_{\alpha,\mu} + \Gamma^{\kappa}_{\mu\omega} A^{\omega\alpha}{}_{\alpha} \tag{1.241}$$

i.e., differentiating (covariantly) a contracted tensor is equal to contracting a (covariant) derivative.

We ought also to remember the form assumed by the covariant derivative in some relevant operations. Thus, the ordinary gradient of a scalar ($f$) just is:

$$f_{;\rho} = f_{,\rho} \tag{1.242}$$

and, since:

$$U_{\tau;\rho} = g_{\tau\mu} U^{\mu}{}_{;\rho} = U_{\tau,\rho} - \Gamma^{\alpha}_{\tau\rho} U_{\alpha} \tag{1.243}$$

covariant and ordinary curls coincide:

$$U_{\tau;\rho} - U_{\rho;\tau} = U_{\tau,\rho} - U_{\rho,\tau} \tag{1.244}$$

The divergence of a (contravariant) vector becomes instead:

$$U^{\rho}{}_{;\rho} = U^{\rho}{}_{,\rho} + \Gamma^{\rho}_{\rho\alpha} U^{\alpha} = \frac{1}{\sqrt{-\mathrm{g}}}\left(\sqrt{-\mathrm{g}}\, U^{\rho}\right)_{,\rho} \tag{1.245}$$

because:

$$\Gamma^{\rho}_{\rho\alpha} = \frac{g^{\rho\sigma}}{2} g_{\rho\sigma,\alpha} = \left(\ln\sqrt{-\mathrm{g}}\right)_{,\alpha} \tag{1.246}$$

and, for any invertible matrix, $\mathrm{Tr}\{G^{-1}G_{,s}\} = (\ln\det G)_{,s}$. In addition, since:

$$g_{\alpha\beta,\rho} = \Gamma^{\kappa}_{\rho\alpha} g_{\kappa\beta} + \Gamma^{\kappa}_{\rho\beta} g_{\kappa\alpha} \tag{1.247}$$

one has the noteworthy property:

$$g^{\nu\alpha}{}_{;\mu} = 0 \tag{1.248}$$

and the expected commutation rule of the semicolon operator with changing contravariant and covariant representations, e.g.:

$$\left(g_{\nu\alpha}U^{\epsilon\nu}\right)_{;\omega} = g_{\nu\alpha}U^{\epsilon\nu}{}_{;\omega} \tag{1.249}$$

We are now in a position to formulate the principle of equivalence by tensor analysis. The Principle of General Covariance requires a couple of points for the validity of any physical relation in the presence of (gravitational) fields. The equations must (a) hold when the gravity field is vanishing and (b) be generally covariant, meaning that it will preserve its form under any coordinate transformation. Therefore, whenever a special-relativistic description is available in a locally inertial system, to rewriting it for a curved frame will only necessitate (i) to replacing Minkowski's tensor with the metric tensor, $\eta_{\nu\alpha} \to g_{\nu\alpha}$, and (ii) to convert any standard derivative with its covariant counterpart, $(\ldots)_{,\rho} \to (\ldots)_{;\rho}$ ("comma goes to semicolon"). Vice versa, the use of locally geodesic coordinates will bring the picture with gravity into an equivalent special-relativistic equation. One might notice also that Einstein's was certainly not the only principle of general covariance that could ever be proposed. Notwithstanding, aiming at economy there was no reason to adopt any other statement than a minimal coupling scheme like his.

We conclude this paragraph by a relevant example, the identities bearing the name of Luigi Bianchi (1902), for the curvature tensor derivatives. They follow in fact from direct calculation, but more conveniently from the locally geodesic expression:

$$R_{\omega\mu\nu\kappa} = \frac{1}{2}(g_{\omega\nu,\kappa\mu} - g_{\mu\nu,\kappa\omega} + g_{\mu\kappa,\nu\omega} - g_{\omega\kappa,\nu\mu}) + \mathrm{O}(\Gamma) \tag{1.250}$$

Differentiating it, $R_{\omega\mu\nu\kappa,\alpha}$, and permuting $\nu$, $\kappa$, $\alpha$ cyclically, the symmetry and commutation properties of the partial derivatives lead quickly to:

$$R_{\omega\mu\nu\kappa,\alpha} + R_{\omega\mu\alpha\nu,\kappa} + R_{\omega\mu\kappa\alpha,\nu} = 0 \tag{1.251}$$

and universally, from any reference frame:

$$R_{\omega\mu\nu\kappa;\alpha} + R_{\omega\mu\alpha\nu;\kappa} + R_{\omega\mu\kappa\alpha;\nu} = 0 \tag{1.252}$$

Bianchi's identities express a geometrical closure relation covering a central role in Einstein's field equations.

## 5.7 Postulate of geodesic motion and free falling frame

We have seen that the (weak) principle of equivalence allows a description of a free falling system in terms of special relativity. It ensures the existence of a class of locally inertial observers, defined on a scale where spacetime can still be regarded unperturbed. In other words, whatever the non-local form of the (curved) spacetime metric, there exists a free falling frame where the motion is still geodesic.

This does not mean that geometry is made Minkowskian everywhere. Rather, in a locally inertial frame, a particle experiencing an external gravitational field will proceed as it were "free" along a "straight," geodesic line. In this spacetime portion, the light cone of special relativity is unchanged, and the (time-like geodesic) curve will join two events by the longest path in time (or by the shortest length, for a space-like curve).

Accordingly, consider a free falling coordinate system where the trajectory is still geodesic, i.e.:

$$\left(\frac{d^2\xi^\mu}{ds^2}\right) = 0 \tag{1.253}$$

with proper time:

$$ds^2 = -\eta_{\mu\nu}\, d\xi^\mu\, d\xi^\nu \tag{1.254}$$

In order to write the relation with another arbitrary frame:

$$ds^2 = -g_{\mu\nu}\, dx^\mu\, dx^\nu \tag{1.255}$$

the free falling system should be worked out in terms of these new coordinates and metric tensor. This is easily done by developing the starting equation as:

$$\left(\frac{d^2\xi^\mu}{ds^2}\right) = \left(\frac{\partial\xi^\mu}{\partial x^\nu}\right)\left(\frac{d^2x^\nu}{ds^2}\right) + \left(\frac{\partial^2\xi^\mu}{\partial x^\nu \partial x^\lambda}\right)\left(\frac{dx^\nu}{ds}\right)\left(\frac{dx^\lambda}{ds}\right) = 0 \tag{1.256}$$

and exploiting:

$$\delta^\tau_\nu \equiv \left(\frac{\partial\xi^\mu}{\partial x^\nu}\right)\left(\frac{\partial x^\tau}{\partial\xi^\mu}\right) \tag{1.257}$$

Multiplying the last but one equation by the second derivative on the right of the previous identity, one obtains in the end the so-called geodesic equation:

$$\left(\frac{d^2x^\tau}{ds^2}\right) + \Gamma^\tau_{\nu\lambda}\left(\frac{dx^\nu}{ds}\right)\left(\frac{dx^\lambda}{ds}\right) = 0 \tag{1.258}$$

The concept of geodesics is joined to that of parallel transport, related in turn to the derivative of a vector along a curve. As it stands, the previous equation may be rewritten by the covariant, "intrinsic" or "absolute" derivative ($\frac{\mathbf{d}}{\mathbf{d}s}$) along a curve $x^\mu = x^\mu(s)$:

$$\left(\frac{\mathbf{d}v^\tau}{\mathbf{d}s}\right) = \left(\frac{dv^\tau}{ds}\right) + \Gamma^\tau_{\nu\lambda}\left(\frac{dx^\lambda}{ds}\right)v^\nu \tag{1.259}$$

applied to $v^\tau$ ($\equiv\frac{dx^\tau}{ds}$). In a locally inertial frame, both contributions on the right will die off, hence:

$$\left(\frac{\mathbf{d}v^\tau}{\mathbf{d}s}\right) = 0 \tag{1.260}$$

in every coordinate system. This relation defines a vector by parallel transport, for all $s$ values given it at some starting $s_0$, and it follows that a geodesics is parallel-transporting its own tangent vector. It points in the same direction along all the curve, where $v^\nu$ keeps parallel to itself with constant magnitude. The rules of covariant differentiation can also be exploited to build any intrinsic tensor derivative, bearing in mind that not all tensors are generally tensor fields along a curve, i.e.:

$$\left(\frac{\mathbf{d}A^{\alpha\omega}}{\mathbf{d}s}\right) = A^{\alpha\omega}{}_{;\mu}\left(\frac{dx^\mu}{ds}\right) \tag{1.261}$$

In any case, a tensor can be defined by parallel transport by asking its covariant derivative to be zero along the path.

## 5.8 Extremal proper time

The law of motion of a freely falling particle descends equivalently from a variational principle, requiring that the proper time, elapsed when the body falls between two events, $P'$ and $P''$:

$$s = \int_{P'}^{P''} ds \tag{1.262}$$

be in extremum. We have already encountered a similar problem, when applied Hamilton's principle to get the free-particle equation of motion in relativistic mechanics. There, the action was chosen proportional to the proper time, and made stationary in the absence of force fields. Here, the same issue transforms into:

$$\delta s \propto \delta \int_{P'}^{P''} \ell_s\big(x^\alpha(u)\big)\, du = 0 \tag{1.263}$$

where $u$ parametrizes the path and:

$$\ell_s \equiv \left\{-\frac{1}{2} g_{\mu\nu}\left(\frac{dx^\mu}{du}\right)\left(\frac{dx^\nu}{du}\right)\right\}^{1/2} \tag{1.264}$$

We will seek the relationships making $s$ stationary under slight deformations of the original curves in a given metric (gravity) field, $x^\mu(u) \to x^\mu(u) + \delta x^\mu(u)$, with $\delta x^\mu(P') = \delta x^\mu(P'') = 0$ (rigid endpoints). At fixed $u$, tangent vector and metric tensor variations are $\delta(dx^\nu/du) = (d\delta x^\nu/du)$ and $\delta g_{\mu\nu} = g_{\mu\nu,\rho}\delta x^\rho(u)$, and the lapse of proper time is:

$$\delta s \propto -\delta \int_{P'}^{P''} \left[ g_{\mu\nu}\left(\frac{dx^\mu}{du}\right)\left(\frac{d\delta x^\nu}{du}\right) + \frac{1}{2} g_{\mu\nu,\omega}\left(\frac{dx^\mu}{du}\right)\left(\frac{dx^\nu}{du}\right)\delta x^\omega \right]\frac{du}{\ell_s} \tag{1.265}$$

Working out the former condition, and let the following "force terms" ($\mathrm{F}_\mu$) be defined via:

$$\ell_s \mathrm{F}_\mu(u) = \frac{d}{du}\left[\frac{g_{\mu\alpha}}{\ell_s}\left(\frac{dx^\alpha}{du}\right)\right] - \frac{1}{2\ell_s} g_{\nu\alpha,\mu}\left(\frac{dx^\nu}{du}\right)\left(\frac{dx^\alpha}{du}\right) \tag{1.266}$$

stationarity is tantamount in the end to requiring, for any variation $\delta x^\mu$ (and parametrization $ds = \sqrt{2\ell_s}\, du$):

$$\int_{P'}^{P''} \mathrm{F}_\mu(s)\delta x^\mu \, ds = 0 \tag{1.267}$$

Free and free-falling particles can both be expressed by a zero force condition, but here $\mathrm{F}_\mu = 0$ does not lead evidently to a zero acceleration. We are left in fact with:

$$g_{\mu\nu}\left(\frac{dx^\lambda}{ds}\right) + \frac{1}{2}(g_{\rho\mu,\nu} + g_{\rho\nu,\mu} - g_{\mu\nu,\rho})\left(\frac{dx^\mu}{ds}\right)\left(\frac{dx^\nu}{ds}\right) = 0 \tag{1.268}$$

from which, raising an index by $g^{\mu\lambda}$ and recalling the affine connection definition, the geodesic equation in a local Lorentz–Poincaré geometry is reobtained:

$$\left(\frac{d^2x^\tau}{ds^2}\right) + \Gamma^\tau_{\nu\lambda}\left(\frac{dx^\nu}{ds}\right)\left(\frac{dx^\lambda}{ds}\right) = 0 \tag{1.269}$$

The four vanishing force equations are sufficient, but not independent. Sliding events along a worldline, $\delta x^\mu = u'(u)(\frac{dx^\mu}{du})$, by an arbitrary "slide factor" ($u'$) will not change the proper time. Working on the starting functional, this leads to a geodesic-like identity $(\delta x^\mu/\delta s)\mathrm{F}_\mu = 0$, anticipating in a way Bianchi's identities in general relativity.

Finally, it will not probably strike us that this geometrical principle has a dynamic counterpart, corresponding to the Euler–Lagrange equations coming from Hamilton's principle rewritten as:

$$\int_{P'}^{P''} \frac{\delta\ell_f}{\ell_s} \, ds = 0 \tag{1.270}$$

i.e.:

$$\frac{d}{ds}\left(\frac{\partial\ell_f}{\partial\dot{x}^\mu}\right) = \left(\frac{\partial\ell_f}{\partial x^\mu}\right) \tag{1.271}$$

where $\ell_f \equiv -\frac{1}{2}g_{\mu\nu}\dot{x}^\mu\dot{x}^\nu$ is the simplest coordinate invariant extension of the kinetic energy, with velocities $\dot{x}^\alpha \equiv v^\alpha$, and $\ell_s = 1$ over the extremal path ($v^\mu v_\mu = -1$).

In summary, a body in free fall from one spacetime point to another will always move on extremal paths, named geodesics, reflecting the spacetime distorsion set by the field. Precisely, geodesics identify the (time-like) worldlines of extremal proper time, which are stationary with respect to any nearby variant of them. Remember the path length is invariant under any arbitrary reparametrization, $s \rightarrow s'(s)$. This property is not independent of the equation $x^\mu = x^\mu(s)$ but, for every solution, immediately indicates other equivalent representations, $x^\mu(s) \to x^\mu(s(s'))$. Unlike dynamical symmetries, which are customarily associated to more "physical" implications, the symmetry in question only produces a mathematical identity and is said to be non-dynamic.

Proper times are not universal, as Newton's absolute. Geodesics each possess an individual "clock," which can be either rescaled by an arbitrary origin shift or a constant scale factor ($s' = c_1 s + c_0$). Furthermore, they do not alter the nature of events. If a geodesic path is once null (i.e., $\|\mathbf{t}_u\| = 0$), time-like ($< 0$) or space-like ($>0$), it will be respectively null, time-like or space-like everywhere. However, evolving along geodesics is not a prerogative of every mechanical system. We may think, as counterexamples, of bodies endowed with internal motion, or of extended material structures.

## 5.9 Energy–momentum tensor and conservation law

Before entering Einstein's field equations, it is opportune to recall and dwell on the 2-rank energy–momentum (or stress-energy) tensor ($T^{\mu\nu}$), defining each current and density associated with the (total) energy–momentum 4-vector ($P^\mu$). As the name says, it brings all matter fields in a tensor formulation, and translates the scalar density field of Newton's mechanics. Intuitively, one might continue using 4-vectors, but this choice would lead in the end to a repulsive gravity. In the special theory, the behavior of energy and momentum is so ascribed to one index, and the (reciprocal of the) volume, which obeys the length contraction rule, to the second index.

We have already derived $T^{\mu\nu}$ in a general field theory, which the analytical and relativistic mechanics definitions follow from at once. Therefore, when $\mathsf{L} = \mathsf{L}(\mathbf{q}_n, \mathbf{q}_{n,k})$, it rewrites:

$$T^{s'}{}_{s} = \mathbf{q}_{n,s} \cdot \left( \frac{\partial \mathsf{L}}{\partial \mathbf{q}_{n,s'}} \right) - \delta^{s'}{}_{s} \mathsf{L} \tag{1.272}$$

while the Minkowskian expression (for $n = 1$) reads:

$$T^{\mu}{}_{\alpha} = q_{,\alpha} \left( \frac{\partial \mathsf{L}}{\partial q_{,\mu}} \right) - \eta^{\mu}{}_{\alpha} \mathsf{L} \tag{1.273}$$

In any of these cases, the formal resemblance to the energy function is evident, the expression $E = p\dot{q} - L$ being the direct analogue of $T^{00}$.

We have seen, if the angular momentum is conserved, that the symmetry property:

$$T^{\mu\alpha} = T^{\alpha\mu} \tag{1.274}$$

applies, and is preserved by any Lorentz–Poincaré transformation, i.e.,

$$T'^{\mu\nu} = \Lambda^{\mu}_{\alpha} \Lambda^{\nu}_{\beta} T^{\alpha\beta} \tag{1.275}$$

However, the most important equation it obeys is that of continuity, required for the sources as is $j^{\alpha}{}_{,\alpha} = 0$ in electromagnetism. In the language of the former section, it comes from the Gauss–Ostrogradsky theorem and the energy–momentum 4-vector conservation:

$$T^{\alpha\mu}{}_{,\mu} = \left(\frac{\delta P^{\alpha}}{\delta v}\right) = 0 \tag{1.276}$$

where the functional derivative can be seen as a density of force (here, for an isolated system). This yields a constraint for two of Noether's currents. One is formed by the energy density ($T^{00}$) and energy flux ($T^{0k}$):

$$T^{0\mu}{}_{,\mu} = 0 \tag{1.277}$$

and another by the momentum density ($T^{k0}$) and momentum flux ($T^{kk'}$):

$$T^{k\mu}{}_{,\mu} = 0 \tag{1.278}$$

The latter is named "stress tensor" ($\sigma^{kk'}$) and models the flow of all components ($k'$) in the unit time through the unit surface perpendicular to each coordinate ($k$). To fix the ideas, and limiting to fluid dynamics, the diagonal entries generally denote in ordinary relativity hydrostatic pressures (normal stresses, $\sigma_{kk} = p_{\mathrm{i}}$), and those off-diagonal are used to characterize the viscous behavior (shear stresses, $\sigma_{k \neq k'}$).

From a stationary reference frame, with $dv_{\rho} = |d\mathbf{r}|\delta^{0}_{\rho}$, total energy and total momentum would be measured as:

$$P^{0} = \int T^{00}\, d\mathbf{r} \tag{1.279}$$

$$P^{k} = \int T^{k0}\, d\mathbf{r} \tag{1.280}$$

where the former groups every energy source (i.e., the Hamiltonian) and should not be confused with a proper mass. This observer would thereby detect the other (12) values to be connected by the continuity equation, i.e.:

$$T^{00}{}_{,0} + \vec{\nabla} \cdot \mathbf{T}^{0} = 0 \tag{1.281}$$

$$T^{k0}{}_{,0} + \vec{\nabla} \cdot \mathbf{T}^{k} = 0 \tag{1.282}$$

and interpret $\mathbf{T}^{\mu} \equiv \{T^{\mu k}\}$ as the (Noether's) currents for the fluxes of the conserved energy (or mass, times $c^2$) and each momentum component ($k$).

The previous notions, though 4-dimensional, refer to a flat spacetime and their understanding is immediate. In the curved spacetime of general relativity, instead, energy and momentum interact to the field, reducing the intuition level by a certain extent. $P^{\alpha}$ will not be a constant of motion anymore, demanding another conservation (variational) principle. We will address it in the next paragraph, where the energy–momentum tensor defined in succession for a curved space is exploited. In a general-relativistic theory, matter action ($S_M$) and Lagrangian ($\mathsf{L}_M$) are introduced as:

$$S_M = \int_{1}^{2} \sqrt{-\mathrm{g}}\, \mathsf{L}_M(g_{\mu\nu}, g_{\mu\nu,\alpha})\, d^4x \tag{1.283}$$

the metric tensor components standing for the fields ($\boldsymbol{\phi}_n = \{g_{\mu\nu}\}$). Varying $g_{\mu\nu} \to \delta g_{\mu\nu}$ produces:

$$\delta S_M = \int_1^2 \left[\left(\frac{\partial \sqrt{-\mathrm{g}}\,\mathsf{L}_M}{\partial g^{\mu\nu}}\right) - \left(\frac{\partial \sqrt{-\mathrm{g}}\,\mathsf{L}_M}{\partial g^{\mu\nu,\alpha}}\right)_{,\alpha}\right]\delta g^{\mu\nu}\, d^4x + (\text{surface terms}) \tag{1.284}$$

and the coefficients proportional to $\delta g^{\mu\nu}$ define the energy–momentum tensor:

$$\frac{1}{2}\sqrt{-\mathrm{g}}\,T_{\alpha\beta} = \left(\frac{\delta \sqrt{-\mathrm{g}}\,\mathsf{L}_M}{\delta g^{\alpha\beta}}\right) \tag{1.285}$$

Furthermore, as $g^{\mu\nu}g_{\mu\nu} = \delta^{\nu}{}_{\nu}$ $(= 4)$:

$$\delta S_M = \frac{1}{2}\int_1^2 \sqrt{-\mathrm{g}}\,T_{\mu\nu}\delta g^{\mu\nu}\, d^4x = -\frac{1}{2}\int_1^2 \sqrt{-\mathrm{g}}\,T^{\mu\nu}\delta g_{\mu\nu}\, d^4x \tag{1.286}$$

but, since the metric variations are not fully independent, a stationary matter action does not necessarily imply a zero energy–momentum tensor. We will see how the previous expression relates to the field (the spacetime geometry) through another invariant functional. Now, from the equivalence principle, the new continuity equation is expected to be nothing but the covariant divergence condition:

$$T^{\alpha\beta}{}_{;\alpha} = 0 \tag{1.287}$$

The (symmetric) energy–momentum tensor, defined by the last but one equation, is conserved if and only if the matter action is a scalar. One needs to regard an infinitesimal coordinate transformation $x'^{\alpha} = x^{\alpha} + \kappa^{\alpha}$, upon which the metric variation (at first order in $\kappa^{\alpha}$) is:

$$\delta g_{\epsilon\nu} = -\left(\frac{\partial \kappa^{\mu}}{\partial x^{\epsilon}}\right)g_{\mu\nu} - \left(\frac{\partial \kappa^{\alpha}}{\partial x^{\nu}}\right)g_{\epsilon\alpha} - g_{\epsilon\nu,\mu}\kappa^{\mu} \tag{1.288}$$

or, after simple developments, $\delta g_{\epsilon\nu} = -\kappa_{\epsilon;\nu} - \kappa_{\nu;\epsilon}$. Using this expression and the symmetry of $T_{\mu\nu}$ lead to:

$$\delta S_M = \int_1^2 \sqrt{-\mathrm{g}}\,T^{\mu\nu}\kappa_{\mu;\nu}\, d^4x = \int_1^2 \sqrt{-\mathrm{g}}\left[\left(T^{\nu}{}_{\mu}\kappa^{\mu}\right)_{;\nu} - \kappa^{\mu}T^{\nu}{}_{\mu;\nu}\right] d^4x \tag{1.289}$$

where the first contribution on the right side can be rewritten as a hypersurface integral, dying off because $\kappa^{\alpha}$ vanish at the boundaries. In this way, if $S_M$ is a scalar:

$$\int_1^2 \sqrt{-\mathrm{g}}\,\kappa^{\mu}T^{\nu}{}_{\mu;\nu}\, d^4x = -\delta S_M = 0 \tag{1.290}$$

the arbitrariness of $\kappa^{\alpha}$ implies that the covariant divergence of the energy–momentum tensor does vanish as well. We take this opportunity to note that the equations:

$$\kappa_{\epsilon;\nu} + \kappa_{\nu;\epsilon} = 0 \tag{1.291}$$

define the infinitesimal coordinate transformations that, at any fixed point, leave the metric tensor "form-invariant," $g_{\mu\alpha}(x^{\nu}) = g'_{\mu\alpha}(x^{\nu})$, or:

$$g_{\mu\alpha}(x^{\nu}) = \left(\frac{\partial x'^{\epsilon}}{\partial x^{\mu}}\right)\left(\frac{\partial x'^{\rho}}{\partial x^{\alpha}}\right) g_{\epsilon\rho}(x'^{\nu}) \tag{1.292}$$

This vector field produces a flow that is a continuous "isometry," discovered by Wilhelm K.J. Killing (1892) in a work on the dynamics of a $n$-dimensional manifold (governed by a free Lagrangian). "Killing's fields" are very useful for classifying metric spaces. For example, homogeneity requires that Killing's vectors can take at any point all possible values, and when $\kappa_{\nu}(P) = 0$ and $\kappa_{\nu;\epsilon}(P)$ can take all possible values, the space is isotropic at $P$. Isotropy at any $P$ then implies homogeneity.

Finally, to treat various situations of interest (point particle systems, electromagnetic fields, and so on), a number of (inequivalent) energy–momentum tensor expressions are available. The simplest definition is for a $n$-particle system with 4-momenta $p_n^{\mu}$:

$$\sqrt{-\mathrm{g}}\, T^{\mu\nu} = \sum_{n} t_n^{\mu\nu} \tag{1.293}$$

and single particle contribution:

$$t_n^{\mu\nu} = \int p_n^{\mu}\left(\frac{dx_n^{\nu}}{ds}\right)\delta^4\left[x - x_n(s)\right] ds = p_n^{\mu}\left(\frac{dx_n^{\nu}}{dt}\right)\delta^3\left[\mathbf{x} - \mathbf{x}_n(t)\right] \tag{1.294}$$

where $\delta^d$ denotes a Dirac's delta distribution in $d$ dimensions and $x_k^0 \equiv t$.

Another simple expression is that employed in ideal (or perfect) fluids, without viscosity and heat conduction:

$$T_{\mathrm{i}}^{\alpha\beta} = p g^{\alpha\beta} + (p + \varrho) v^{\alpha} v^{\beta} \tag{1.295}$$

where $v^{\mu}$ $(=\frac{dx^{\mu}}{ds})$ is still the local value of the $\mu$th 4-velocity component in the fluid element, with $-g_{\alpha\beta} v^{\alpha} v^{\beta} = 1$. Hydrostatic pressure ($p_{\mathrm{i}}$) and energy density ($\varrho$) are measured from a locally inertial frame that, at the instant of measurement, happens to be moving with the fluid (or "comoving") at given relative velocity ($\mathbf{v}'$). In the absence of gravity the metric again becomes Minkowskian, $g^{\alpha\beta} = \eta^{\alpha\beta}$, while the 0-velocity component equals Lorentz's factor, $v^0 = \gamma_L$, and $\mathbf{v} = v^0\mathbf{v}'$. Thus, when the fluid is at rest at some position and time, $v^{\alpha}v^{\beta} = \mathrm{diag}(1, \mathbf{0})$, the energy–momentum tensor assumes the (diagonal) form which is typical of spherical symmetry:

$$T_{\mathrm{i}}^{\alpha\beta} = \mathrm{diag}(\varrho, p\mathbf{I}) \tag{1.296}$$

It can be used to describe (celestial) bodies in hydrostatic equilibrium, without dissipative phenomena. In non-ideal (or imperfect) viscous fluids, it is amended instead by an extra-term ($\tau^{\alpha\beta}$):

$$T^{\alpha\beta} = T_{\mathrm{i}}^{\alpha\beta} + \tau^{\alpha\beta} \tag{1.297}$$

and a commonly adopted expression is:

$$\tau^{\alpha\beta} = -\zeta_B \theta_V h^{\alpha\beta} - \eta_S h^{\alpha\mu} h^{\kappa\beta} \sigma_{\mu\kappa} \tag{1.298}$$

where $h_{\alpha\beta} = g_{\alpha\beta} + v_\alpha v_\beta$ is the projector on the rest frame of the observer comoving with the fluid, $\theta_V$ ($=v^\rho_{;\rho}$) is the volume expansion, $\zeta_B$ and $\eta_S$ are respectively the bulk and shear viscosity coefficients, and the (shear) stress tensor is:

$$\sigma_{\alpha\beta} = v_{\alpha;\beta} + v_{\beta;\alpha} - \frac{2}{3}\theta_L g_{\alpha\beta} \tag{1.299}$$

Remember that the term proportional to $\zeta_B$ quantifies the internal friction accompanied by a volume change, while the other (in $\eta_S$) expresses the effect of changing shape at constant volume.

## 5.10 Einstein's field equations

Up to now, only the effect of gravity on matter has been considered (e.g., geodesics). In this paragraph, matter will be tackled instead as an active gravity source. Intuitively, just as Poisson's equation extends Laplace's, for a field in vacuum ($\nabla^2\phi = 0$), and accounts for Newton's gravity source as:

$$\nabla^2\phi = 4\pi G\varrho \tag{1.300}$$

a similar generalization is equally expected in the Einsteinian view. Letting $G_{\mu\nu} = 0$ be the gravity equations in vacuum, this extension should be written as:

$$G_{\mu\nu} = \text{something related to matter} \tag{1.301}$$

The equivalence principle does not indicate the relations that the metric tensor must comply with, and Einstein realized they ought to be postulated as well. To go ahead, he made use of his extraordinary scientific imagination and stated the famous relationship, curvature $\sim$ matter. This guided him to deriving the set of differential equations bringing his name, in which an overall geometry contribution connects the energy–momentum tensor.

In short, there are a couple of main approaches to them. In a first, more physical, one avails of the properties of $T_{\mu\nu}$ (symmetry and conservation) and the equivalence principle in the stationary and weak field limit. In this case, the time-time metric component for a non-relativistic matter distribution is $g_{00} \simeq -(1 + 2\phi)$, while $T_{00} \simeq \varrho$ and:

$$\nabla^2 g_{00} \simeq -8\pi G T_{00} \tag{1.302}$$

recovers Poisson's equation for Newton's gravity. It may well seem too simple but, under the equivalence principle, a comparison between the last and the last but two equations does suffice to write straight off the following law, valid for fields of arbitrary intensity:

$$G_{\mu\nu} = -8\pi G T_{\mu\nu} \tag{1.303}$$

The quantity on the left generally consists of a linear combination of the metric tensor and its derivatives up to the second order. However, some of the ambiguity on $G_{\mu\nu}$ can be removed by supposing it to be expandible into a sum of products of $g_{\mu\nu}$ derivatives up to a total number of $N_d = 2$ differentiations. By this assumption, it is meant that all possible choices are restricted to second derivatives and products of first derivatives. Because $G_{\mu\nu}$ is set dimensionally to a second derivative, every term which gets negligible for large ($N_d > 2$) or small ($< 2$) enough spacetime scales will be consequently ignored. This corresponds to a gravity field propagating uniformely in scale, "stabilizing" the sensitivity of the field equations to it.

A tensor field with $N_d = 2$ is generally built by contracting the Riemann–Christoffel tensor, that is, in terms of Ricci's and the curvature scalar:

$$G_{\mu\nu} = \alpha R_{\mu\nu} + \beta g_{\mu\nu} R \tag{1.304}$$

with $\alpha$, $\beta$ constant coefficients. Bianchi's identities, $G^{\mu}_{\mu;\nu} = (\beta + \frac{\alpha}{2}) R_{;\nu}$, and the weak and stationary approximation, $G_{00} \simeq \alpha \nabla^2 g_{00}$, imply $\beta = -\frac{\alpha}{2}$ and $\alpha = 1$, thence Einstein's equations take their definite form:

$$R_{\mu\nu} - \frac{g_{\mu\nu} R}{2} = -8\pi G T_{\mu\nu} \tag{1.305}$$

whereupon, taking the trace $8\pi G T^{\rho}{}_{\rho} = R$:

$$R_{\mu\nu} = -8\pi G \left( T_{\mu\nu} - \frac{g_{\mu\nu}}{2} T^{\rho}{}_{\rho} \right) \tag{1.306}$$

Observe the mass and momentum distributions (on the right sides) related to the geometrical features (left sides) of the spacetime where they lie. It is not a coincidence that, contracting twice Bianchi's identities, Einstein's tensor divergence turns out to inevitably die off:

$$0 = R_{;\alpha} - R^{\mu}_{\alpha;\mu} - R^{\nu}_{\alpha;\nu} = \left( g^{\mu}{}_{\alpha} R - 2R^{\mu}{}_{\alpha} \right)_{;\mu} = 2G^{\mu}_{\alpha;\mu} \tag{1.307}$$

concording to the divergence condition expected for the energy–momentum tensor. This sound result, spelling out the conservation rules of physics into a closure relation of Riemannian geometry, cannot pass unnoticed.

In a different, more axiomatic derivation, the field equations stem from a principle of stationary action, accounting for the balance of two, matter ($S_M$) and gravity ($S_G$), contributions:

$$S = S_M + S_G \tag{1.308}$$

Again, the metric tensor (the field) is made to undergo an arbitrary infinitesimal variation, $g_{\mu\nu} \to g_{\mu\nu} + \delta g_{\mu\nu}$, with $\delta g_{\mu\nu}(|x^{\tau}| \to \infty) = 0$, and:

$$\delta S \equiv S(g_{\mu\nu} + \delta g_{\mu\nu}) - S(g_{\mu\nu}) = 0 \tag{1.309}$$

independently of coordinate transformations, as the principle of general covariance requires. Technically, it is said that Einstein's equations come from the "diffeomorphism invariance" (or diffeomorphism covariance) of the action. To proceed, the (total) Lagrangian density is written as a sum of matter and gravity terms:

$$\delta S = \delta S_M + \delta S_G = \int \delta\left(\sqrt{-\mathrm{g}}\,\mathsf{L}_M\right) d^4x + \int \delta \mathsf{L}_G \, d^4x \tag{1.310}$$

where the coefficient in the former was seen to define the energy–momentum tensor, and the geometry contribution is contained in the latter, pointing out the Einstein–Hilbert action ($S_G$):

$$k\mathsf{L}_G \, d^4x = \frac{1}{2}\sqrt{-\mathrm{g}}\,R \tag{1.311}$$

Apart from the constant $k$ ($=8\pi G/c^4$, in standard units), introduced to recover Newton's theory in the non-relativistic limit, it is the integral of the curvature scalar density, invariant over any 4-dimensional region. Thus, we consider the sum of three infinitesimal changes in the adjustable $\delta g^{\mu\nu}$:

$$\delta\left(\sqrt{-\mathrm{g}}\,R\right) = R\delta\sqrt{-\mathrm{g}} + \sqrt{-\mathrm{g}}\,\delta\left(g^{\mu\nu}R_{\mu\nu}\right) \tag{1.312}$$

and ought to calculate $\delta\sqrt{-\mathrm{g}}$ and $\delta R_{\mu\nu}$. From $\delta(g^{\mu\nu}g_{\mu\nu}) = 0$, the metric tensor variation rules are:

$$g^{\mu\nu}\delta g_{\mu\nu} = -g_{\mu\nu}\delta g^{\mu\nu} = \delta \ln(-\mathrm{g}) \tag{1.313}$$

and:

$$\delta g^{\mu\alpha} = -g^{\mu\omega}g^{\alpha\rho}\delta g_{\omega\rho} \tag{1.314}$$

while that of the Ricci's tensor is computed by an elegant method thanks to Attilio Palatini (1919). He realized that, together with the ten metric components, the variational problem could more coveniently involve Christoffel's forty symbols for the Levi-Civita connection, whose differences $\delta\Gamma^{\iota}_{\mu\alpha}$ build in turn a tensor. Armed with the definition of locally geodesic frame, in which Christoffel's symbols are vanishing (but their variations are not), it may be deduced that every observer will detect:

$$\delta R_{\mu\nu} = \left(\delta\Gamma^{\iota}_{\mu\iota}\right)_{;\nu} - \left(\delta\Gamma^{\iota}_{\mu\nu}\right)_{;\iota} \tag{1.315}$$

and the following quantity:

$$\begin{aligned} g^{\mu\nu}\delta R_{\mu\nu} &= \left(g^{\mu\nu}\delta\Gamma^{\iota}_{\mu\iota}\right)_{;\nu} - \left(g^{\mu\nu}\delta\Gamma^{\iota}_{\mu\nu}\right)_{;\iota} \\ &= \frac{1}{\sqrt{-\mathrm{g}}}\left[\left(\sqrt{-\mathrm{g}}\,g^{\mu\nu}\Gamma^{\iota}_{\mu\iota}\right)_{,\nu} - \left(\sqrt{-\mathrm{g}}\,g^{\mu\nu}\Gamma^{\iota}_{\mu\nu}\right)_{,\iota}\right] \end{aligned} \tag{1.316}$$

is a covariant divergence that, from the Gauss-Ostrogradsky theorem in covariant form, disappears after integrating over the whole domain:

$$\int \sqrt{-\mathrm{g}}\,g^{\mu\nu}\delta R_{\mu\nu}\,d^4x = 0 \tag{1.317}$$

We are so left with the two contributions in Einstein's tensor density:

$$\delta \mathsf{L}_G = -\frac{1}{2}\sqrt{-\mathrm{g}}\, g^{\mu\nu} R \delta g_{\mu\nu} + \sqrt{-\mathrm{g}}\, R^{\mu\nu} \delta g_{\mu\nu} \tag{1.318}$$

obeying, for any variation:

$$\int \sqrt{-\mathrm{g}} \left( R^{\mu\nu} - \frac{g_{\mu\nu} R}{2} \right) \delta g_{\mu\nu}\, d^4x = -k \int T^{\mu\nu} \sqrt{-\mathrm{g}}\, \delta g_{\mu\nu}\, d^4x \tag{1.319}$$

and bringing again to the (contravariant) field equations. We have seen this variational criterion is valid upon changing the metric tensor and its first derivatives, vanishing on the boundary of the integration domain. More general variations are certainly possible, but would require additional terms, such as further surface integrals or contributions coming from smaller spacetime scales. This would be accomplished, for instance, by adding to the Einstein–Hilbert action other terms with higher powers of the curvature scalar ($R^k, k \geqslant 2$). Nowadays, the validity domain of Einstein's equations seems to cover spacetime scales not exceeding the one of the solar system, beyond which general relativity could no longer continue to hold.

General relativity has raised the complexity of mechanics. Newton's theory deals with interactions as functions of simultaneous particle locations, whereas in special relativity they depend on separations among events. In this context, interactions are direct counterparts of geometrical features, but the functional dependence of the metric tensor on particle events is normally unknown. Another point to realize is the non-linearity of Einstein's equations, arising from the (gravity) field self-interaction. If they supply explicit solutions for rather simple (or simplified) systems, only a handful of them actually are physically meaningful. To work out more realistic cases, approximation and numerical techniques are normally inescapable. An often used analytical method is to start from an exactly solvable lowest-order background metric (e.g., Minkowskian), and calculate the perturbations characterizing the real model. In any case, this complexity limited over the years the theory verification to weakly interacting systems, strong fields still providing the matter for intriguing speculations.

Field equations should clearly not to be in conflict with the postulate of geodesic motion, but some authors noticed they would not be fully independent of it. Isolating a test particle from its mass distribution is a fictitious operation, and deducing this postulate from Einstein's equations may be expectable, instead of imposing it axiomatically. This was the line followed by Hermann K.H. Weyl (1921) and by Einstein himself, in cooperation with Jacob Grommer (1927), noting that the field equations would fix certain limitations on motion. In orher words, metric singularities would not be arbitrary, their form being set by Einstein's equations themselves. A central reason of this clearly lies in their non-linearity. In a linear theory, one can find further solutions by superimposing one solution with point singularities. Here, the influences of distinct bodies cannot be summed up to get a resultant effect (as, instead, in classical gravity). Any field contains energy and is part of its own source, thus it should be treated as an inseparable whole.

To understand the separate roles of space and time, it can be helpful to resort to the seminal works by John A. Wheeler, Richard L. Arnowitt, Stanley Deser and

Charles W. Misner (1957–1963). Wheeler baptized it "geometrodynamics," to indicate that the Einsteinian picture of gravity arises in a dynamic framework of spatial metrics, as well elucidated by the Arnowitt–Deser–Misner initial value reformulation of general relativity. In classical mechanics, when the boundary conditions (positions and velocities) are known, the laws of motion determine each particle trajectory. Here, a "foliation" of spatial surfaces, catalogued by a continuous time, is slicing up spacetime. We have, rephrasing it better, a Hamiltonian dynamics, evolving by the field equation constrained to an initial space-like hypersurface, with given (intrinsic and extrinsic) geometries. Curvatures cannot be given independently but, closely to the electromagnetism equations $\vec{\nabla} \cdot \mathbf{E} = 0$ and $\vec{\nabla} \cdot \mathbf{B} = 0$, must solve Cauchy's initial value problem for Einstein's equations, as in the original formulation due to Yvonne Foures-Bruhat (1952) and André Lichnerowicz (1967). The evolution of the hypersurface deformation gives rise to a "geometrodynamic history," within which the spatial geometry acts as a time information carrier. The cost to be paid for it is the indistinguishability of time instants from space points, however, the Arnowitt–Deser–Misner approach has the advantage of affording a more intuitively understandable level.

As a final aside, it is worth recalling that Einstein, in trying to account for the gauge invariance, lost some time around 1913. He thought that the field equations had to set the metric unambiguously and, when discovered it was not true, inferred (erroneously) that his principle of general covariance was to be restricted. Both $G_{\mu\nu}$ and $g_{\mu\nu}$ possess in fact 10 independent components, but the conservation laws (or Bianchi's identities) reduce their number to 6, leaving us with 4 degrees of freedom. Einstein, actually, didn't realize that the metric tensor components can be determined only up to a change of coordinate system (acting similarly to a gauge transformation), and the energy–momentum conservation is just a consequence of this. Precisely, if $g_{\mu\nu}(x^\alpha)$ is a solution of the field equations, so will be $g'_{\mu\nu}(x'^\omega)$, with $x'^\omega = x'^\omega(x^\alpha)$ forming a system of 4 arbitrary functions. He discovered his misinterpretation, reaching his celebrated equations a few years later. Some forty years later, Ryoyu Utiyama (1956) proved that general relativity may alternatively be reformulated by bringing the global coordinate transformations of the special theory to be local. Gravity would come thereafter as a field "compensating" the local invariance requirement, as in the electromagnetic gauge theory.

## 6. PARTICULAR SOLUTIONS AND REFERENCE FRAMES

### 6.1 Weak and stationary field approximation

To check if the equivalence principle extends Newton's second law consistently, consider the geodesic equations for (i) a slow particle in (ii) a weak and (iii) stationary field. The last two points require respectively that (ii) the metric is nearly Minkowskian, $g_{\mu\nu} \simeq \eta_{\mu\nu} + h_{\mu\nu}$ ($|h_{\mu\nu}| \ll 1$), and (iii) the time derivatives of each metric component are vanishing:

$$\Gamma^{\omega}_{00} = -\frac{1}{2} g^{\omega\rho} g_{00,\rho} = -\frac{1}{2} \eta^{\omega\rho} h_{00,\rho} + O\big(|h_{\mu\nu}|^2\big) \tag{1.320}$$

Since the particle slowness implies $|\frac{d\mathbf{x}}{ds}| \ll |\frac{dt}{ds}|$, or:

$$\left(\frac{d^2 x^\tau}{ds^2}\right) + \Gamma^{\tau}_{00} \left(\frac{dt}{ds}\right)^2 = 0 \tag{1.321}$$

the geodesic equation reduces to:

$$\begin{gathered} \left(\frac{d^2 \mathbf{x}}{ds^2}\right) = \frac{1}{2} \left(\frac{dt}{ds}\right)^2 \vec{\nabla} h_{00} \\ \left(\frac{d^2 t}{ds^2}\right) = 0 \end{gathered} \tag{1.322}$$

or:

$$\left(\frac{d^2 \mathbf{x}}{ds^2}\right) = \frac{1}{2} \vec{\nabla} h_{00} \tag{1.323}$$

This relation equals the Newtonian limit upon choosing $\frac{1}{2}\vec{\nabla} h_{00} = -\vec{\nabla}\phi$, where $\phi$ is Newton's potential, implying $h_{00} = -2\phi$, unless an additive constant reflecting the boundary condition at large distances. It will clearly be vanishing with $\frac{1}{r}$ ($\phi = -\frac{GM}{r}$), guaranteeing that the reference frame is nearly Cartesian at infinity ($-g_{00} = 1 + 2\phi$). Correspondingly, for non-relativistic matter, Einstein's equations become:

$$\vec{\nabla}^2 g_{00} = -8\pi G T_{00} \tag{1.324}$$

and, let $T_{00} \simeq \varrho$, Newton's potential is set by Poisson's equation:

$$\vec{\nabla}^2 \phi(\mathbf{r}) = 8\pi G \varrho \tag{1.325}$$

Newtonian gravity comes from the Einsteinian theory as a singular limit, $c \to \infty$. It may be thought of as the opening of light cones into space-like hypersurfaces at a simultanous (absolute) time, where actions at a distance may take place.

There is another (singular) limit, called "ultrarelativistic," otherwise said of ultralocal approximation, where $c \to 0$ and (every velocity) $v \to c$. In this case, light cones shrink and spacetime reduces to a null hypersurface, embedding a 5-dimensional space. The resulting formalism is rather simple and closer to the Newtonian. The elliptic differential equations for Newton's potential, or those hyperbolic of general relativity, are replaced in the ultrarelativistic limit by ordinary differential equations. Regarding causality, the interaction among spatially separated events vanish and, aside from objects moving faster than light ("tachyions"), no true motion can actually occur. Inspired by Louis Carroll's tale, "Alice in Wonderland," this picture is sometimes referred to as "Carroll's causality." Galilei's group, extended in special relativity to Lorentz–Poincaré's, leaves thus the place to Carroll's group, first discussed by Jean M. Lévy–Leblond (1965).

## 6.2 Riemann's normal and harmonic coordinates

The choice of a reference frame in general relativity has some analogy with that of a gauge in electrodynamics. One of the simplest possible is the normal coordinate system, centered at some origin O:

$$x^{\alpha} g_{\alpha\mu}\left(x^{\rho}\right) = x^{\alpha} \hat{g}_{\alpha\mu} \tag{1.326}$$

with the condition of being locally inertial:

$$\hat{g}_{\alpha\mu} \equiv g_{\alpha\mu}(\mathrm{O}) = \eta_{\alpha\mu} \tag{1.327}$$

In this setting, the coefficients in Taylor's expansion of the metric components within $\delta x^{\nu} \equiv x^{\nu} - 0$:

$$\begin{aligned} g_{\alpha\mu} = \eta_{\alpha\mu} &+ \hat{g}_{\alpha\mu,\kappa}\delta x^{\kappa} + \frac{1}{2!}\hat{g}_{\alpha\mu,\gamma\kappa}\delta x^{\kappa}\delta x^{\gamma} \\ &+ \frac{1}{3!}\hat{g}_{\alpha\mu,\varepsilon\gamma\kappa}\delta x^{\kappa}\delta x^{\gamma}\delta x^{\varepsilon} + \cdots \end{aligned} \tag{1.328}$$

are expressible by the curvature tensor centered at the origin. Evidently, the first-order term $\hat{g}_{\alpha\mu,\kappa} = 0$. Working on the affine connection then gives:

$$\hat{\Gamma}^{\mu}_{\alpha\alpha',\rho} = -\frac{1}{3}\left(\hat{R}^{\mu}{}_{\alpha\alpha',\rho} + \hat{R}^{\mu}{}_{\alpha'\alpha,\rho}\right) \tag{1.329}$$

implying:

$$\hat{g}_{\alpha\mu,\gamma\kappa}\delta x^{\kappa}\delta x^{\gamma} = -\frac{2}{3}\hat{R}_{\alpha\kappa\mu\gamma}\delta x^{\kappa}\delta x^{\gamma} \tag{1.330}$$

while the third-order contribution turns out to be:

$$\hat{g}_{\alpha\mu,\varepsilon\gamma\kappa}\delta x^{\kappa}\delta x^{\gamma}\delta x^{\varepsilon} = -\hat{R}_{\alpha\kappa\mu\gamma;\varepsilon}\delta x^{\kappa}\delta x^{\gamma}\delta x^{\varepsilon} \tag{1.331}$$

Normal coordinates parametrize geodesics by straight lines passing through O, i.e.:

$$\Gamma^{\mu}_{\alpha\alpha'}x^{\alpha}x^{\alpha'} = 0 \tag{1.332}$$

and fix the reference frame up to a rigid rotation.

Another notable representation is given by asking coordinates to be "harmonic," i.e.:

$$g^{\alpha\mu}\Gamma^{\rho}_{\alpha\mu} = -\frac{1}{\sqrt{-\mathrm{g}}}\left(\sqrt{-\mathrm{g}}\,g^{\rho\omega}\right)_{,\omega} = 0 \tag{1.333}$$

The condition of harmonicity normally defines the vanishing of the covariant d'Alembertian, written in full as:

$$\square = g^{\alpha\mu}\left(\frac{\partial}{\partial x^{\alpha} x^{\mu}} - \Gamma^{\rho}_{\alpha\mu}\frac{\partial}{\partial x^{\rho}}\right) \tag{1.334}$$

in fact, from the last but one equation, coordinates are themselves harmonic functions, generalizing the harmonic equation ($\vec{\nabla}^2\mathbf{x} = 0$) to:

$$\square\, x^{\rho} = 0 \tag{1.335}$$

## 6.3 General static isotropic metric

The metric tensor reflects the symmetry properties implied by the field and can sometimes be simplified to a remarkable extent. This is the general "static isotropic" case, whenever it is possible to find a nearly-Minkowskian system in which the invariant interval is not dependent on time (staticity), but on space, so to be equal in every point equidistant from that taken as the center (isotropy). The most general time-independent and spherically symmetric expression will therefore comprise four metric components, reading:

$$\begin{aligned} ds^2 = B(r')\,dt'^2 &- 2E(r)\,dt'(\mathbf{x}'\cdot d\mathbf{x}') \\ &- D(r')(\mathbf{x}'\cdot d\mathbf{x}')^2 - C(r')\,d\mathbf{x}'^2 \end{aligned} \tag{1.336}$$

which can be written conveniently in diagonal form and spherical polar coordinates. Time can be reset by a new coordinate:

$$t = t' + \tau(r'), \qquad B(r')\,d\tau = -r'E(r')\,dr' \tag{1.337}$$

bringing the former representation into the so-called "standard form":

$$ds^2 = b(r)\,dt^2 - a(r)\,dr^2 - r^2\,d\Omega^2 \tag{1.338}$$

where $d\Omega^2 = d\theta^2 + \sin^2\theta\,d\varphi^2$ denotes the standard element of solid angle, while $r^2 = r'^2 C(r')$, $b(r) \equiv B(r')$, $a(r) \equiv (1+\frac{G}{C})(1+\frac{1}{2}\frac{d\ln C}{d\ln r'})^{-2}$ and $G(r') = r'^2 D + (\frac{d\tau}{dr'})^2 B$.

In the "isotropic form," instead, this metric is represented by:

$$ds^2 = \overline{B}(\bar{r})\,dt^2 - \overline{A}(\bar{r})\,dl^2(\bar{r},\theta,\varphi) \tag{1.339}$$

where $dl = \sqrt{d\mathbf{l}^2}$ is the Euclidean length element in three dimensions. Here, $\ln\bar{r} = \int\sqrt{1+G(r')/C(r')}\,d\ln r'$, $\overline{B}(\bar{r}) \equiv B(r')$, and $\overline{A}(\bar{r}) \equiv (r/\bar{r})^2$.

Finally, when coordinates are harmonic, the proper time can be rewritten as:

$$ds^2 = b(r)\,dt^2 - \left(\frac{a(r)}{R'^2R^2} - \frac{r}{R^4}\right)\mathbf{x}\cdot d\mathbf{x} - \frac{r^2}{R^2}\,d\mathbf{x}^2 \tag{1.340}$$

where the function $R = R(r)$ replaces the radial position in the harmonic coordinates, prime denoting a derivative with respect to $r$. Appendix A reports the main quantities of interest for a general static isotropic metric in standard form (affine connection, Ricci's tensor, curvature scalar).

## 6.4 Geodesic light deflection and parametrized metric

One of the simplest, yet remarkable, applications of the former metric is calculating the deflection angle of light rays, bending near a spherically symmetric (large) mass source (i.e., the sun). We start thus from the geodesic equation in a static isotropic field, generally parametrized by $u = u(s)$:

$$\left(\frac{d^2x^\alpha}{du^2}\right) + \Gamma^\alpha_{\nu\lambda}\left(\frac{dx^\nu}{du}\right)\left(\frac{dx^\lambda}{du}\right) = 0 \tag{1.341}$$

to be solved in each $x^\mu$. Working with a metric in standard form, the conditions to be satisfied are:

$$
\begin{aligned}
0 &= \frac{d^2t}{du^2} + \frac{d\ln b}{dr}\frac{dt}{du}\frac{dr}{du} \\
0 &= \frac{d^2r}{du^2} + \frac{1}{2a(r)}\frac{db}{dr}\left(\frac{dt}{du}\right)^2 + \frac{1}{2}\frac{d\ln a}{dr}\left(\frac{dr}{du}\right)^2 \\
&\quad - \frac{r}{a(r)}\left(\frac{d\theta}{du}\right)^2 - \frac{r\sin^2\theta}{a(r)}\left(\frac{d\varphi}{du}\right)^2 \\
0 &= \frac{d^2\theta}{du^2} + \frac{2}{r}\frac{d\theta}{du}\frac{dr}{du} - \frac{\sin 2\theta}{2}\left(\frac{d\varphi}{du}\right)^2 \\
0 &= \frac{d^2\varphi}{du^2} + \frac{2}{r}\frac{d\varphi}{du}\frac{dr}{du} + 2\cot\theta\frac{d\varphi}{du}\frac{d\theta}{du}
\end{aligned}
\tag{1.342}
$$

As in classical mechanics, a convenient way to proceed is to seek the integrals of motion. Isotropy implies that limiting the description to the equatorial plane is sufficient, $\theta = \frac{\pi}{2}$. This makes the condition for $\theta$ identically satisfied, and those for $t$, $\varphi$ reducing to:

$$\frac{d}{du}\left[\ln\left(r^2\frac{d\varphi}{du}\right)\right] = \frac{d}{du}\left[\ln\left(b(r)\frac{dt}{du}\right)\right] = 0 \tag{1.343}$$

The second equality to zero suggests the reparametrization:

$$\left(\frac{du}{dt}\right) = b(r) \tag{1.344}$$

while the first leads to another integral of motion:

$$r^2\left(\frac{d\varphi}{du}\right) = L_\varphi \tag{1.345}$$

$L_\varphi$ being an angular momentum density (i.e., per unit mass). These conditions, employed in the equation for $r$, yield after some manipulations:

$$a(r)\left(\frac{dr}{d\sigma}\right)^2 - \frac{1}{b(r)} + \left(\frac{L_\varphi}{r}\right)^2 = -E \tag{1.346}$$

where $\sqrt{E} = \frac{d\sigma}{du} \geqslant 0$ is the square root of a constant (dimensionless) energy per unit mass (equal to zero for $v = c$).

Now, instead of focusing on the time history of orbits (the explicit trajectory of motion), we dwell on their shape. To describe it, one has to get rid of the temporal coordinate, and express $\varphi = \varphi(r)$. This can be done by eliminating $u$ from the last two equations, yielding:

$$\frac{a(r)}{r^4}\left(\frac{dr}{d\varphi}\right)^2 - \frac{1}{b(r)L_\varphi^2} + r^{-2} = -\frac{E}{L_\varphi^2} \tag{1.347}$$

from which, a quadrature implies:

$$\varphi = \pm L_\varphi \int \sqrt{\frac{a(r')}{r'^2/b(r') - Er'^2 - L_\varphi^2}}\, d\ln r' \tag{1.348}$$

The last relation can be applied to light rays in proximity of a planet mass, deflecting by the angle $\Delta\varphi$:

$$\frac{\Delta\varphi}{2} = \left|\varphi(r_m) - \varphi_\infty\right| - \frac{\pi}{2} \tag{1.349}$$

where $\varphi_\infty$ is the incident direction (at infinity, where $a = b = 1$) and $r_m$ is the distance of closest approach to the mass:

$$\left(\frac{dr}{d\varphi}\right)_{r_m} = 0 \tag{1.350}$$

Light rays are manifestly characterized by $E = 0$, thus the previous condition returns:

$$L_\varphi = \frac{r_m}{\sqrt{b(r_m)}} \tag{1.351}$$

therefore:

$$\Delta\varphi(r) = \int_r^\infty \sqrt{\frac{a(r')}{B(r')}}\, d\ln r' \tag{1.352}$$

with $B(r) \equiv \frac{r^2}{r_m^2}\frac{b(r_m)}{b(r)} - 1$. If spacetime were everywhere Minkowskian (with no mass, $a = b = 1$), light would proceed unperturbed ($\Delta\varphi = 0$). For arbitrary fields, working out this integral equation explicitly can be a tough task. Nevertheless, for fields which are weak enough, it is convenient to employ a numerical solution, derived by expanding each component in power series of the (small) gravitational parameter, $\kappa_M(r)$. This "parametrized post-Newtonian" metric is normally acknowledged to Howard P. Robertson and Eddington (1923), who availed of it in the epoch of the classical general relativity tests, and in standard form may be written as:

$$\begin{aligned} ds^2 = {} & \left[1 - 2\alpha\kappa_M + 2(\beta - \alpha\lambda)\kappa_G^2 + \cdots\right] dt^2 \\ & - \left[1 + 2\lambda\kappa_M + \cdots\right] d\mathbf{l}^2 \end{aligned} \tag{1.353}$$

The values of $\alpha$, $\beta$ and $\lambda$ catalogue any possible theory and can be extrapolated from the experiments. Recovering Newton's gravity requires $\alpha = 1$, from which clock frequency-shift experiments turned out to be well posed for any metric theory (see the Principle of Equivalence). Perihelion precessions generally depend on $\lambda$ and $\beta$, while light deflection is sensitive to $\lambda$. Since general relativity is shown to correspond to $\alpha = \beta = \lambda = 1$, and the leading order expansion in $\kappa_M(r_m)$ gives:

$$\frac{\Delta\varphi}{2} = (1 + \lambda)\kappa_M(r_m) + \mathrm{O}\left(\kappa_G^2\right) \tag{1.354}$$

the light deflection angle in Einstein's prediction reads $\Delta\varphi = 4\kappa_M(r_m)$. For light grazing the sun, this calculation returns $\kappa_M \simeq 0.44''$ and $\Delta\varphi \simeq 1.75''$.

## 6.5 Schwarzschild's metric

The principles of classical mechanics often enable us to get meaningful qualitative results without entering the details of mathematical solutions. Unfortunately, this is not the case in general relativity, but particular situations exist which are more instructive and of greater interest. Among them, the solution written by Karl Schwarzschild (1915–1916), some weeks after Einstein's paper, was the first exact non-trivial solution of general relativity, and covers a special role in several applications. Schwarzschild's solution (or Schwarzschild's vacuum) has a certain analogy to Kepler's problem in celestial mechanics, and can be perturbed in the analysis of more complicated issues. It comes from the spherically symmetric field equations for a curved and empty space:

$$R_{\mu\nu} = 0 \tag{1.355}$$

and, as from the theorem demonstrated by George D. Birkhoff (1923), provides the most general solution for this case. Schwarzschild's metric models thus the space-time outside a spherical (non-rotating) mass source (as a planet or black-hole), and is determined by solving the previous equation with a general static isotropic metric. To proceed, one needs the non-vanishing components of Ricci's tensor ($R_{\alpha\alpha}$) reported in Appendix A. Working on those with $\alpha = 0, r$, it is not difficult to arrive at:

$$\frac{R_{rr}}{a(r)} + \frac{R_{tt}}{b(r)} + \frac{1}{ra(r)}\left(\frac{d\ln a}{dr} + \frac{d\ln b}{dr}\right) = 0 \tag{1.356}$$

and:

$$a(r)b(r) = \text{const} \tag{1.357}$$

At a point infinitely distant from the mass source, Minkowski's flat metric must be recovered, $g_{\alpha\beta}(r \to \infty) = \eta_{\alpha\beta}$, fixing const $= 1$. Substituting $a(r) = 1/b(r)$ in the vacuum equations finally returns $(rb)' = 1$, which is solved by:

$$b(r) = 1 + \frac{\text{const}'}{r} \tag{1.358}$$

We know that, far away from the mass, $b(r) \simeq 1 + 2\phi(r)$, while for $r \to 0$ the same singularity of Newton's potential, $\phi(r) = -\frac{GM}{r}$, is to be met. This fixes $-\text{const}' = 2MG \equiv r_S$ and, finally, the proper time to:

$$ds^2 = \left(1 - \frac{r_S}{r}\right) dt^2 - \frac{dr^2}{1 - \frac{r_S}{r}} - r^2\, d\Omega^2 \tag{1.359}$$

where $r_S$ is named Schwarzschild's radius. Perhaps against the intuition, it can be shown that the curvature tensor is regular at $r = r_S$, meaning that this radius only denotes an apparent ("coordinate") singularity, promptly removed upon an opportune choice of the coordinate system. Rather, its existence reflects the impossibility of describing the spacetime overly well. The origin, $r = 0$, stands instead for a true "gravitational singularity." When regarded $\forall r \geqslant 0$, this metric defines the spacetime around Schwarzschild's "black hole," bounded by the "event horizon" at $r = r_S$ (the black hole size). It would specify the innermost domain where the escape and light speeds coincide, and which any particle or body (including light) would be indefinitely trapped inside.

Finally, it is noteworthy to underline that, at a fixed spatial location:

$$\frac{dt_0}{dt} = \sqrt{1 - \frac{r_S}{r}} \tag{1.360}$$

that is, the proper time ($t_0$) is locally affected by the radial distance, running thus differently at different distances. On the other hand, any radial length will change into ($\Delta l$):

$$\frac{dl}{dr} = \frac{1}{\sqrt{1 - \frac{r_S}{r}}} \tag{1.361}$$

returning a first-order logarithmic distortion to the ordinary distance:

$$\Delta l \simeq \Delta r + \frac{r_S}{2} \ln \frac{r + \Delta r}{r} \tag{1.362}$$

## 6.6 Friedmann–Lemaître–Robertson–Walker metric

It was often pointed out that relativistic cosmology cannot be reduced to general relativity and, reading the literature on the subject, there seems to be a certain feeling that some postulates or assumptions of Einstein's theory should be relaxed or even renounced. Here, among the basic concepts worth recalling, are the Cosmological Principle and the "co-moving" observer. The former supposes the universe to be spatially homogeneous (with curvature equal at every point) and isotropic. The latter indicates a class of (privileged) reference frames, from which the universe would conform to special relativity and appear fully isotropic. All co-moving observers see each other linked to the whole universe expansion, and measure a common "cosmic" time. The occurrence of three co-moving frames implies an infinity of them, each per spacetime point, and all of them sharing an isotropic universe.

Under validity of the Cosmological Principle, an effective spacetime description comes from the metric introduced independently by Alexander Friedmann (1922) and Georges Lemaître (1927), proved then to be the only homogeneous and isotropic solution of Einstein's equation by Robertson (1935–1936) and Arthur G. Walker (1936):

$$ds^2 = dt^2 - R^2(t)\left(\frac{dr^2}{1 - kr^2} + d\Omega^2\right) \tag{1.363}$$

where $R = R(t)$ is a time-dependent scale factor, giving the length expansion inflating on a spatial section at a fixed time, and $k$ is a constant curvature index. By a suitable unit choice for the radial coordinate, it can always be fixed to $k = 0$

(flat), 1 (closed-spherical) and −1 (open-hyperbolic), setting once and for all the spatial geometry at any time. The spacetime depicted by this metric actually belongs to the family of "maximally symmetric spaces," attaining a much simpler tensor description and algebra, settled unambiguously by a curvature constant and the number of positive or negative eigenvalues of the metric. Furthermore, it can be shown that a homogeneous space with the isotropy property about some point is maximally symmetric.

On this basis, the energy–momentum tensor is proved to take the perfect fluid-form ($T_{\mathrm{i}}^{\alpha\mu}$) and, working out the continuity equation, the above metric brings to:

$$\frac{d(\varrho R^3)}{dR} = -3p_{\mathrm{i}}R^2 \tag{1.364}$$

each quantity being here a function of time. When pressure can be ignored, the solution of this differential equation joins the energy density ($\varrho$) to the proper 3-dimensional volume simply as:

$$\varrho(t)R^3(t) = \mathrm{const} \tag{1.365}$$

This metric affords a remarkably intuitive simplification but, because of the lack of operational meaning, may raise some difficulties. Once the curvature value is decided, and the physical distance thus assigned, one is left with a Newtonian-like time combined to an instantaneous distance, which is not universal.

Furthermore, as it cannot yield $R = R(t)$, it is necessary to suppose some matter distribution, from which determining the previous metric as a solution of the field equations. This was pioneered by Alexander Friedmann's (1922), and all approches in which the scale factor is derived that way are called Friedmann's models. We ought, in short, to solve Einstein's equations:

$$R_{\mu\nu} = -8\pi G S_{\mu\nu} \tag{1.366}$$

where the pure temporal (00) and spatial $(s, s')$ components of the source tensor are:

$$S_{\mu\nu} = T_{\mu\nu} - \frac{g_{\mu\nu}}{2}T^{\rho}{}_{\rho} = \begin{cases} \frac{1}{2}(\varrho + 3p) & (\mu = \nu = 0) \\ \frac{1}{2}(\varrho - p)R^2 g_{ss'} & (\mu, \nu = s, s') \\ 0 & \text{elsewhere} \end{cases} \tag{1.367}$$

and, correspondingly:

$$R_{\mu\nu} = \begin{cases} 3\ddot{R}/R & (\mu = \nu = 0) \\ -g_{ss'}(R\ddot{R} + 2\dot{R}^2 + 2k) & (\mu, \nu = s, s') \\ 0 & \text{elsewhere} \end{cases} \tag{1.368}$$

The scale factor is thus determined by:

$$\dot{R}^2 - A\varrho R^2 = -k \tag{1.369}$$

with $A = \frac{8\pi G}{3}$ and where $\varrho = \varrho(R)$ comes from the energy conservation law for a specific state equation, $p = p(\varrho)$. Friedmann's models are very popular in the determination of the curvature sign of the universe (flat, contracting, expanding), which is presently believed to be expanding.

A last point, somewhat noteworthy here, is the concept of observability limit, or spacetime horizon relative to an observer. In short, there are two types of it, contemporary (or current) and ultimate. The first regards observability at present time, indicating the furthest distance detectable at a certain instant ($t = T$):

$$\rho_c(T) = \int_{T_0}^{T} dt_R \tag{1.370}$$

with $dt_R \equiv \frac{dt}{R(t)}$. It is the distance ($\rho_c$) of the light source emitting at the "beginning" ($T_0$) a light ray which has just reached the observer. The second evaluates the distance ($\rho_u$) of the light ray that will get the observer at the "end" ($T_\infty$):

$$\rho_u(T) = \int_{T}^{T_\infty} dt_R \tag{1.371}$$

At fixed $\theta$ and $\varphi$, these integrals are generally related to those in the radial coordinate, $\int \sqrt{g_{rr}}\, dr$, according to the value of the curvature index:

$$\rho(r) = \int \frac{dr}{\sqrt{1-kr^2}} = \begin{cases} \sinh^{-1} r & (k=-1) \\ \sin^{-1} r & (k=1) \\ r & (k=0) \end{cases} \tag{1.372}$$

## Appendix A

The general static isotropic metric (in standard form) is a diagonal tensor, thus its contravariant components are the reciprocals of those covariant ($g^{\mu\alpha} g_{\alpha\nu} = \delta^{\mu}{}_{\nu}$). It follows that the affine connection is fully specified by:

$$\begin{aligned} \Gamma^r_{rr} &= \frac{1}{2}\psi_a \\ \Gamma^r_{\theta\theta} &= -\frac{r}{a(r)} \\ \Gamma^r_{\varphi\varphi} &= -\frac{r\sin\theta}{a(r)} \\ \Gamma^r_{00} &= \frac{1}{2a(r)}\frac{db}{dr} \end{aligned} \tag{A.1}$$

$$\begin{aligned} \Gamma^\theta_{r\theta} &= \Gamma^\theta_{\theta r} = \frac{1}{r} \\ \Gamma^\theta_{\varphi\varphi} &= -\frac{\sin 2\theta}{2} \end{aligned} \tag{A.2}$$

$$\Gamma^{\varphi}_{r\varphi} = \Gamma^{\varphi}_{r\varphi} = \frac{1}{r}$$
$$\Gamma^{\varphi}_{\varphi\theta} = \Gamma^{\varphi}_{\theta\varphi} = \cot\theta \tag{A.3}$$

$$\Gamma^{0}_{0r} = \Gamma^{0}_{r0} = \frac{1}{2}\psi_b \tag{A.4}$$

with $\psi_{\ldots} \equiv \frac{d\ln\ldots}{dr}$. Continuing with Ricci's tensor (from top, $\alpha = 0$, $r$, $\theta$ and $\varphi$):

$$R_{\alpha\alpha} = \begin{cases} -\frac{1}{2a(r)}\frac{d^2b}{dr^2} + \frac{1}{4a(r)}\frac{db}{dr}(\psi_a + \psi_b) - \frac{1}{ra(r)}\frac{db}{dr} \\ \frac{1}{2b(r)}\frac{d^2b}{dr^2} - \frac{1}{4a(r)}\frac{db}{dr}(\psi_a + \psi_b) - \frac{1}{ra(r)}\frac{db}{dr} \\ \frac{r}{2a(r)}(\psi_b - \psi_a) + \frac{1}{a(r)} - 1 \\ \sin^2\theta\, R_{\theta\theta} \end{cases} \tag{A.5}$$

being $R_{\alpha\alpha'} = 0$ for $\alpha \neq \alpha'$. Its trace, the curvature scalar, thus obeys:

$$a(r)R = \psi_b\left[\psi_{\frac{db}{dr}} + \frac{2}{r} - \frac{1}{2}(\psi_a + \psi_b)\right] + \frac{2}{r}\left(\frac{1}{r} - \psi_a - \frac{a(r)}{r}\right) \tag{A.6}$$

and the corresponding components of Einstein's tensor, $G_{\mu\nu} \equiv R_{\mu\nu} - \frac{1}{2}g_{\mu\nu}R$, are ($G_{\alpha\neq\alpha'} = 0$):

$$G_{\alpha\alpha} = \begin{cases} \frac{b(r)}{r^2a(r)}[1 - a(r) - r\psi_a] \\ \frac{1}{r^2}[a(r) - 1 - r\psi_b] \\ \frac{r^2}{2a(r)}\psi_b \mathrm{h}(a, b; r) \\ \sin^2\theta\, G_{\theta\theta} \end{cases} \tag{A.7}$$

where the function h obeys:

$$1 + r\mathrm{h}(a, b; r) = \frac{\psi_a}{\psi_b} + r\left(\frac{\psi_{ab}}{2} - \psi_{\frac{db}{dr}}\right) \tag{A.8}$$

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CHAPTER TWO

# THE SPECIAL THEORY OF BROWNIAN RELATIVITY

## Contents

## 1. BROWNIAN MOTION AND DIFFUSION (NOTES)

### 1.1 Historical summary

"Brownian movement" takes the name from the botanist Robert Brown (1827–1829), who made microscopic observations of pollen of several plants in water. His plant-pollen dispersed into a large amount of tiny particles, moving about

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by highly irregular and uninterrupted "swarming" paths. Astonished, since many organic substances gave rise to the same behavior, he concluded he had found in this phenomenon the "primitive molecule" of "living matter." The roots of this finding, however, date back the microscopy observations of Anthonie van Leeuwenhoek (1674), the founder of microbiology, and Jan Ingenhousz (1784–1785), the discoverer of photosynthesis, who documented forty years earlier the highly irregular motion exhibited by fine powders of charcoal floating in alcohol. Brown himself reported more than ten previous observations, before his 1828 publication. Nevertheless, it has only been since the 1860 publication that Brownian motion has become the subject of many scores of articles in the literature, paving the way over the years to the probability approach of Einstein's seminal work.

Also from the theoretical side, his 1905 paper was not the earliest investigation. The first probabilistic treatment is to be acknowledged to the mathematician Louis Bachelier (1900) that, in his Ph.D. thesis on the analytical valuation of financial stocks and options, anticipated both the Einstein's ideas and the mathematical description of Norbert Wiener (1921). He developed a probability analysis of the market that pioneered the theory of Brownian movement, of which Einstein himself seemed to be unaware. In a chapter entitled, "The Radiation of Probability," he made a formal comparison with the analytical theory of heat, which is analogous to matter diffusion. Bachelier, despite the very positive report by H. Poincaré, was not much appreciated by the scientific community of that time, and lived rather ahead of his age. His work was severely misjudged by Paul P. Lévy, and was recovered thirty years later by a citation within another pioneering work on probability, of Andrey N. Kolmogorov (1931). This is why, in his elegant treatise, William Feller proposed to remedy it by renaming the stochastic process defining a Brownian motion as Bachelier–Wiener process.

The intuition that this movement arises from collisions driven by the random thermal motion of atoms and molecules may be found in other authors, such as Ludwig Chr. Wiener (1863), Giovanni Cantoni (1867), Ignace Carbonelle (∼1874), Joseph Delsaulx (1877), Louis G. Gouy (1888) and Felix M. Exner (1900). L.C. Wiener and Cantoni ascribed the motion irregularity to the molecular structure of the liquid hosting the particle, a thesis which was explained correctly by Carbonelle and Delsaux in terms of particle impulses (or pressures). Gouy's experiments established once and for all that the source of such impulses could not be in the Brownian particles, but in the liquid molecules, observing in particular that the smaller the liquid solvent viscosity ($\eta_S$, the ratio of force to rate of strain) was, the more lively the movements were. Exner noticed that the velocity decreased with increasing particle size ($r_a$) and increased with increasing temperature ($T$). In the meantime, kinetic theory and statistical mechanics were initiated by J.C. Maxwell (1859–1860) and Ludwig Boltzmann (1872–1878), the former with the (Maxwell-Boltzmann) distribution function of molecular speeds in thermal equilibrium of a gas, the latter with the microscopic (probabilistic) explanation of irreversibility (entropy) and the introduction of his famous (Boltzmann's) constant, by which the energy of thermal fluctuation could be expressed ($\sim k_B T$). Exner's quantitative interpretations, making use of an energy equipartition between liquid molecules and suspended particles, went therefore in support of the kinetic theory, for which the Brownian motion had to be in thermal equilibrium with the molecules around.

We thus arrive at the famous analysis by A. Einstein (1905) who, with surprise, admitted later of being unaware of its concrete phenomenological existence. His main goal was to develop the statistical mechanics and kinetic theory that could predict the existence of atoms. He himself wrote, "... according to the atomistic theory, there would have to be a movement of suspended microscopic particles open to observation, without knowing that observations concerning the Brownian motion were already long familiar." His work, together with Max Planck's evaluation of the molecular size by the radiation law at high temperatures, let the "atomism" prevail against the so-called "energetism," an antimechanical (too positivistic) school of thought encompassing outstanding believers as Mach and Wilhelm Ostwald. It denied the fundamentals of the kinetic theory, that is, the thermal agitation of molecules, driven in random motion by intrinsic thermodynamic fluctuations, and temperature reflecting their (average) kinetic energy.

Einstein's work comprises two main arguments, the analysis of Brownian movement as a probabilistic process and the derivation of the diffusion coefficient. Owing to molecular collisions, colloid particles and molecules would move with "aleatory" (or random) velocity, undergoing systematically random changes of magnitude and direction. Einstein discovered that the probability equation for a Brownian motion, reaching a certain position at a given time, is just the diffusion second law discovered by Adolf Fick (1955), thence the mean square value of the particle displacement had to linearly increase with time and be multiplied by the diffusion constant, $\overline{r^2} \sim Dt$. This conception was accurately verified by the experiments on colloids of Jean B. Perrin (1908) and his collaborators (among whom, Niels Bjerrum), proving that Brownian motion is random and possesses well defined equilibrium properties. By availing the diffusion coefficient equation, he and his group also evaluated Loschmidt's (or, equivalently, Avogadro's or Boltzmann's) constant within a relative error equal to $\sim 0.19$ of the current value, giving an irrefutable proof of the existence of atoms and molecules. Perrin (1916) noticed also the self-similarity of the Brownian paths, bringing the attention from particle or molecular details to the mechanism by which the random collision may come to cooperate.

In a second step, the diffusion coefficient is related to the main physical quantities by the theory of friction of George G. Stokes (1851), leading to the so-called Stokes–Einstein equation, $D \propto k_B T/(\eta_S r_a)$. This law, however, was derived one year earlier by William Sutherland (1904) who, in a report of a meeting at the Australasian Association for the Advancement of Science, published a method of calculating the mass of a Brownian particle. The result, this time corrected from an unfortunate misprint in the 1904 manuscript (a missing Avogadro's constant) was then resubmitted in March 1905 to the Philosophical Magazine, and appeared in the June issue, one month before Einstein's paper was sent out to Annalen der Physik.

Einstein was also credited for opening new prospects towards the theory of stochastic processes, any family of random variables depending on an evolutionary parameter (a continuous or discrete "time"), whose developments had over the years a great impact on deepening Brownian motion. His model, in fact, is in essence a Markovian process (a process with short memory), despite the fact that Andrey A. Markov (1906) had still to introduce his "Markovian chains." Marian R. Smoluchowski (1906), however, had already formulated independently a dynamic theory, reobtaining (unless a numerical forefactor) the Sutherland–Stokes–Einstein equation. Paul Langevin (1908), considered the father of the theory of stochastic differential equations, invented another method and arrived at a stochastic (Newton's) equation of motion. It was of the greatest importance to the next contributions to the program (not yet completed) of reducing Brownian movement to Newtonian mechanics, as the "mean-reverting" process of Leonard S. Ornstein and George E. Uhlembeck (1930). Meanwhile, the equation by Adriaan D. Fokker (1914) and Max Planck (1917), known also as Kolmogorov's forward (or first) equation, and the discovery of another family of (stable and "exceptional") distributions by Paul P. Lévy (1924), could attain the analysis of ample classes of stochastic processes. Lévy, in particular, baptized the class of all processes in continuous time, with stationary and independent increments, including the Brownian motion with a drift term.

Langevin argued that the total force on a single Brownian particle comprises two main contributions. One is a frictional force, exerted by the medium, whereby the particle dissipates energy into the degrees of freedom of the liquid. The other, due to the random collisions with the surrounding molecules and very rapidly fluctuating, is that assigning the motion its typical zig-zag look. We can therefore average out the motion equation at the time scale of the friction force, and relate the statistical properties of such an irregular walk to quantities defined at the longest time scale. Remember Langevin's equation has no straight relationship with thermodynamics, but is very effective in describing ample classes of stochastic motions. Fokker–Planck's descends instead from the more general Chapman–Kolmogorov equation for Markov's processes. It is a deterministic partial second-order differential equation for a probability distribution function, involving velocity, time and space coordinates, with coefficients equal to the first two statistical moments calculated in a macroscopically infinitesimal time interval. Smoluchowski's is another phenomenological equation, essentially tantamount to Langevin's, and formulates the problem in the relevant phase space portion, corresponding to the longest time scale (said to be Smoluchowski's scale). It has evident connection with thermodynamics of irreversible processes, but is normally less versatile than the others, in particular the Fokker–Planck's, from which it can be inferred as a special case.

Smoluchowski's work on kinetic theory provides the opportunity of turning to another standpoint of stochastic processes, the random walk (or "drunkard's walk"), identifying a neat (mathematical) analogue of Brownian motion. It denotes a stochastic process produced by summing arbitrary numbers of not necessarily independent random variables (e.g., $d$-dimensional vectors) and its history dates back to Einstein's annum mirabilis, when the statistician Karl Pearson (1905) formulated in a letter sent to Nature "The problem of random walk." Lord Rayleigh (1905), in the subsequent issue, quickly gave an answer and referred to the asymptotic (Gaussian) solution of another issue, which he confronted in two publications in the years 1880 and 1899. He noted that the Pearson's walk corresponds to the problem of addition of (sound) waves with the same frequency and arbitrary phase. It was later recognized that the origins of random walk can actually be ascribed to the dawn of probability approaches to the games of chance, as in the analysis by Christiaan Huygens (1657) and Jakob Bernoulli (1713), the scientific importance of which remained hidden for a long time. The paradigmatic relevance of the random walk for Brownian motion was noticed by Smoluchowski, who described the path of a Brownian molecule in a gas as a broken line, where the angle between adjacent segments is held fixed. Although his kinetic model appeared one year later than Pearson's letter, he did not name it random walk. His was a typical example of persistent (or correlated) random walk, while Pearson's, setting this angle to a uniform random variable, falls into the category called "unrestricted." Random walks on a lattice were then introduced by György Pólya (1919–1921), studying the (unbiased) motion described by a sequence of elementary steps ($\pm 1$) between nearest-neighbor positions (sites), and suggesting the application to diffusion of gas molecules in a 3-dimensional crystal lattice. He asked himself if the probability that a given site is visited at least once (or the initial position visited twice) tends to certainty with increasing step numbers. His answer, first stated without demonstration, "Yes, if $d = 1, 2$; no, if $d = 3, 4, 5, \ldots$" encloses one of the main random walk properties, its discontinuous behavior as the space dimension ($d$) increases.

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## 1.2 Einstein's probability approach and Bachelier–Wiener process

Behind Einstein's approach to Brownian motion is, as already said, the kinetic theory of matter, whereby both suspended and dissolved particles in a liquid solvent were expected to manifest the same qualitative behavior. The main difference is quantitative. Because of a much larger size, the number of collisions per unit time experienced by a Brownian particle will remarkably exceed that of a solvent molecule, assigning different motion parameters. It seems to be plausible thus to introduce a short elementary time step $\tau$, with the criterion that any path increment over $\Delta t \geqslant \tau$ be (statistically) independent of each other. Molecular collisions, in other words, will tend to destroy the memory that Brownian trajectories hold of their initial location, $\tau$ being a measure of this persistence. Einstein did not suppose explicitly the (total) stochastic independence of the random position among adjacent time intervals, and seemed to concentrate on a sort of kinetic gas theory. This is why the existence of an elementary time appears to be uninfluential in his analysis ($\tau \to 0$) and, as many scientists and Einstein himself criticized, likely the weakest point of his investigation. We will be brought to a stochastic process for the random position ($\mathbf{x}(t)$) that, at any time and regardless of the auxiliary step, may be specified in essence by $|d\mathbf{x}(t)| = \sqrt{dt}$. Some authors observed what Einstein actually needed was Markov's property, and not the full independence of all paths temporally separated by $\tau$.

Formally, working in the simplest one-dimensional case, the fraction of particles experiencing a displacement ranging in $(x', x' + dx')$ and $(t, t + \tau)$ will be modeled by a given probability function ($\mathsf{P}$). In a homogeneous system, where driving forces and diffusion coefficients are independent of position and time, it is simply specified by $\mathsf{P} = \mathsf{P}(x', \tau)$, in terms of which the particle probability (or concentration) is expanded as follows. If $W = W(\mathbf{x} = x, t)$ denotes the particle number per unit volume at the spatial point $x$ and some (earlier) time $t$, then:

$$W(x, t+\tau) = W(x,t) + \left(\frac{\partial W}{\partial t}\right)\tau + \mathrm{O}(\tau^2) \tag{2.1}$$

and, at second order in the random displacement, the same quantity can be obtained from integrating over a large enough particle ensemble, i.e.:

$$\begin{aligned} &= \int_{-\infty}^{\infty} W(x+x', t)\mathsf{P}(x')\,dx' \\ &= \int_{-\infty}^{\infty} \left[W(x,t) + \left(\frac{\partial W}{\partial x}\right)x' + \frac{1}{2}\left(\frac{\partial^2 W}{\partial x^2}\right)x'^2\right]\mathsf{P}(x')\,dx' \end{aligned} \tag{2.2}$$

The function $\mathsf{P}$ "propagates" the particle probability, from one position to one other in a time step, and was a formal keypoint in Einstein's work. A simple comparison of the latter expansions, with $\overline{\mathbf{x}'(t)} = 0$ and the (local) definition $\overline{\mathbf{x}'^2(t)} = 2D\tau$, led Einstein to Fick's second law:

$$\left(\frac{\partial W}{\partial t}\right) = D\left(\frac{\partial^2 W}{\partial x^2}\right) \tag{2.3}$$

known in three spatial dimensions as the heat-diffusion equation. Otherwise, a drift term as $\frac{\overline{\mathbf{x}'}}{\tau}\frac{\partial W}{\partial x}$ must be added to the right side. The former equation admits, as a fundamental solution, the Gaussian (or normal) density, with $D$ giving a measure of variability:

$$W(x,t) = (4\pi Dt)^{-\frac{1}{2}}\mathrm{e}^{-\frac{x^2}{4Dt}} \tag{2.4}$$

It flattens in fact as time elapses, with $\overline{\mathbf{x}(t)} = 0$ and variance provided by Einstein's (or Einstein–Smoluchowski) law:

$$\overline{\mathbf{x}^2(t)} = \int_{-\infty}^{+\infty} x^2 W(x,t)\,dx = 2Dt \tag{2.5}$$

that, in the time-step limit, reduces (independently of driving forces) to the above diffusion coefficient definition. This typical concentration behavior, to spread out with time, is actually a consequence of dissipative (friction) forces, but does not exhaust every diffusion process. Anyway, such results are clearly in line with the "central limit theorem," asserting that the convolution of many (arbitrary) density functions of finite width always converges to a Gaussian distribution. The total particle displacement is the sum in fact of many independent elementary contributions, each of them with zero mean and characteristic time $\sim\tau$. Note also the same time-dependence of "mean" and "root mean square" displacements, as $\overline{|\mathbf{x}|}^2/\overline{\mathbf{x}^2} = 2/\pi$.

The former 1-dimensional calculation can promptly be extended to any space of higher dimensionality ($x \to \mathbf{r}$). In that case, a symmetric diffusion (or mobility) tensor will generally replace $D$ ($\overline{\mathbf{x}'_s \mathbf{x}'_{s'}} = 2D_{ss'}\tau$) but, if isotropy applies, ($\bar{\mathbf{x}}_s^2 = \overline{\mathbf{r}^2}/d$), still involves one diffusion coefficient alone. This also lays the basis for the simplest random walk analysis, of Fick's first and second laws for a particle performing a sequence of random jumps in a regular lattice, as in the diffusion kinetics of atoms in a crystal, driven by interstitial mechanisms. Remember that, while atoms of "ideal solids" can only vibrate around their equilibrium positions, real solids too always exhibit (random walk) diffusive processes over long enough time scales.

Stepping back to the probability density $W = W(x,t)$, its significance goes as follows. When a large amount of particles, located at the beginning ($t = 0$) at the origin ($x = 0$), are released to themselves ($t^+ = 0$), its number density between (planes at) $x$ and $x + dx$ will spontaneously establish in a time interval $t$ to be $\mathsf{P}(x,t)\,dx$, and the calculation of the average distribution, performed at a fixed time over many particles, will finally return $W = W(x,t)$. This "collective" interpretation fits evidently well the scope of the diffusion equation, modeling the total variation of a solute concentration, but may also be reverted to describe an individual Brownian movement. In this view, $W(x,t)\,dx$ is the probability to find a single path in a time $t$ in (between planes at) $(x, x + dx)$. Thus, whenever a large number of observations are carried out, the relative frequency of particle displacements between subsequent time steps will be ruled by $W(x,t)$. This "time-summation" over a single Brownian path is the counterpart of the former "space-summation" over many-particle ensembles, and their equivalence lies at the basis of understanding what is called as "ergodicity." "Ergodic theorems" are key tools of statistical physics, their applications to (Markov's or not) diffusion processes and (free or not) Brownian movements are still under investigation. In brief, a stochastic process is ergodic ($\mathbf{x}(t)$) whenever the ensemble and (the infinite) time averages are proved to be equal, whereby any statistical feature can be deduced from a single (long enough) "sampling path" ($\mathbf{x}_k(t)$). An intuitive example of ergodic hypothesis is regarding the statistics of "residence times" ($\mathbf{T}$) of a Gaussian Brownian motion in a system of finite size ($L$) and without fields of force. On waiting for long observation periods ($t$), the residence time in half the system should approach $\overline{\mathbf{T}}(t, L/2) \sim t/2$.

Brownian movement in the Einstein's (and Smoluchowski's) view is known as the Bachelier–Wiener process (or Bachelier–Wiener–Lévy's), $\mathbf{x}_B(t) \equiv \mathbf{x}(t)$. Actually, Brownian motion can denote a wider class of stochastic processes, but here is restricted to describe the random motion of a free particle with negligible acceleration. Bachelier–Wiener's so is an "almost surely" ("a.s.," with probability one) continuous Markov's process on coordinate space (not differentiable everywhere), characterized by $\mathbf{x}_B(0) = 0$ and joint probability ($P$):

$$P\left\{\bigcap_{s=1}^{m} \mathbf{x}_B(t_s) \in X_s\right\} = \int_{X_1} \cdots \int_{X_m} \prod_{s=1}^{m} dP_s \tag{2.6}$$

to observe the movement in any sequence of intervals $X_s$ at times $t_0 = 0 < t_1 < \cdots < t_m$. Each probability differential $dP_s = W_s\,dx_s$ can be developed in terms of a "transition density," depending upon time increments ($t_s - t_{s-1}$) as:

$$\begin{aligned} W_s(x_{s-1}, t_{s-1}; x_s, t_s) &= W(x_{s-1}, x_s; t_s - t_{s-1}) \\ &= \left[2\pi(t_s - t_{s-1})\right]^{-1/2} \exp\left[-\frac{(x_s - x_{s-1})^2}{2(t_s - t_{s-1})}\right] \end{aligned} \tag{2.7}$$

where the semicolon replaces for convenience the intersection symbol (; ≡ ∩). It points out a continuous, isotropic and translationally invariant diffusion law. Concisely, the above density function (in Euclidean space) is just one of the main characteristics of what is generally a Brownian movement. The others are its continuous paths and the "strong" Markov's property, that is, a Markovian property that is not limited to a constant time step but holds for arbitrary times.

Concerning the most important expectations, it turns out:

$$\overline{\mathbf{x}_B(t)} = 0 \tag{2.8}$$

$$\overline{\mathbf{x}_B(t)\mathbf{x}_B(t')} = \min(t, t') \tag{2.9}$$

$$\overline{\left|\mathbf{x}_B(t) - \mathbf{x}_B(t')\right|^2} = |t - t'| \tag{2.10}$$

which, working in (twice) diffusion coefficient units, $2Dt \equiv t - t' > 0$, coincides with the Einstein's law. The increments of the Bachelier–Wiener process, $\mathbf{x}_B(t_s) - \mathbf{x}_B(t_{s'})$, are so "stationary," their statistics is not affected by changing the time origin to "scratch" from. Consequently, their probability density and self-correlation (or auto-correlation) functions only depend on the time shift $\tau = t_s - t_{s'}$. In general, when this property applies to some process $\mathbf{x}(t)$, then:

$$W_n(x_1, t_1; \ldots; x_n, t_n) = W_n(x_1, t_1 + \tau; \ldots; x_n, t_n + \tau) \tag{2.11}$$

and the following "moments," forming the family of self-correlation functions at any order ($n$) as:

$$\overline{\mathbf{x}(t_1)\ldots\mathbf{x}(t_n)} \equiv \int \ldots \int x_1 \ldots x_n W_n(x_1, t_1; \ldots; x_n, t_n)\, dx_1 \ldots dx_n \tag{2.12}$$

will be also functions of time increments alone. In particular:

$$W_1(x, t) \equiv \overline{W}(x) \tag{2.13}$$

$$W_2(x_1, t_1; x_2, t_2) \equiv W(x_1, x_2; t_2 - t_1) \tag{2.14}$$

implying a couple of properties already met above, for $\mathbf{x}_B(t)$:

$$\overline{\mathbf{x}(t)} = \text{const} \tag{2.15}$$

$$\overline{\mathbf{x}(t)\mathbf{x}(t + \tau)} = \overline{\mathbf{x}(t - \tau)\mathbf{x}(t)} \tag{2.16}$$

which, since infinitely remote statistics are not correlated:

$$\lim_{\tau\to\infty} \overline{\mathbf{x}(t)\mathbf{x}(t + \tau)} = \overline{\mathbf{x}(t)}^2 \tag{2.17}$$

When the last but two conditions are met, irrespective of the behavior of probability functions at any higher order ($n > 2$), the process obeys a weaker constraint that is named "wide sense stationarity." Finally, Brownian motion increments form clearly a set of (pairwise) independent aleatory variables:

$$P\left\{\bigcap_{s=1}^{m}\left[\mathbf{x}_B(t_s)-\mathbf{x}_B(t_{s-1})\right]\in X_s\right\}=\prod_{s=1}^{m}P\left\{\mathbf{x}_B(t_s)-\mathbf{x}_B(t_{s-1})\in X_s\right\} \tag{2.18}$$

as they are normally distributed, with zero mean, and "orthogonal":

$$\overline{\left[\mathbf{x}_B(t_1)-\mathbf{x}_B(t_2)\right]\ldots\left[\mathbf{x}_B(t_{m-1})-\mathbf{x}_B(t_m)\right]}=\prod_{s=1}^{m}\overline{\left[\mathbf{x}_B(t_s)-\mathbf{x}_B(t_{s-1})\right]}=0 \tag{2.19}$$

It is worth remembering that, while there are numerous examples of (well-posed) discrete sequences of independent random variables, strictly speaking, stochastic processes in continuous time can never be truly independent. Other properties are those said to be "scaling" and "time inversion," saying respectively that $a^{-1}\mathbf{x}_B(a^2t)$ $(a > 0)$ and $t\mathbf{x}_B(t^{-1})$ have the same statistics of $\mathbf{x}_B(t)$, and are still Brownian movements. In particular, a hint for the first of these two "self-affinities" comes from the invariance of the partial differential equation under the rescaling $(x,t)\to(\sqrt{a}x,at)$, which will also be met in the basic scaling behavior of (ideal) polymer chains.

The great importance of the Bachelier–Wiener process lies mainly in the fact that its increments embody a wealth of relevant properties, and the whole knowledge of it only needs a second-order analysis (the first two moments). In a way, Brownian motion may be regarded the very statistical paradigm of natural phenomena.

## 1.3 Sutherland–Stokes–Einstein equation

Another milestone of statistical physics, coming from Einstein's work on Brownian movement, is the expression of the diffusion constant. The central question in this derivation was whether a liquid suspension of Brownian particles may or may not exert an osmotic pressure. Supporters of the energetism were convinced that the answer had to be negative. On the contrary, the kinetic–atomic view of matter conceives a dispersion of fine particles as a "dispersion of atoms" (a solution), for which an osmotic pressure had to take place. Due to the difficulty of detecting it experimentally, Einstein (1905) proposed measuring the number density $n=n(z)$ as a function of the height of particles $(z)$ dispersed in a vertical column. With no osmotic pressure, $\Pi = nk_BT$, the gravity force $(f=-mg)$ would drag the Brownian particles to the bottom. Otherwise, at equilibrium, the osmotic force per unit volume:

$$F_\Pi(z)=-k_BT\nabla_z n(z) \tag{2.20}$$

will balance the gravity contribution, $F_g(z)=n(z)f$, so to have:

$$f=k_BT\nabla_z\ln n(z) \tag{2.21}$$

and the profile, $n(z)/n(0)=\mathrm{e}^{fz/(k_BT)}$, confirmed experimentally.

Now, when a concentration gradient establishes, Fick's second law predicts a net (upward) particle flux proportional to the diffusion coefficient. In dynamic equilibrium, it equates the flux driven by $f$ against friction, thence:

$$\mu_m f = D\nabla_z \ln n \tag{2.22}$$

where the right-handed side is the particle velocity necessary to neutralize the osmosis, and the new quantity on the left defines the particle "mobility." It is the reciprocal of a characteristic frequency times the particle mass, $\mu_m = 1/(\nu_S m)$, or, if one prefers, of a "friction coefficient" ($\alpha = \nu_S m$). Since force and number density cancel out, one is left with the "Einstein–Smoluchowski" equation:

$$D = \mu_m k_B T \tag{2.23}$$

which is not affected by the physical origin of $f$ and can either be applied in the absence of forces or to single Brownian particles. Smoluchowski, in his dynamic theory, got to the same equation with a different numerical prefactor ($\frac{32}{27}$, on the right).

Experimentally, the largest uncertainty source clearly comes from the mobility coefficient, which depends in turn on particle details. However, if the Brownian particle is a sphere of radius $r_a$, Stokes's law asserts that the force necessary to drag it at velocity $v$ across an incompressible viscous fluid is $F = 6\pi\eta_S v$. This means that the friction coefficient is related to the (shear) viscosity of the solvent ($\eta_S$) by $\alpha_S = 6\pi r_a \eta_S$, from which the Sutherland–Stokes–Einstein equation follows at once:

$$D = \frac{k_B T}{6\pi r_a \eta_S} \tag{2.24}$$

Stokes's theory supplies some weak points that should be kept in mind in every application. The friction constant, for instance, is supposed to be fully independent of pressure, which is clearly untenable in rarefied liquids. Furthermore, in his lectures on the kinetic theory, Lorentz (1911–1912) pointed out that Brownian motion might even be incompatible with Stokes's formula. In calculating the resistance to friction, a term like $r_a(\bar{\varrho} n_\omega / 2\eta_S)^{\frac{1}{2}}$ was ignored, $\bar{\varrho}$ and $n_\omega$ denoting respectively the fluid density and the frequency of the vibrational motion. This means that the characteristic time over which the random velocity changes appreciably should (greatly) exceed the neglected contribution, $m/(6\pi r_a \eta_S) \gg \pi\bar{\varrho} r_a^2/\eta_S$, or $2\bar{\varrho}_a \gg 9\pi\bar{\varrho}$. Notwithstanding, depending on the particle density ($\bar{\varrho}_a$), this inequality may not be automatically satisfied. Nowadays, the name "Stokesian dynamics" still indicates any particle motion driven by thermal, hydrodynamic and direct external forces.

## 1.4 Notes on hydrodynamics

When a Brownian particle in a solvent reaches a certain velocity value, the flow arisen in the liquid will interplay with the surroundings. As recalled, Smoluchowski's formalism arrives at Newton's equation for the probability distribution function in the presence of such interactions, but requires the particle size to be (much) larger than the molecular dimension of the liquid. If so, the flow perturbation is so fast that particle positions and momenta cannot vary very much during the time interval in which the disturbance can get to the other molecules. This means, in practice, to deal with "instantaneous" hydrodynamic interactions and write forces as $\mathbf{F}_i = \mathbf{F}_i[\mathbf{r}_k(t), \mathbf{p}_k(t)]$. In this case, particle momenta relax to thermal equilibrium with the heat liquid bath, and the friction acting on each particle is balanced by the other (stochastic) interactions. This is, in a few words, the physical picture characterizing the true diffusive regime (the "Brownian time scale"). Another feasible approximation is the neglect of non-linear inertial contributions, implying that hydrodynamic forces linearly depend on velocities. This stems from the typical orders of magnitude of Reynolds's number ($Re = \bar{L}\bar{\varrho}\bar{\mathbf{v}}/\eta_S$), the ratio between inertial forces (needed to accelerate masses) and viscous forces (produced by the viscous shear) over the linear scale ($\bar{L}$) of the motion (e.g., the particle size). At the typical particle size and velocity scales, one has $Re \ll 1$, allowing the Navier–Stokes equation (i.e., Newton's second law):

$$\bar{\varrho}\left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \vec{\nabla}\mathbf{v}\right) = \eta_S \vec{\nabla}^2 \mathbf{v} - \vec{\nabla} p_{\mathrm{i}} + \mathbf{F} \tag{2.25}$$

to be linearized in the fluid velocity, keeping on the left the unsteady acceleration, $(\frac{\partial \mathbf{v}}{\partial t})$, but getting rid of that convective, $(\mathbf{v} \cdot \vec{\nabla})\mathbf{v}$.

Consider now an ensemble of $N$ particles, with velocities collected by the super-vector $\mathbf{v} = (\mathbf{v}_1, \ldots, \mathbf{v}_N)$. To model the hydrodynamic interactions between two of them, $i$ and $k$, one may introduce a super-force $\mathbf{F} = (\mathbf{F}_1, \ldots, \mathbf{F}_N)$ and $(3N)^2$ microscopic friction matrices ($\mathbf{A}$):

$$\mathbf{F} = -\mathbf{v} \cdot \mathbf{A} \tag{2.26}$$

that depends on all particle positions and is independent of all velocities, i.e.:

$$\mathbf{F}_k = -\sum_{i=1}^{N} \mathbf{v}_i \cdot \mathbf{A}_{ik}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{2.27}$$

Due to feedback flow effects ("backflow," decreasing as $1/r$ in the Stokesian approximation), it should not be overlooked that diagonal matrices ($kk$) do not stand simply for the friction coefficients of single particles. However, when their distance is very large on the average, then:

$$\mathbf{F}_k = -\alpha_S \mathbf{v}_k \tag{2.28}$$

as the friction tensor in the limit of infinite dilution expresses the Stokesian constant of an isolated particle, $\mathbf{A}_{ik} = \alpha_S \delta_{ik} \mathbf{I}$. Note that, in a rotational motion without inertial effects, the friction constant tensor replaces the moment of inertia. Finally, the inverse $(\mathbf{A}_{ik})^{-1} \equiv (k_B T)^{-1} \mathbf{D}_{ik}$ defines the microscopic diffusion tensor, whose matrices embody scalar "mobility functions." They generally refer to a many-body system and, aside from low density regimes, cannot be represented by pairwise expansions, nor ever by closed-form analytical expressions. At low densities, in comparison with particle pairs, $n$-body configurations ($n \geqslant 3$) more rarely comprise particles which get close enough.

The diffusion tensor can solely depend on particle positions only for spherical bodies. When they are non-spherical, positions and orientations are hydrodynamically coupled, as in the relevant case of rigid rods. Here, particles exert forces and torques onto each other, and the translational friction constant is influenced by the rod orientation. A noteworthy situation is given by homogeneous systems where, regardless of the orientational anisotropy, the coupling between translations and rotations will not affect the (uniform) positional distribution of the molecules. Anyway, when the diffusive regime is reached, the instantaneous relaxation to thermal equilibrium with the liquid implies again that the total force and torque die off. This is generally true also for spherical particles, but the analysis of translational and rotational movements can be performed therein independently. In particular, the (vanishing) total torque is purely hydrodynamic, and hydrodynamic interactions are expressible via translational velocities only.

To give a brief account of these considerations, let us write now the microscopic tensors. They admit a $2^2$ compact writing, in which the diagonal entries stand for pure translational (T) and rotational (R) terms, and those off-diagonal for the mixed ones. When no hydrodynamic interaction comes into play, the friction tensor is diagonal:

$$\mathbf{A}_{ss}^{(\mathrm{T})} = \alpha_{\parallel}\mathbf{v}_s\mathbf{v}_s + \alpha_{\perp}(\mathbf{I} - \mathbf{v}_s\mathbf{v}_s) \tag{2.29}$$

$$\mathbf{A}_{ss}^{(\mathrm{R})} = \alpha_r\mathbf{I} \tag{2.30}$$

where $\alpha_r$, $\alpha_{\parallel}$, $\alpha_{\perp}$ separate a rotational constant from parallel and perpendicular translational frictions, evaluated with respect to the (cylindric) symmetry axis of the rod. Similarly, the microscopic diffusion matrices read:

$$\mathbf{D}_{ss}^{(\mathrm{T})} = D_{\parallel}\mathbf{v}_s\mathbf{v}_s + D_{\perp}(\mathbf{I} - \mathbf{v}_s\mathbf{v}_s) \tag{2.31}$$

$$\mathbf{D}_{ss}^{(\mathrm{R})} = D_r\mathbf{I} \tag{2.32}$$

where each diffusion coefficient is defined via the corresponding mobility relation, $D_k = \mu_{mk}k_BT$, of course with $\alpha_k \equiv 1/\mu_{mk}$.

Another notable quantity is the tensor carrying the name of Carl W. Oseen (1927), arising in the velocity calculation at a position $\mathbf{R}$ when a pointwise force $\mathbf{F} = \mathbf{f}\delta(\mathbf{r})$ is applied somewhere else in the fluid ($\mathbf{r} \neq \mathbf{R}$). It stands for Green's function of the stationary and linearized Navier–Stokes equation:

$$\mathbf{F} = \vec{\nabla}p - \eta_S\vec{\nabla}^2\mathbf{v} \tag{2.33}$$

for an incompressible medium, where the continuity equation (mass conservation):

$$\left(\frac{\partial\bar{\varrho}}{\partial t}\right) = -\vec{\nabla}\cdot(\bar{\varrho}\mathbf{v}) \tag{2.34}$$

reduces to the volume conservation, $\vec{\nabla}\cdot\mathbf{v} = 0$. Switching to the wavevector domain ($\mathbf{q}$) by a spatial Fourier transform ($\mathbf{v} \rightarrow \mathbf{v}_{\mathbf{q}}$), it turns out:

$$\eta_S q^2\mathbf{v}_{\mathbf{q}} = \left(\mathbf{I} - \frac{\mathbf{q}\mathbf{q}}{q^2}\right)\cdot\mathbf{f} \tag{2.35}$$

from which, the inverse transform brings back to:

$$\mathbf{v}(\mathbf{R}) = \mathbf{f} \cdot \mathbf{T}(\mathbf{r} - \mathbf{R}) \tag{2.36}$$

and the Green function on the right is Oseen's hydrodynamic interaction tensor:

$$\mathbf{T}(\mathbf{r}) = \frac{1}{8\pi\eta_S r}\left(\mathbf{I} + \frac{\mathbf{rr}}{r^2}\right) \tag{2.37}$$

A dynamic generalization, for time-dependent point interactions, can be attained if the unsteady acceleration is put back in the Navier–Stokes equation. In a linear hydrodynamic theory, a particle ensemble with identical friction constants will be characterized by:

$$\mathbf{v} - \mathbf{v}_0 = -\alpha_S \mathbf{v} \cdot \mathbf{T} \tag{2.38}$$

where the super-vector $\mathbf{v}_0$ joins the velocities ($\mathbf{v}_{s_0}$) with which the position of each particle ($\mathbf{r}_s$) would flow if $s$ were removed from the fluid. $\mathbf{T}$ is formed by Oseen's matrices, $\mathbf{T}_{ss'} = \mathbf{T}(\mathbf{r}_s - \mathbf{r}_{s'})$, determining the velocity perturbation produced in $\mathbf{r}_s$ by a force concentrated in $\mathbf{r}_{s'}$. As velocities are related to the microscopic friction via $\alpha_S \mathbf{v} = \mathbf{A} \cdot \mathbf{v}_0$, the diffusion tensor turns out to be no longer diagonal:

$$\mathbf{D}_{ss} = D\mathbf{I}, \qquad \mathbf{D}_{ss'} = k_B T \mathbf{T}_{ss'} \tag{2.39}$$

This is Oseen's approximation, reasonable for hydrodynamic interactions between spherical particles at large distances. Moreover, the incompressibility condition joint to Oseen's tensor definition can prove that there is no concentration (or density) gradient, $\vec{\nabla}_{\mathbf{r}_s} \cdot \mathbf{D}_{ss'} = 0$. In general, the small distance behavior is vital for a correct analysis of the concentration dependence, and Oseen's approximation must be renounced. This problem, tough to be worked out (theoretically) with great accuracies, was solved for hard-spheres by George K. Batchelor (1976) and B. Ubbo Felderhof (1978).

## 1.5 Smoluchowski's formalism

Smoluchowski's equation is basically Newton's equation for the probability distribution function of the Brownian position, evolving in the phase space at the diffusive (or "Smoluchowski's," or Brownian) time scale. It is often adopted as the basic point of numerous out-of-equilibrium theories, including especially colloid and polymer solution dynamics. We still work in a super-vector notation, $\mathbf{r} \equiv (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$, $\vec{\nabla}_{\mathbf{r}} \equiv (\vec{\nabla}_{\mathbf{r}_1}, \vec{\nabla}_{\mathbf{r}_2}, \ldots, \vec{\nabla}_{\mathbf{r}_N})$ and $\mathbf{p} = m\mathbf{v}$. The friction tensor can be used to express the balance of hydrodynamic and other interaction forms, such as direct forces stemming from the total potential, $-\vec{\nabla}_{\mathbf{r}} U(\mathbf{r})$, and any term $\mathbf{F}_B \equiv (\mathbf{F}_{B1}, \mathbf{F}_{B2}, \ldots, \mathbf{F}_{BN})$ grouping the unknown forces neglected in the (diffusive) time scale coarsening:

$$\mathbf{A} \cdot \mathbf{v} = -\vec{\nabla}_{\mathbf{r}} U(\mathbf{r}) + \mathbf{F}_B \tag{2.40}$$

The continuity (Liouville's) equation for the probability distribution function, $W = W(\mathbf{r}, t)$, is a conservation law for the number of representative points in an arbitrary phase space volume. It must equate the integral of the current density, $\mathbf{J} = \mathbf{v}W(\mathbf{r}, t)$, over the surface boundaries (e.g., $\partial\Gamma$):

$$\frac{d}{dt}\int_{\Gamma} W(\mathbf{r},t)\,d\mathbf{r} = -\oint_{\partial\Gamma} \mathbf{J}\cdot d\mathbf{S} \tag{2.41}$$

and can be determined by setting a model operator such that:

$$\left(\frac{d\mathbf{r}}{dt}\right) = \mathbf{B}\big[\mathbf{r}(t)\big] \tag{2.42}$$

Accordingly:

$$\left(\frac{\partial W}{\partial t}\right) = -\vec{\nabla}_{\mathbf{r}}\cdot\big[\mathbf{B}(\mathbf{r})W(\mathbf{r},t)\big] \tag{2.43}$$

and, from the initial balance equation, $\mathbf{B} \equiv \mathbf{A}^{-1}\cdot(\mathbf{F}_B - \vec{\nabla}_{\mathbf{r}}U(\mathbf{r}))$. At dynamic equilibrium:

$$\lim_{t\to\infty} W(\mathbf{r},t) \simeq \mathrm{e}^{-\frac{U}{k_BT}} \tag{2.44}$$

the Brownian force is constrained to:

$$\mathbf{F}_B = -k_BT\vec{\nabla}_{\mathbf{r}}\ln W(\mathbf{r},t) \tag{2.45}$$

thus, the final form of Smoluchowski's equation is:

$$\left(\frac{\partial W}{\partial t}\right) = \mathcal{L}_{\mathrm{s}}\big[W(\mathbf{r},t)\big] \tag{2.46}$$

Smoluchowski's (Liouvillian) operator is a double sum over the particle ensemble that, in terms of the diffusion tensor writes:

$$k_BT\mathcal{L}_{\mathrm{s}} = \vec{\nabla}_{\mathbf{r}}\cdot\mathbf{D}\cdot(\vec{\nabla}_{\mathbf{r}}U + k_BT\vec{\nabla}_{\mathbf{r}}) \tag{2.47}$$

embodying the hypothesis of linear rate equations of thermodynamics of irreversible processes, with phenomenological coefficients in each $\mathbf{D}_{ks}$. When hydrodynamic interactions do not occur, the microscopic tensors are diagonal ($\mathbf{D}/D = \mathbf{A}/\alpha_S = \mathbf{I}$), simplifying the model a lot.

This is what happens in a single Brownian motion under an external field:

$$\left(\frac{\partial W}{\partial t}\right) = \vec{\nabla}\cdot(D\vec{\nabla}W + W\vec{\nabla}U) \tag{2.48}$$

where, if the applied (conservative) force is weak enough, the drift velocity imparted to the particle comes from the linear rate equation:

$$\mathbf{v} = \frac{\vec{\nabla}U}{\alpha_S} \tag{2.49}$$

and the matter flux comprises the additional current density:

$$\mathbf{J}_M = -D\vec{\nabla}W - \mathbf{J} = -\frac{W}{\alpha_S}\vec{\nabla}\mu \tag{2.50}$$

Note the gradient of the diffusion coefficient, whose spatial variations influence the approach to equilibrium. As expected from thermodynamics, Boltzmann's distribution function, constraining the Brownian force at dynamic equilibrium, originates from setting the gradient of the chemical potential ($\mu$) to zero. For non-interacting particles, concentration and probability only differ by a normalization term, and $\mu = k_B T \ln W + U$. More generally, when fields are time-independent and the boundary flux is vanishing, distribution functions always assume the Boltzmann's form, setting the functional for the Helmoltz's free energy ($\mathcal{A}$):

$$\mathcal{A}[W] = \overline{\mu(\mathbf{r},t)} = \int \mu W(\mathbf{r},t)\, d\mathbf{r} \tag{2.51}$$

at a stationary minimum. Remember that, close to the (temporal) limitations in Einstein's approach, Smoluchowski's disregards the small length scale, and external forces are not allowed to vary sensibly on a distance $\sim\sqrt{m\mu_m D}$.

For rigid rod-particles, the route to Smoluchowski's equation is conceptually analogous, but the formal complexity increases. They perform two Brownian movements, one translational, if we observe their center of mass, the other rotational, depicted by the (unit) vector parallel to them. Thus, the position vector has to include each particle orientation, $(\mathbf{r}, \mathbf{u})$, with super-vectors $\mathbf{u} \equiv (\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_N)$ and $\boldsymbol{\omega} \equiv (\boldsymbol{\omega}_1, \boldsymbol{\omega}_2, \ldots, \boldsymbol{\omega}_N)$, of angular velocities specified by the equation for the orientational rate of change:

$$\boldsymbol{\omega}_s = \mathbf{u}_s \wedge \left(\frac{d\mathbf{u}_s}{dt}\right) \tag{2.52}$$

Note that the latter is a simply kinematic equation, without reference to specific particle features (motion and shape). All $\mathbf{u}_s$ are vectors defined over a unit spherical surface, bringing the description to a $6N$-dimensional product space, with $U = U(\mathbf{r}, \mathbf{u})$ and:

$$\left(\frac{\partial W}{\partial t}\right) = \mathcal{L}_{\mathrm{r}}\big[W(\mathbf{r}, \mathbf{u}, t)\big] \tag{2.53}$$

In short, with the balance equation for the total force, there is one more for the rate of change of angular momentum, or total torque (i.e., $\boldsymbol{\tau} = \mathbf{r} \wedge \mathbf{F}$):

$$\boldsymbol{\tau} = \boldsymbol{\tau}_B + \boldsymbol{\tau}_H + \boldsymbol{\tau}_U = \mathbf{0} \tag{2.54}$$

where the subscripts $H$ and $U$ indicate again hydrodynamic and direct contributions. Similarly, one arrives at:

$$\boldsymbol{\tau}_B = -k_B T \vec{\mathbf{R}} \ln W(\mathbf{r}, \mathbf{u}, t) \tag{2.55}$$

$$\boldsymbol{\tau}_U = -\vec{\mathbf{R}} U(\mathbf{r}, \mathbf{u}) \tag{2.56}$$

where $\vec{\mathbf{R}}$ is the "rotational operator," dual to the gradient operator for translational diffusion:

$$\vec{\mathbf{R}} = \mathbf{u} \wedge \vec{\nabla}_{\mathbf{r}} \tag{2.57}$$

Accordingly, Smoluchowski's operator can be written symbolically as:

$$k_B T \mathcal{L}_{\mathrm{r}} = (\vec{\nabla}_{\mathbf{r}}\ \vec{\mathbf{R}}) \cdot \begin{pmatrix} \mathbf{D}_{\mathrm{TT}} & \mathbf{D}_{\mathrm{TR}} \\ \mathbf{D}_{\mathrm{RT}} & \mathbf{D}_{\mathrm{RR}} \end{pmatrix} \cdot \begin{pmatrix} \underline{\vec{\nabla}}_{\mathbf{r}} \\ \underline{\vec{\mathbf{R}}} \end{pmatrix} \tag{2.58}$$

with the notation:

$$\underline{\ldots} \equiv \ldots U + k_B T \ldots \tag{2.59}$$

and where the diffusion tensor has been subdivided in four roto-translational parts, on the basis of their contributions to translational (T) and rotational (R) velocities:

$$k_B T \mathbf{v} = -\mathbf{D}_{\mathrm{TT}} \cdot \mathbf{F}_H - \mathbf{D}_{\mathrm{TR}} \cdot \boldsymbol{\tau}_H \tag{2.60}$$

$$k_B T \boldsymbol{\omega} = -\mathbf{D}_{\mathrm{RT}} \cdot \mathbf{F}_H - \mathbf{D}_{\mathrm{RR}} \cdot \boldsymbol{\tau}_H \tag{2.61}$$

This setting is rather complicated and, normally, of no particular avail. Notwithstanding, in the absence of hydrodynamic forces, it can be simplified to a certain extent, and expressed as:

$$k_B T \mathcal{L}_{\mathrm{r}} = \vec{\nabla}_{\mathbf{r}} \cdot (D_+ \mathbf{I} + D_- \mathbf{S}_{(\mathbf{u})}) \cdot \underline{\vec{\nabla}}_{\mathbf{r}} + D_r \vec{\mathbf{R}} \cdot \underline{\vec{\mathbf{R}}} \tag{2.62}$$

in which $3D_+ = D_\parallel + 2D_\perp$, $D_- = D_\parallel - D_\perp$, and the quantity:

$$\mathbf{S}_{(\mathbf{u})} = \mathbf{uu} - \frac{1}{3}\mathbf{I} \tag{2.63}$$

is an "order parameter" tensor, quantifying anisotropy and yielding a zero contribution for any isotropic distribution function. If the potential field is negligible too (e.g., in dilute systems), one is left with three terms, of evident significance:

$$\mathcal{L}_{\mathrm{r}} = D_+ \vec{\nabla}_{\mathbf{r}}^2 + D_r \vec{\mathbf{R}}^2 + D_- \vec{\nabla}_{\mathbf{r}} \cdot \mathbf{S}_{(\mathbf{u})} \cdot \vec{\nabla}_{\mathbf{r}} \tag{2.64}$$

## 1.6 Langevin's equation and spatio-temporal scales

Brownian motion can be faced exactly by a phase space description, taking the stochastic velocity process into account. This work was carried out by Langevin, whose stochastic equation recovers Einstein's results over much longer time intervals than the typical velocity correlation time. The large difference between relaxation times of Brownian particles ($\gtrsim 10^{-9}$ s) and liquid molecules ($\tau_L \sim 10^{-14}$ s), caused by their different mass (and volume), has important implications in the stochastic analysis of Brownian movement. We have already seen that such particles, as colloids, undergo numerous random collisions with solvent molecules, resulting in the stochastic force $\mathbf{F}_B(t)$, rapidly fluctuating on the molecular time scale, in the liquid. It may be striking to note that a small diffusing molecule may step to the "left or right" $\sim 10^6$ times in $\sim 10^{-6}$ s. However, remember that the typical zig-zag appearance of a Brownian path is mainly due to the fluctuations in the sum of huge amounts of small velocity perturbations. A second force, still arising from random collisions, is the friction exerted by the liquid on the particle, and acting on a distinct time scale. Molecular impacts will more frequently take place on the particle "front," than on its "back" side, causing a systematic force that tends to slow down with increasing velocity.

As already said, when the Brownian volume greatly exceeds that molecular, it will equate $-\alpha_S \mathbf{v}$. This is the hydrodynamic friction of a macroscopic body reaching a given velocity, re-expressible then by the Sutherland–Stokes–Einstein relation if $|\mathbf{v}|$ does not take too large values. These observations imply that Newton's second law of motion must lead to a stochastic equation in the momentum (and position) phase space coordinates, familiarly known as Langevin's equation:

$$\left(\frac{d\mathbf{p}}{dt}\right) = -\nu_S \mathbf{p} + \mathbf{F}_B(t) \tag{2.65}$$

where the characteristic frequency $\nu_S \equiv \frac{\alpha_S}{m}$ is the inverse of the characteristic time after which the friction felt by the Brownian particle is balanced by all other forces. Observe that Langevin's and Smoluchowski's representations are equivalent whenever the spatial gradient of the diffusion constant is zero, a condition already seen to be implied by Oseen's approximation. Otherwise, the random velocity is clearly corrected by the contribution of $\vec{\nabla} D$, compensating the flux driven by the position-dependence of the random force.

Since collisions keep briefly correlated, one may take advantage of the central limit theorem, and regard $\mathbf{F}_B(t)$ as a Gaussian delta-correlated (or "white-in-time") process:

$$\overline{\mathbf{F}_B(t)} = 0, \qquad \overline{\mathbf{F}_B(t)\mathbf{F}_B(t')} = \delta(t - t')\mathbf{S}_F \tag{2.66}$$

the ($3^2$) matrix $\mathbf{S}_F$ being the so-called "fluctuation strength." From the previous relations, it is clear that the general approach sacrifices any deterministic solution, and concentrates on the statistical description allowed by the ensemble properties of the (Brownian) stochastic forces. These averages witness in particular that the random acceleration changes much faster than velocity and, from a certain time instant on ($t \gg \tau_L$), will get stochastically independent of it. Essentially, velocity will behave as a Markovian process. In addition, the shortest interval ($\tau_{\mathrm{FP}} \gg \tau_L$) over which they become statistically meaningful is said to be the "Fokker–Planck time scale." Note also that the above infinitely sharply peaked time correlation behavior identifies the self-correlation function for the derivative of the Bachelier–Wiener process, more popularly known as "white noise." Such a differentiation could not be done in itself, but may be rendered meaningful by its integral definition (i.e., $\mathbf{x}_B = \int \dot{\mathbf{x}}_B \, dt$).

In the following, a full solution of Langevin's equation will be given in tensor form by the stochastic analysis of each phase-space coordinate. We need, of course, to integrate it out:

$$\mathbf{p}(t) = \varsigma(t)\mathbf{p}_0 + \int_0^t \mathbf{F}_B(t')\varsigma(t - t')\, dt' \tag{2.67}$$

where the second addendum on the right is a convolution between functions evolving over very different scales with, for convenience, $\varsigma(t) \equiv \mathrm{e}^{-\nu_S t}$, and heretofore $\ldots_0 \equiv \ldots(0)$. Close to Einstein's theory, a time interval can be chosen which is much longer than the solvent relaxation time, and much shorter than the Brownian one. Owing to this temporal resolution, the friction term in the integral may be considered constant, and the random force would show so many independent realizations that the central limit theorem can be applied. The second addendum on the right side thus identifies a sum of independent Gaussian variables with zero mean, implying that $\mathbf{P}(t) \equiv \mathbf{p}(t) - \varsigma(t)\mathbf{p}_0$ is also normal with $\overline{\mathbf{P}(t)} = 0$. Obviously, this should not give the wrong suggestion to set the stochastic force to zero, as it remains delta-correlated at any time.

Proceeding with the calculations, one arrives at:

$$\alpha_S\big[\mathbf{r}(t) - \mathbf{r}_0\big] = \big[1 - \varsigma(t)\big]\mathbf{p}_0 + \int_0^t \mathbf{F}_B(t')\big[1 - \varsigma(t - t')\big]\,dt' \tag{2.68}$$

so that $\mathbf{R}(t) \equiv \Delta\mathbf{r}(t) - [1 - \varsigma(t)]\mathbf{p}_0/\alpha_S$ is again a Gaussian variable, with $\Delta\mathbf{r} \equiv \mathbf{r} - \mathbf{r}_0$ and $\overline{\mathbf{R}(t)} = 0$. The joint stochastic process, $\mathbf{H} = (\mathbf{R}, \mathbf{P})$, lies so in a 6-dimensional space with the (same) normal distribution function of the phase-space aleatory vector $(\mathbf{r}, \mathbf{p})$:

$$W(\mathbf{r}, \mathbf{p}, t \mid \mathbf{r}_0, \mathbf{p}_0, 0) = (2\pi)^{-3}(\det \mathbf{C}_H)^{-\frac{1}{2}} \mathrm{e}^{-\frac{1}{2}\mathbf{H}\cdot\mathbf{C}_H^{-1}\cdot\mathbf{H}} \tag{2.69}$$

The latter denotes a "multivariate" Gaussian distribution function, where $\mathbf{C}_H$ is a $6^2$ "correlation tensor" (or "covariance matrix"), generally defined by:

$$\mathbf{C}_X = \overline{(\mathbf{X} - \overline{\mathbf{X}})(\mathbf{X} - \overline{\mathbf{X}})} \tag{2.70}$$

and simplifying into $\mathbf{C}_X = \mathrm{diag}(\overline{\mathbf{X}}_1^2, \ldots, \overline{\mathbf{X}}_n^2)$ whenever all of its components can benefit from the independence property:

$$\overline{\mathbf{X}_s\mathbf{X}_{s'}} = \overline{\mathbf{X}}_s\overline{\mathbf{X}}_{s'} \tag{2.71}$$

Here, they comply with:

$$2\nu_S\alpha_S^2\overline{\mathbf{R}(t)\mathbf{R}(t)} = \big[2\nu_S t - \varsigma(2t) - 3 + 4\varsigma(t)\big]\mathbf{S}_F \tag{2.72}$$

$$2\nu_S\overline{\mathbf{P}(t)\mathbf{P}(t)} = \big[1 - \varsigma(2t)\big]\mathbf{S}_F \tag{2.73}$$

$$\nu_S\alpha_S\overline{\mathbf{R}(t)\mathbf{P}(t)} = \big[1 - \varsigma(t)\big]^2\mathbf{S}_F \tag{2.74}$$

and symmetrically for $\overline{\mathbf{P}(t)\mathbf{R}(t)}$. At long times, the second component reduces to:

$$2\nu_S\overline{\mathbf{p}(t)\mathbf{p}(t)} \simeq \mathbf{S}_F \qquad (\nu_S t \gg 1) \tag{2.75}$$

and, from the equipartition theorem (the average value of each independent quadratic term in the Hamiltonian contributes to $k_BT/2$), $\overline{\mathbf{p}^2} = mk_BT$:

$$\mathbf{S}_F = 2\alpha_S k_B T\mathbf{I} \tag{2.76}$$

This relationship, between force correlation function and friction, which dissipates kinetic energy into heat, is a version of the "fluctuation–dissipation" theorem, better commented in the next subsection. We are finally in a position to calculate the full variance expressions for the random position and momentum:

$$\alpha_S^2\overline{\Delta\mathbf{r}(t)\Delta\mathbf{r}(t)} = \big[\varsigma(t)-1\big]^2\mathbf{p}_0\mathbf{p}_0 + mk_BT\big[2\nu_S t - \varsigma(2t) - 3 + 4\varsigma(t)\big]\mathbf{I} \tag{2.77}$$

$$\overline{\mathbf{p}(t)\mathbf{p}(t)} = mk_BT\big[1-\varsigma(2t)\big]\mathbf{I} + \varsigma(2t)\mathbf{p}_0\mathbf{p}_0 \tag{2.78}$$

in line with a theorem of Joseph L. Doob (1942), stating that the correlation function of a Gaussian and Markovian process is exponential.

From the former treatation, the crossover condition $\nu_S t = 1$ (or $t = \tau_B \simeq 10^{-9}$ s) turns out immediately to demarcate a pair of relevant regimes. When $t \ll \tau_B$, the Brownian particle does not experience (yet) the friction caused by the collisions with the solvent molecules, and behaves as it were moving "ballistically":

$$\overline{(\Delta\mathbf{r})^2} \simeq (\mathbf{v}_0 t)^2 \tag{2.79}$$

otherwise, Einstein's law is recovered ($D \equiv k_BT/\alpha$) in the so-called "hydrodynamic limit" ($t \gg \tau_B$):

$$\overline{(\Delta\mathbf{r})^2} \simeq 2Dt\mathbf{I} \tag{2.80}$$

It means that, as a consequence of the systematic collisions, the random velocity undergoes so many changes that the particle displacement slows down significantly, evolving asymptotically with $\sim t$.

The relevant spatio-temporal scales of a natural phenomenon (always) define the minimum resolution intervals over which the physical quantities are averaged, and their knowledge is equivalent to handle the whole phenomenon. This expresses quantitatively the idea that the responses of a system are perceived differently at different scales. Here, there are basically four, ordered as $\tau_L \ll \tau_{\mathrm{FP}} \ll \tau_B \ll \tau_D$. Besides the solvent relaxation time ($\tau_L$), the Fokker–Planck ($\tau_{\mathrm{FP}}$) points out the maximum time interval in which the motion is still ballistic. Over this scale, the Brownian particle phase-space is the only one to matter, as that of the liquid molecules can be regarded at thermal equilibrium. Remember, for whatever correlation function, that the short-time domain can generally be studied in detail by Maclaurin's expansions in powers of time, with coefficients equal to statistical frequency moments, and characterizing the (liquid) system at equilibrium. To get rid of particle momenta, and get back to Einstein's model, one must wait for the inertial forces to become irrelevant, that is, for another scale, the diffusive Einstein–Smoluchowski's ($\tau_D$).

Time scales will have counterparts in the corresponding coarsening of the spatial resolution, and a very important one is the diffusive length scale ($\ell_D$). For a Brownian particle performing large enough displacements, it is the largest length scale of interest and, from the equipartition theorem:

$$\ell_D/\mu_m = \overline{|\mathbf{p}_0|} \simeq \sqrt{3mk_BT} \tag{2.81}$$

Using the Sutherland–Stokes–Einstein relation helps us to realize that space will be resolved into tiny fractions of the particle size, $\lambda_D/r_a \simeq (10^{-4}{\div}10^{-3})$. The value of the diffusive length scale, in the term $-\ell_D^2$, also appears in the intercept onto the spatial axis, obtained by prolonging the tangent of the time-dependent mean square displacement at $t = \tau_D$. Of course, other time scales will emerge whenever Brownian particles interact together. One is the "interaction" scale and one other is the "hydrodynamic" scale, but while the latter is comparable to $\tau_D$, the former can exceed it a lot, according to the nature of the involved interparticle and surface forces.

## 1.7 Markov's processes and Fokker–Planck formalism

According to the extent of "memory" retained of the "past," two are in essence the simplest examples of stochastic process. One is that "completely random," with no memory ($t_{s-1} < t_s$):

$$W_n(x_1, t_1; \ldots; x_n, t_n) = \prod_{s=1}^{n} W_1(x_s, t_s) \tag{2.82}$$

that, from the definition of conditional probability (density), of an event $\{x_n, t_n; \ldots; x_{n-j}, t_{n-j}\}$ given the knowledge of $\{x_{n-j-1}, t_{n-j-1}; \ldots; x_1, t_1\}$:

$$\begin{aligned} &W(x_n, t_n; \ldots; x_{n-j}, t_{n-j} \mid x_{n-j-1}, t_{n-j-1}; \ldots; x_1, t_1) \\ &\quad = \frac{W_n(x_1, t_1; \ldots; x_n, t_n)}{W_{n-j}(x_1, t_1; \ldots; x_{n-j-1}, t_{n-j-1})} \end{aligned} \tag{2.83}$$

implies:

$$W(x_n, t_n \mid x_{n-1}, t_{n-1}; \ldots; t_1, x_1) = W_1(x_n, t_n) \tag{2.84}$$

and the property of statistical independence at any two times ($t \neq t'$). These processes are fully determined by $W_1$ and, when stationarity holds, $W = W_2(x_1, x_2; t_2 - t_1) = W_1(x_1)W_1(x_2)$, regardless of time increments.

A little more complicated, yet more interesting, are Markov's short memory processes, where the probability for $(x_n, t_n)$ is only conditioned by the (preceding) closest time:

$$W(x_n, t_n \mid x_{n-1}, t_{n-1}, \ldots, x_1, t_1) = W(x_n, t_n \mid x_{n-1}, t_{n-1}) \tag{2.85}$$

the function on the right determining the "transition probability" between times $t_n > t_{n-1}$. Every distribution function, from $n = 3$ on, will be clearly deduced from the knowledge of the second-order statistics ($W_2$). For stationary Markov's processes (or "homogeneous chains"), the memory of the initial state is gradually lost, $W(x_2, t \to \infty \mid x_1) = W_1(x_2)$. We saw this feature to hold in the classical Brownian motion treatment, so as in the sharply peaked behavior at infinitely short times, $W(x_2, t \to 0^+ \mid x_1) = \delta(x_2 - x_1)$, keeping in mind of course that not all matter diffusion or self-diffusion phenomena can be described by homogeneous Markov's chains. More generally, there are (physically real) processes that can be Gaussian but are not (strictly) Markovian.

The short-memory property leads to the Chapman–Kolmogorov equation which, in a continuous time, expresses an identity relation for the transition densities:

$$W(x_{s+1}, t_{s+1} \mid x_{s-1}, t_{s-1}) = \int W_1(x_{s+1}, t_{s+1} \mid x_s, t_s) W(x_s, t_s \mid x_{s-1}, t_{s-1})\, dx_s \tag{2.86}$$

the integral summing over all "intermediate" Markovian states ($s$). By removing the conditioning symbol, one gets back to "Bachelier's chain equation," compatible again with the convolution features of Gaussian density functions. Anyway, Chapman–Kolmogorov's gives the basis to the Fokker–Planck equation that, for a Brownian movement, yields a deterministic description for the temporal variation of the probability distribution function of the random velocity ($\mathbf{v}$). After setting $x_{s-1} \to v_0$, $x_s \to v'$, and $x_{s+1} \to v$, it returns another "Smoluchowski's equation":

$$W(v, t + \tau \mid v_0) = \int_{-\infty}^{\infty} W\big(v, \tau \mid v'\big) W\big(v', t \mid v_0\big)\, dv' \tag{2.87}$$

being $t_{s+1} - t_s \to \tau$ and $t_s - t_{s-1} \to t$. Let $\tau$ be a short time and $\delta v \equiv v - v'$, the following expansion holds:

$$\begin{aligned}\tau\left(\frac{\partial W}{\partial t}\right) &= -W(v, t \mid v_0) \\ &\quad + \int_{-\infty}^{\infty} W(v, \tau \mid v - \delta v) W(v - \delta v, t \mid v_0)\, d\delta v \end{aligned} \tag{2.88}$$

that, in terms of moments $\mu_{i\tau} \equiv \overline{[\Delta \mathbf{v}(\tau)]^i}$, of the aleatory velocity increment in a time $\tau$:

$$\tau \mu_{i\tau} \equiv \int_{-\infty}^{\infty} v^i W(v + \delta v, \tau \mid v)\, d\delta v \tag{2.89}$$

becomes a differential equation for $W = W(\mathbf{v} = v, t \mid \mathbf{v}_0 = v_0)$:

$$\left(\frac{\partial W}{\partial t}\right) = \sum_{i=1}^{\infty} \frac{(-1)^i}{i!} \left(\frac{\partial^i \mu_{i\tau} W}{\partial v^i}\right) \tag{2.90}$$

The integral domain mostly contributing to the Chapman–Kolmogorov equation lies in a small neighborhood of $\delta v = 0$, at which any moment is centered and $W(v, \tau \mid v - \delta v)$ expected to be sharply peaked. We consider now the limit of macroscopically infinitesimal time increments (say, $\tau \to 0$), and each moment with $i > 2$ to approach zero faster than $\tau$. As $\mu_{i\tau}$ converges to a finite function only for $i = 1, 2$, one is carried to the Fokker–Planck, or "forward" equation ("future from past"):

$$\left(\frac{\partial W}{\partial t}\right) = -\left(\frac{\partial \mu_1 W}{\partial v}\right) + \frac{1}{2}\left(\frac{\partial^2 \mu_2 W}{\partial v^2}\right) \tag{2.91}$$

where the adjoint "backward" version of it ("past from future"), still due to Kolmogorov, comes from differentiating with respect to earlier times. Note that, once the short-time behavior of $\mu_{1,2}$ is determined, the probability function is set at every time. However, while $\mu_2$ relates the asymptotic solution at thermal equilibrium, and is easier to work out, $\mu_1$ may require perturbation techniques. By recalling the previous theories, it can also be argued that in the Fokker–Planck formalism for a set of random variables, $\mu_1$ will be replaced by a drift vector and $\mu_2$ by a diffusion tensor.

For a Brownian movement, initially fluctuating with $\mathbf{v}_0 = v_0$, it models the stationary process for the particle approach to equilibrium. Because $\mu_1 = \overline{\Delta \mathbf{v}(\tau)}/\tau = -\nu_S v$, $\mu_2 = \overline{[\Delta \mathbf{v}(\tau)]^2}/\tau = 2\nu_S k_B T/m$ $(\mu_{n>2} = 0)$ and the boundary condition $W(v, t \to 0^+ \mid v_0) = \delta(v - v_0)$, one obtains a standard diffusion equation in the rescaled quantities $t \to [\varsigma(-2t) - 1]/(2\nu_S)$, $v \to \varsigma(-t)v$, and $D \to \nu_S k_B T/m$. It is solved, evidently, by the same normal density function of Einstein's approach, thence $(d = 1)$:

$$W(v, t \mid v_0) = \left\{\frac{2\pi k_B T}{m}\left[1 - \varsigma(2t)\right]\right\}^{-\frac{1}{2}} \exp\left(-\frac{[v - \overline{\mathbf{v}(t)}]^2}{\frac{2\pi k_B T}{m}[1 - \varsigma(2t)]}\right) \tag{2.92}$$

with average $\overline{\mathbf{v}(t)} = \varsigma(t)v_0$. At thermal equilibrium $(t \to \infty)$, Maxwell's distribution is thus regained with $\overline{\mathbf{v}(t)} = 0$ and $\overline{\mathbf{v}^2(t)} = k_B T/m$.

## 1.8 Rotational Brownian motion

It was seen that, in a rotational Brownian motion (or diffusion), the particle orientation changes irregularly under a random torque generated by the thermal environment. We may thus inquire ourselves for the rotational analogue of Einstein's approach. The simplest (though unrealistic) situation is that of a spherical particle of constant diameter, rotating about a fixed axis. Orientations will be specified by the random angle $\widehat{\mathbf{u}_0\mathbf{u}(t)} \equiv \boldsymbol{\theta} \in [0, \pi)$, and its family of correlation functions. Evidently, the same arguments adopted for translational diffusion will equally hold, and a Fokker–Planck equation can be written as:

$$\left(\frac{\partial W}{\partial t}\right) = D_r\left(\frac{\partial^2 W}{\partial \theta^2}\right) \tag{2.93}$$

Since the orientational distribution function, $W = W(\boldsymbol{\theta} = \theta, t)$, must be periodic in any multiple of $2\pi$, $W(2z\pi, t) = W(2z'\pi, t)$ $(z, z' \in \mathrm{Z})$, the main difference with the translational case is in the boundary conditions. In addition, every statistical moment of the random angle is bounded at every instant, thus will increase limitedly with increasing time. To solve the previous equation, it is convenient to multiply it by $\sin^2\theta$, averaging over $\theta$:

$$\left(\frac{d\overline{\sin^2\boldsymbol{\theta}}}{dt}\right) = D_r\left(1 - 2\overline{\sin^2\boldsymbol{\theta}}\,\right) \tag{2.94}$$

and, after fixing $\overline{\sin^2\boldsymbol{\theta}_0} = 0$, it turns out:

$$2\overline{\sin^2\boldsymbol{\theta}} = 1 - \mathrm{e}^{2D_r t} \tag{2.95}$$

Taylor's expansion near $t = 0$ returns the short-time behavior:

$$\overline{\Delta\boldsymbol{\theta}^2(t)} \simeq D_r t \tag{2.96}$$

again, with a crossover value $D_r^{-1}$, demarcating the linear transient ($D_r t \ll 1$) from the asymptotically constant ($D_r t \geqslant 1$) regimes.

A more precise analysis can follow, of course, from using stochastic processes, and the simplest Langevin's (or Euler–Langevin) equation holding for a rotating sphere (or a spherical top molecule) is, explicitly:

$$\mathrm{I}\left(\frac{d\boldsymbol{\omega}}{dt}\right) = -\alpha_r\boldsymbol{\omega} + \boldsymbol{\tau} + \boldsymbol{\phi} \tag{2.97}$$

where I is the moment of inertia, $\alpha_r$ is the friction coefficient for rotational motion, so that $-\alpha_r\boldsymbol{\omega}(t)$ is a Brownian damping torque, and $\boldsymbol{\phi}(t)$ denotes a stochastic external field. In the non-inertial regime, the smallest (negligible) torque is obviously that due to the angular acceleration, and $\boldsymbol{\omega}$ can be canceled out:

$$\alpha_r\left(\frac{d\mathbf{u}}{dt}\right) = \boldsymbol{\tau} \wedge \mathbf{u} + \left(\frac{d\mathbf{u}}{dt}\right)_{\phi} \tag{2.98}$$

the last term being the force field contribution to the orientational rate of change. Note that, as expected from the meaning of continuity equation, the operator in Smoluchowski's (equivalent) formalism:

$$\mathcal{L}_{\mathrm{rU}} = D_r\vec{\nabla}^2 - \alpha_r^{-1}\vec{\nabla}\cdot\left(\frac{d\mathbf{u}}{dt}\right)_{\phi} \tag{2.99}$$

is (minus) the divergence of a current density, taking a diffusive and a field flux into account.

Rotational diffusion takes a central role in (the relaxation processes of) many polarized systems (e.g., dielectrics and N.M.R. measurements), and the pioneering approach to it is credited to Peter J.W. Debye (1913–1929). In the framework of dielectric theory, he employed Smoluchowski's formalism to get the effect of a constant field on the relaxation of the dipole moment of a rigid particle. Generally, there are two (antagonistic) contributions to the medium polarization, as the alignment of polar molecules, with torques fixed by the external field, tends to be broken by the Brownian collisions. Debye, in essence, expressed the Laplacian and divergence operator in the azimuth and zenith angles, and proceeded to solve Smoluchowski's equation. He found in the end that the (mean) dipole moment relaxes exponentially with "Debye's relaxation time," just equal to twice a rotational diffusion coefficient given by $D_r = k_B T/\alpha_r$.

However, diffusing particles are seldom perfect spheres, and rotational dynamics may actually become a tough task. From analytical mechanics, it is known in fact that rotations about distinct axes are not compatible (do not commute). Moreover, one could be no longer allowed to reasonably express the angular velocity as a simple time derivative of a unit orientation vector. If inertial contributions are ignored, the rotatory friction (or diffusion) tensor replaces that of inertia, usefully classified by its "principal moments of inertia" ($\mathrm{I}_s$), the eigenvalues it has in the basis of "principal axes of rotation" ($\mathbf{o}_s$). As a result, the solutions become increasingly difficult with increasing (rotational) asymmetry. When "spherical tops" ($\mathrm{I}_k = \mathrm{I}$) are abandoned for symmetrical tops ($\mathrm{I}_1 = \mathrm{I}_2 \neq \mathrm{I}_3$), one can resort to Smoluchowski's formalism, with operator specified by the principal axes of rotation (and eigenvalues $D_s$):

$$\mathcal{L}_{\mathrm{o}} = \sum_s \frac{\partial}{\partial \mathbf{o}_s} D_s \frac{\partial}{\partial \mathbf{o}_s} \tag{2.100}$$

while, for asymmetric tops ($\mathrm{I}_1 \neq \mathrm{I}_2 \neq \mathrm{I}_3$), approximated solutions are only available.

## 1.9 Notes on fluctuation–dissipation theorem

The concept of fluctuation is one of the most ubiquitous and densely meaningful in all sciences. It can be recovered in Darwin's theory of evolution, in the deep insight of spontaneous fluctuations of living systems, as well as in relativistic cosmology, where Dimitrii I. Blokhintsev (1975) envisaged that the spacetime metric should fluctuate at a length scale $\sim 10^{-34}$ m. In general, a physical body is constantly subject to fluctuating forces, coming from the environment with which it exchanges energy continuously. When they show no correlation in space and time, nor obey any dynamic law, physical variables will be correspondingly uncorrelated. The understanding of Brownian fluctuations at thermal equilibrium is to this end paradigmatic. As suspended particles cannot get energy from the surroundings incessantly, a major point to be solved at Einstein's time was how to conciliate these two, apparently conflicting, phenomenologies. Evidently, there had to be some dissipation mechanism which does not prevent the fluctuating particles from approaching equilibrium and, intuitively, the answer had to be sought in the host medium, acting as a common source for both random and dissipative forces.

One so arrives at a fundamental detailed-balance condition of statistical mechanics, bearing the name of "fluctuation–dissipation theorem." It asserts that, when a thermodynamic system lies at equilibrium, the responses to a small external perturbation and to a spontaneous internal fluctuation without that disturbance, are the same. In this way, the theories of equilibrium fluctuations and linear response become intimately related. Despite it lies much behind Brownian motion, Einstein's probability approach resulted in an elegantly simple realization of it, in which particle diffusion and mobility coefficients connect through the Einstein–Smoluchowski equation. In other words, (the responses to) particle fluctuations at rest ($D$) and (to) friction forces ($\alpha_S$) would have the same origin. This theorem was argued by Harry Nyquist (1928), who applied classical statistical mechanics arguments to explain the mean square fluctuation voltage in a resistor, in the experiment on electrical noise published in the same year by John B. Johnson (the "Johnson–Nyquist noise"). Herbert B. Callen and Theodore A. Welton (1951) gave a first (quantum) demonstration, widening its applicability to an ample class of phenomena. Over the years, it was clearly exploited in two manners, to link the (microscopic) molecular dynamics at thermal equilibrium to the (macroscopic) dynamic response detected experimentally. It can predict the behavior of fluctuations from dissipative features (Nyquist's theorem) and vice versa, as in the demonstration of the symmetry of kinetic coefficients provided by Lars Onsager (1931).

Consider thus the (linear) expectation change of a time-dependent quantity ($Q$), with and without application of a (weak) field $\phi$:

$$\overline{Q(t)} - \overline{Q_0} = \int_{-\infty}^{t} \mathrm{M}(t-t')\phi(t')\,dt' \tag{2.101}$$

meaning $Q(t) \equiv Q(\phi = \phi(t))$, $Q_0 \equiv Q(\phi = 0)$ and $\mathrm{M}(t)$ specifying the "response function" (or "susceptibility"), as in the formulation by Ryogo Kubo (1956–1957). If potential and scalar fields are related via a "conjugate" observable ($Q^*$), $U(\mathbf{r}, t) = -Q^*(\mathbf{r})\phi(t)$, the fluctuation–dissipation theorem implies that correlation and response functions relate in turn through:

$$\frac{d}{dt}\overline{Q_0^* Q(t)} = -k_B T \mathrm{M}(t) \tag{2.102}$$

However, the most appropriate working space for the fluctuation analysis is the frequency domain and, when Langevin's is the starting equation, a first version of this theorem is:

$$2\nu_S \overline{|\mathbf{p}^2|} = \mathrm{S}_{BB}(\omega) \tag{2.103}$$

expressing the balance of dissipation ($\nu_S$) and fluctuation ($\overline{|\mathbf{p}^2|}$) terms by the power spectral density of the Brownian force (e.g., in vector form):

$$\mathrm{S}_{BB}(\omega) = \int_{-\infty}^{\infty} \overline{\mathbf{F}_B(0) \cdot \mathbf{F}_B(t)}\mathrm{e}^{\mathrm{i}\omega t}\,dt \tag{2.104}$$

whose existence is ensured to any (wide sense) stationary process, for which Fourier's transform does not exist, by the Wiener–Khinchin–Kolmogorov theorem. Note that the last but one equation could be rewritten for any Langevin's formalism, provided the characteristic frequency, momentum and force be replaced by the corresponding quantities. When $\mathbf{F}_B$ is regarded pointwise correlated in time ("white" spectral density, constant in the whole $\omega$-domain), a "second fluctuation–dissipation theorem" can be written as:

$$\alpha_S = \frac{1}{k_B T d} \int_{0}^{\infty} \overline{\mathbf{F}_B(0) \cdot \mathbf{F}_B(t)}\,dt \tag{2.105}$$

the equipartition theorem being exploited again. There is finally a third version, using the zero-frequency spectral density of a fluctuating quantity, i.e., ($X$):

$$\lim_{\omega\to 0} S_{XX}(\omega) = 2\int_0^\infty \overline{X(0)X(t)}\,dt \tag{2.106}$$

Therefore, let $X \to \mathbf{p}$, the first formulation returns:

$$D = \frac{1}{d}\int_0^\infty \overline{\mathbf{v}(0)\cdot\mathbf{v}(t)}\,dt \tag{2.107}$$

as it had to be, from the definition:

$$2dD \equiv \lim_{t\to\infty}\left[\frac{d\overline{(\Delta\mathbf{r})^2}}{dt}\right] \tag{2.108}$$

the spatial displacement being the integral of the random velocity, thence the square particle position:

$$(\Delta\mathbf{r})^2 = \int_{-\infty}^{t}\int_{-\infty}^{t} \mathbf{v}(t')\cdot\mathbf{v}(t'')\,dt'\,dt'' \tag{2.109}$$

With absolute molecular disorder, the sign of velocity is as often positive as negative, and the mean value of the last expression (the variance) is the lowest-order statistical moment which does not vanish. It may be worth while remembering that averaging is performed here over a particle track ensemble, when many particles are released at the same time at different positions in a spatially homogeneous medium. Furthermore, if stationarity applies, it turns out:

$$\overline{(\Delta\mathbf{r})^2} = 2\int_0^t (t-t')\overline{\mathbf{v}(0)\cdot\mathbf{v}(t')}\,dt' \tag{2.110}$$

bringing to the former equation for $D$, as well as to the fundamental law of stochastic dynamics:

$$\frac{1}{2}\left[\frac{d^2\overline{(\Delta\mathbf{r})^2}}{dt^2}\right] = \overline{\mathbf{v}(0)\cdot\mathbf{v}(t)} \tag{2.111}$$

By this way, remember that the velocity autocorrelation function obeys in turn ($m\mathbf{f} \equiv \mathbf{F}$):

$$\overline{\mathbf{f}(0)\cdot\mathbf{f}(t)} = -\frac{d^2}{dt^2}\overline{\mathbf{v}(0)\cdot\mathbf{v}(t)} \tag{2.112}$$

so that force and position self-correlation functions connect by a fourth-order time derivative. The diffusion coefficient (and any close) expression belongs to the family of "Green–Kubo" relations, written for instance as:

$$k_B T L_k = V \int_0^\infty \overline{\mathbf{j}_k(0) \cdot \mathbf{j}_k(t)}\, dt \tag{2.113}$$

derived by Melville S. Green (1954) and Kubo (1957) to get the linear transport coefficients ($L_k$) from the autocorrelation function of the conjugate flux ($j_k$) in a system with volume $V$ at temperature $T$. They hold irrespective of the nature of the transport process, with the obvious prescription it be taken again in the small force field limit (i.e., an infinitely slow process). For instance, the shear viscosity coefficient ($L_k = \eta$) follows from the time integral of the stress tensor (or momentum-flux) autocorrelation function.

The assumption of a systematically constant friction has the great advantage to allowing for the simplest of Langevin's descriptions, but can only be reasonable when particle accelerations are negligible. We are also used to dealing with random force and velocity self-correlation functions which are respectively pointwise correlated and decaying exponentially in time:

$$\overline{\mathbf{v}(0) \cdot \mathbf{v}(t)} = \overline{\mathbf{v}^2(0)}\varsigma\big(|t|\big) \tag{2.114}$$

Actually, friction is often a dispersive phenomenon, with frequency dependence that is strongly influenced by the specific fluid dynamics, and these features are not generally true. Stochastic force and friction are normally coupled, in particular at high frequency (or large dynamic coherence), when Brownian movement is affected by a few collisions, and the exponential velocity autocorrelation function no longer applies. Another relevant effect originates from the fluid inertia, producing an exponential self-correlation decay like $t^{-\frac{3}{2}}$ and $t^{-\frac{5}{2}}$, respectively in translational and rotational Brownian movements. The high-frequency behavior of the medium inertia, compressibility and viscosity, may generate strong couplings with random force spectra and velocity correlation functions, and the internal rotation of fluid molecules can also influence the particle dynamics, either in high or low frequency domains.

Ryogo Kubo (1965) supplied this deficiency by extending the friction constant to a frequency-dependent behavior. For the second fluctuation–dissipation theorem to hold, it has to become Fourier's time-dependent transform of the (stationary) correlation function of the Brownian force at equilibrium. In line with this, a more detailed fluctuation analysis can be afforded by "Langevin's generalized equation," as in the formulation due to Hazime Mori (1965) and Kubo (1966). The former, in particular, put forward an earlier approach, initiated by Robert W. Zwanzig (1961), who devised the tool of projection operator to get the relevant information without calculating the distribution function over the entire phase space (the so-called Zwanzig–Mori "projection–operator" technique). Aside from dynamic details of the host molecules, Mori could so focus on the properties of the Brownian particle alone.

In its deepest significance, the "Langevin's generalized equation" states that as the state of a system in equilibrium varies with time, any aleatory variable identifies a stationary stochastic process with equation:

$$\left(\frac{d\mathbf{x}}{dt}\right) = -\int_{0}^{t} \widehat{\nu}(t-t')\mathbf{x}(t')\,dt' + \mathbf{f}(t) \tag{2.115}$$

the force term being uncorrelated to the initial variable value, $\overline{\mathbf{x}(0)\mathbf{f}(t)} = 0$, and $\widehat{\nu}(t)$ being now a "memory" function, or "retardation" kernel. In our case, it stands evidently for a numerically valued time-dependent friction, slowing down the aleatory velocity $\mathbf{v}(t)$ ($\equiv\mathbf{x}(t)$) in the presence of $\mathbf{F}_B \equiv \mathbf{f}$. The random force can also include external fields and an imaginary-valued term ($\propto i\mathbf{x}$), which always dies off provided the stochastic process does not consist of a sum of time-reversal symmetry contributions (actually, an infrequent situation). It may also comprise aleatory interactions exerted on a "tagged" (or "tracer") particle by the surrounding medium, as the particle distribution around departs instantaneously from the equilibrium average. In any of these general cases, the above equation models a non-Markovian process at any time scale, and the customary Brownian movement conditions (particles which are heavier and larger than host molecules, white random forces, and so on) can be finally relaxed or abandoned.

## 2. POSTULATES OF BROWNIAN RELATIVITY: IDEAL POLYMER AND UNIVERSALITY

### 2.1 Equivalence of time-like and shape-like observers

Consider the relative motion of a tagged particle pair, consisting of two reference frames, $(t, \mathbf{X}')$ and $(t, \mathbf{X}'')$, in stationary diffusion across a common medium. The random variables $\mathbf{X}'$ and $\mathbf{X}''$ denote the position vectors of the two particles, and $t$ is a common time. When, at an initial instant, they are simultaneously released, the stochastic process associated with the relative displacement at time $t$:

$$\mathbf{r}(t) = \mathbf{X}'(t) - \mathbf{X}''(t) \tag{2.116}$$

can be detected by measuring the mean square separation:

$$\overline{\mathbf{r}^2(t)} = \overline{\mathbf{X}'^2(t)} + \overline{\mathbf{X}''^2(t)} - 2\overline{\mathbf{X}'(t)\cdot\mathbf{X}''(t)} \tag{2.117}$$

the last cross average denoting the particle correlation at equal times. For the present purposes, the first (ballistic) stage of motion, when particles are initially close and start to move apart, will not be taken here into account. We will limit instead on the hydrodynamic regime, focusing on those characteristic long wavelength (or time) values, over which the cross correlation vanishes and movements can be regarded independent:

$$\overline{\mathbf{r}^2(t)} = 2dDt + O(\sqrt{t}\,) \tag{2.118}$$

with:

$$D = D' + D'' \tag{2.119}$$

being $D' = \frac{d\overline{\mathbf{X}'^2}}{dt}$ and $D'' = \frac{d\overline{\mathbf{X}''^2}}{dt}$. Remember that the separation between short-time and long-time scales (in a liquid) will never be put into question. We will continue to rely on Gaussian fields and the possibility of identifying a well-posed hydrodynamic regime. Outside this limiting behavior, $D$ should be therefore replaced by:

$$\Delta = D - 2D_c \tag{2.120}$$

where:

$$D_c = \left( \frac{d\overline{\mathbf{X}' \cdot \mathbf{X}''}}{dt} \right) \tag{2.121}$$

is the contribution to diffusion of motion correlations. When particles are uncorrelated, the relative mean square displacement is described by the positive sum of the single mean square distances. Thus, if diffusion is isotropic ($\mathbf{X}' = \mathbf{X}''$), the Einstein's final law will be with twice diffusion coefficient. To decrease the mean particle separation, the only option is correlating the motions.

Consider now the three following frames of reference: A single molecule ($O'$), self-diffusing in a liquid with diffusion coefficient $D'$, a chain molecule ($O''$), diffusing in the same medium with $D'' < D'$, and the laboratory frame ($O$), with own diffusion coefficient $D_0$. A Newtonian conception of motion would give $O$ a privileged status, whereas in a special-relativistic formulation, Einstein's postulates need to be spelled out in diffusion language. Unfortunately, the different working context does not make this task directly feasible. Needless to say that any pair of distinct Brownian frames, such as $O'$ and $O''$, will not witness the same statistical description, and diffusion coefficients of fluids cannot be regarded as relativistic limit properties. Brownian relativity will actually lie in between, an absolute and a covariant description of the (statistical) laws of nature. We will call these laws "universal," to denote a privileged observation, carried out from the rest frame of the laboratory ($O$) and in agreement with any class of reference systems ($O', O,'' O''', \ldots$).

To infer the quantity preserved in such observations, consider now the frame $O'$, moving along a Brownian path from point $P$ to a point $Q$ at rest ($O$). Wishing to bring $Q$ in motion by the observer $O''$, independent of $O'$, the relative diffusion coefficient ($D$) will comply with:

$$D - D_0 = D' + D'' \tag{2.122}$$

Thus, provided to correlate $O'$ and $O''$ by the opposite amount, $D_c = D''/2$, this difference will be left equal to the diffusion coefficient of $O'$, i.e.:

$$D - D_0 = D' + D'' - 2D_c = D' \tag{2.123}$$

In particular, when the laboratory is at rest ($D_0 = 0$), the relative diffusion coefficient ($D$) will coincide with that of the liquid molecules ($D'$). We so name as "diffusive horizon" ($\Delta'$) the difference between the diffusion coefficients of the (liquid) molecules, forming the background medium, and of the laboratory frame:

$$\Delta' \doteq D' - D_0 \tag{2.124}$$

It will be verified that, absorbing the laboratory diffusion into this definition brings to an interesting setting. This "hidden zero," to be subtracted to the diffusion coefficient of liquid molecules, varies the definition of (unperturbed) reference frame quite substantially.

A special relativity example illustrating a direct analogue of this invariance property is the following. If $P$ and $Q$ would be rigidly joined together in vacuum, the time required by a light ray sent from one of such extremities to reach the other will always equal $\overline{PQ}/c$, irrespective of the velocity of the rigid frame connecting $P$ and $Q$. In our experiment, the two Brownian movements, one relative to the rest frame and the other to a polymer chain, are equivalent. They have the same diffusion coefficient and take the same time to go from $P$ to $Q$.

In a medium where $\Delta'$ is preserved, liquid and chain molecules lend themselves to an effective representation. We may borrow, for simplicity, the scheme used by the mean-field theory for polymer solution thermodynamics, credited to Paul J. Flory (1942) and Maurice L. Huggins (1942), where liquid and chain molecules are distributed over a homogeneous and isotropic lattice. For any molecular arrangement, the polymer solution will partition into a given proportion of liquid-like and chain-like sites or, which is better here, of reference frames. Those macromolecular will not be rigidly constrained in a unique state, but fluctuate continuously around it as a consequence of thermal energy and molecular collisions, which keep conformations mixed up and do not allow the chain molecule to settle down in that of minimum energy. With no mass transformations, a polymer frame of reference with $N$ repeat units can be linked to that liquid by a sort of "shish-kebab" model, merging together an equal number of single units. This operation is similar to embodying a number of pearls by some (immaterial) string, as in a necklace for example, and is equivalent to increasing the spacetime scale by creating a molecular ensemble with given shape and dimension ($1 \rightarrow N$). Despite the abstraction, it summarizes everything that counts here to describe a macromolecule in solution as a coordinate change. Of course, decreasing the spacetime scale is equivalent to inverting observation ($N \rightarrow 1$). We will for simplicity assume at the beginning an infinitely extended background liquid, so as to make the diffusive horizon insensitive to any scale exchange ($1 \leftrightarrow N$). Otherwise, for systems lying in finite spacetimes, the influence of the polymer fraction should be accounted for.

In Brownian relativity, random snapshots have another dual significance. Any path, from point $P$ to point $Q$, may either consist of a part, i.e., from $P$ to $K$, indicating a Brownian movement along it, and another, from $K$ to $Q$, standing for some chain shape. Due to the invariance of the diffusive horizon, exchanging a site lying in $\widetilde{PK}$ with any other in $\widetilde{KQ}$ does not have to alter the whole diffusion coefficient along $\widetilde{PQ}$. Therefore, the special theory of Brownian relativity acts in a spacetime where temporal trajectories and static shapes can be exchanged at will (Fig. 2.1). This feature will be seen to give an extended definition of the model known indifferently as ideal, random, Gaussian or "phantom" chain (or coil), and

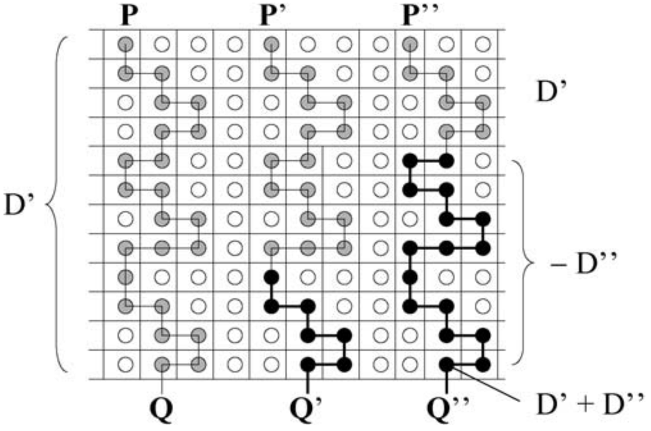

**Figure 2.1** The second postulate of (special) Brownian relativity. We can exchange $\circ(t) \rightleftharpoons \bullet(N)$.

translating in statistical physics the "shape" of a polymer that continuously fluctuates between local and overall (equiprobable) conformations. This situation is representative of the Flory's "$\Theta$" point, the temperature value (or the solvent conditions) at which the second virial coefficient vanishes ($A_2 = 0$). It will stand here for the Brownian–relativistic counterpart of a perfect gas at equilibrium that, following the physical idea ascribing correlations in a classical system to particle interactions, is fully uncorrelated. Accordingly, liquid-like and chain-like frames of reference will be renamed as "time-like" and "shape-like," respectively.

Remember the known formal equivalence between time and repeating unit number in (ideal) polymer problems. Because of the phantom chain immateriality, the random monomer position in a Gaussian coil can be described by Einstein's law, where time is replaced by the unit number. Since $\overline{\mathbf{r}^2(t)} \propto Dt$ and $\overline{\mathbf{r}^2(N)} = Nl^2$, a particle diffusing in time and a monomeric unit, "diffusing" in an ideal chain, formally correspond. Special Brownian relativity may thus be conceived as a physical extension of the equivalence $t \leftrightarrow N$, making a molecular trajectory equivalent to a macromolecular snapshot. In summary, its postulates can be set to:

1. From the rest frame of the laboratory, static shapes and dynamic trajectories point out universal Brownian observers for the laws of statistics;
2. The diffusive horizon is invariant from any universal frame or random path.

Note that, if special relativity may be defined as the theory of inertial frames, the Brownian one starts as the statistical theory of uncorrelated (or unperturbed) random paths, irrespective of the variable by which they may vary or evolve. The first postulate describes a "universal" principle of relativity among time-like and shape-like stochastic realizations. The second introduces the quantity taking place of the light speed. Otherwise seen, they provide an alternative definition of an "ideal" polymer solution, each Gaussian chain "conformation" being equivalent to a random trajectory of a single molecule in the large wavelength limit.

Imagine finally observing the motion of a polymer particle of mass $M = Nm_0$ (the molecular weight), embedding a (simple) liquid formed by molecules of mass $m_0$. Approaching the universal state requires bringing the chain at the rest frame, $m_0/M = N^{-1} \to 0$. This limit, of infinitely large molecular weights, is well known to imply several universality (or "criticality") classes in the segment number. In this state, a central issue is to determine the scaling (or critical) exponents for all those polymer quantities behaving as $\sim A_i N^{a_i}$ when $N \to \infty$. In this and the next chapters, we will seek those values of $a_i$ that are universal for certain classes of models, and will not take much care of the forefactors $A_i$, specific to the concrete phenomenology, the adopted model and its parameters. Now, from the first Brownian postulate, random realizations built either on time (liquid molecules) or repeat units (chain molecules) provide "equivalent," in the sense of universal, statistical observations. It would be as if, upon $1 \to N$ (up to $N \to \infty$), a static chain shape were tending to "collect" all statistical information on the molecular motion in the liquid.

Brownian relativity also sets a relation between two translational invariances (when they exist), one in space at the thermodynamic limit and the other in time, in the asymptotic regime. The former refers to a spatially extended system, of linear size ($\ell_t$) that is infinitely larger than its elementary constituents and with negligible boundary effects. Physical quantities are then expressed per unit volume ($\times \ell_t^{-d}$), and the limit $\ell_t \to \infty$ taken at a constant density. The latter is analogous to the former, with time $\mathrm{T} \leftarrow \ell_t$, and observes the system in $\tau \leqslant t \leqslant \tau + \mathrm{T}$, both the boundary value ($\tau$) and T being large enough. Criticality is accompanied by a diverging correlation (or fluctuation) range, and can only occur in the thermodynamic limit or the asymptotic regime. The above Brownian postulates wish so to bring two such descriptions into an united universal mechanism.

## 2.2 The invariant diffusive interval

To see how the formalism of special relativity modifies in light of the two Brownian postulates, let us work in Minkowski's spacetime where any event comprises a time and a mean square displacement, both observed at the hydrodynamic limit. In particular, at the diffusive horizon, the frame of reference $O' = (t', \overline{\mathbf{r}'^2})$ will detect:

$$\overline{\mathbf{r}'^2} = \Delta' t' \tag{2.125}$$

where $\mathbf{r}'(t')$ is the stochastic process in (continuous) time $t'$ for the aleatory position $\mathbf{r}'$, and the barycenter of motion is set to $\mathbf{r}'(0) = \mathbf{0}$. The quantity $\overline{\mathbf{r}'^2}$ is averaged over all path configurations, and may either refer to the distance traveled by a single tagged particle, or to the endpoint contraction of a polymer snapshot. Throughout this analysis, the numerical constant ($2d$) accounting for the space dimensionality in the diffusion coefficient will be included into the diffusive horizon, and therefore ignored. As will be seen, the scaling picture raised by Brownian relativity is insensitive to "absolute" and homogeneous diffusion coefficient variations of the host liquid, which would rather act as physical unit changes. Mostly its "relative" and local variations, still evaluated from the rest laboratory frame, will matter in the following.

To continue, from another frame $O'' = (t'', \overline{\mathbf{r}''^2})$ in the same physical and chemical conditions, one will have:

$$\overline{\mathbf{r}''^2} = \Delta' t'' \tag{2.126}$$

The invariance of diffusive horizons preserve the intervals between events in $O'$ and $O''$ that are arbitrarily close to each other, thus:

$$d\sigma'^2 = d\sigma''^2 \tag{2.127}$$

with:

$$d\sigma'^2 = \Delta' \, dt' - d\overline{\mathbf{r}'^2} \tag{2.128}$$

and similarly for the other observer. Working with the differentials upon constant $\overline{\mathbf{r}'^2}$ leads us to a time dilation rule of the form:

$$\left(\frac{dt'}{dt''}\right) = 1 - \frac{1}{\Delta'}\left(\frac{d\overline{\mathbf{r}''^2}}{dt''}\right) \tag{2.129}$$

where the derivative on the right needs to be explicited (in the system $O'$). Generally, for a reference frame $O^{(k)}$ diffusing with $D^{(k)} \in (D_0, D^{(p)}]$, The second postulate implies that the incremental ratio between mean square length and time equates a "relative" diffusive horizon. By introducing the notation ${}^{(k)}\Delta^{(p)} = D^{(p)} - D^{(k)}$, it reads:

$$\left(\frac{d\overline{\mathbf{r}''^2}}{dt''}\right) = {}''\Delta' \tag{2.130}$$

where, from here on, primes on the left will indicate the diffusing system and those on the right the reference frame from which it is observed. This quantity complies of course with the composition laws:

$$\begin{gather} {}'\Delta'' + {}''\Delta' + {}'''\Delta'' + \cdots + {}^{'''\cdots'}\Delta^{''\cdots'} = {}'\Delta^{''\cdots'} \tag{2.131} \\ \Delta' - \Delta'' = {}''\Delta' \tag{2.132} \end{gather}$$

which, once exploited in the time dilation rule, imply:

$$\left(\frac{dt'}{dt''}\right) = \gamma_B^{-1} \tag{2.133}$$

The ratio $\gamma_B = \frac{\Delta'}{\Delta''}$, taking the place of Lorentz's factor of special relativity, will be called "Brownian–Lorentz factor" and is dually found in the (square) length contraction rule:

$$\left(\frac{d\overline{\mathbf{r}'^2}}{d\overline{\mathbf{r}''^2}}\right) = \gamma_B \tag{2.134}$$

Finally, when the laboratory frame is at rest, $D_0 \equiv 0$ and $\gamma_B \equiv \frac{D'}{D''}$:

$$\left(\frac{dt'}{dt''}\right) = \gamma_B^{-1} \quad \text{(time dilation)} \tag{2.135}$$

$$\left(\frac{d\overline{\mathbf{r}'^2}}{d\overline{\mathbf{r}''^2}}\right) = \gamma_B \quad \text{(length contraction)} \tag{2.136}$$

These relations give the basis for the spatio-temporal scaling in (ideal) polymer solutions.

Before going ahead, some remarks on the diffusion coefficient are in order. It is a central quantity for the invariance of the diffusive interval, and we should not overlook the fact that there are more than one type of diffusion coefficient (or "diffusivity") only. That connecting matter flux and density gradient in Fick's laws is a "collective" (or "mutual") diffusivity. It conceptually differs from the self-diffusion coefficient, describing instead the movement of single tracers in homogeneous media, at constant concentration, as in Einstein's interpretation. They get coincident in the limit of infinite dilution, but may be very different at finite concentrations. Furthermore, if tracer and host particles interact together, their diffusion coefficients generally depend on time, wavevector and, with the notable exception of Oseen's approximation, on concentration. One can find here a second classification, into short-time and long-time diffusivities, coming back to the Sutherland–Stokes–Einstein value in the non-interacting limit.

It is clear, given the breadth of this framework, that to state an enlarged formalism in the wavevector and frequency domains might be desirable in a near future, clearly recovering our (static) diffusive interval upon $|\mathbf{q}|, \omega \to 0$. Nevertheless, a central purport of Brownian relativity is the establishment of (weakly) covariant relations among molecular and macromolecular observers in the long-wavelength (scaling) regime, with the main prescription having a (weakly) Lorentz–Poincaré invariant diffusion law ($\overline{\mathbf{r}^2} \propto t$). What matters, again, is the "form-invariance of motion," regardless of its kinematic details.

## 2.3 Time dilation and length contraction: Random walk and Rouse's chain

To ascertain what the length contraction and time dilation mean in a polymer solution, consider a time-like frame ($O'$), collecting an ensemble of $N$ liquid units, each of average dimension $l$. The latter may either denote the "real size" of liquid molecules and monomer bonds, in the chemical structure of the macromolecule, or the "statistical length" (or step size) introduced by Werner Kuhn (1936–1939) to partition the chain into a walk of hypothetic freely hinged segments, with vector distribution obeying the central limit theorem. At initial time ($t' = 0$), before starting their motion, they may be viewed as an instantaneous shot of $N$ single units, confined to a "tube" of "rectilinear" shape and given extension. For simplicity, the tube will have a diameter equal to $l$, and a (contour) length $L_c = Nl$. Consider then a shape-like frame ($O''$), consisting of a chain formed by the same liquid molecules, placed initially ($t'' = 0$) in the same tube. In $O'$, when molecules are released and start to disengage from the tube independently, their fluctuations will soon have the effect of breaking the rectilinear shape taken on at the beginning. In $O''$, the same stochastic process will bring instead to another chain shape, with average spacetime features. Aim is to understanding how such measurements, in $O'$

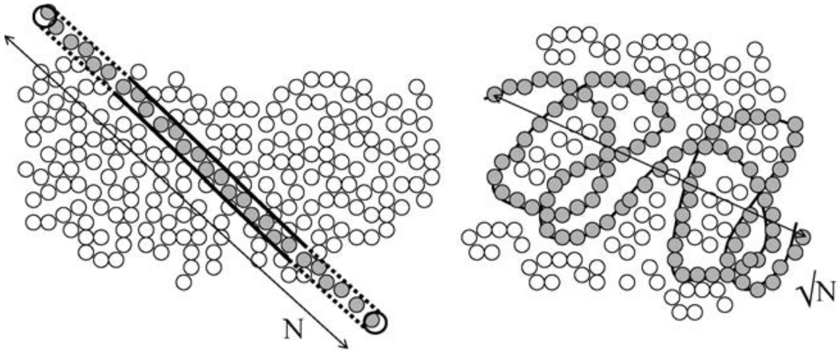

**Figure 2.2** Molecular (rod-shaped) and macromolecular (coil-shaped) reference frames.

and $O''$, are related. First remember, as in any transformation law, that the invariance of diffusive intervals can raise two formally equivalent, but conceptually different, conceptions. We may imagine, for instance, that events in $O''$ are the images of events in $O'$ (active interpretation). Otherwise, each of them will stand for the same spacetime point seen from two Brownian frames (passive interpretation). Though that passive is the more physical of the two, it will be equally suitable to think of a system as the image of another molecular system.

As already stated, passing from "molecules in a tube" ($O'$) to a "chain in a tube" ($O''$), one may increase the spacetime scale ($1 \rightarrow N$) by merging $N$ liquid molecules into a macromolecule of equal "contour length" and chemical nature (Fig. 2.2). We have also seen that, in a medium preserving $\Delta'$, this scale change fails to introduce statistical correlations among molecular sites, and thus between frames of reference. The only effect it has is to decrease the mobility in the local portion of the medium where the transformation $1 \rightarrow N$ occurs. Thus, the universal state arising from the rules of length contraction and time dilation should simply follow from expliciting $D'' = D''(N)$.

To check this point, step back to the observer $O'$. It will measure a length $\overline{r'^2} = L_C^2 = N^2 l^2$ and a time $t' = N t_0$, for some characteristic molecular time ($t_0$). Then, if $O$ is at rest, $O''$ and $O'$ detect their diffusive horizons according to the ratio of their diffusion coefficients:

$$\frac{{}''\Delta'}{\Delta'} = 1 - \frac{D''}{D'} \tag{2.137}$$

Since the mobility coefficient of the ideal coil is additive in the segment number, the rest state is approached as $D''/D' = N^{\delta}$, with $\delta = -1$. One could also say that, with increasing $N$ ($1 \rightarrow \infty$), a macromolecule "annulls" the diffusive horizon of the liquid molecules, nearly a locally inertial frame of reference, which in relativity annuls the gravity effect. In other words, universality in polymer solutions arises from ordering a (Brownian–relativistic) space indistinguishably disordered.

If $\nu$ and $\vartheta$ indicate the universal exponents for the average "end-to-end distance" (or "diameter of gyration," when they coincide) and characteristic time, $\overline{\mathbf{r}''^2} \sim N^{2\nu}$ and $t'' \sim N^{\vartheta}$, the length contraction and time dilation rules take the form:

$$\overline{\mathbf{r}''^2} = \frac{D''}{D'} L_C^2 = Nl^2 \tag{2.138}$$

giving the ideal size scaling for a random walk polymer ($\nu_\mathrm{i} = \frac{1}{2}$) and Rouse's time ($\vartheta = 2$), the longest relaxation time in the "bead-spring" model due to Prince E. Rouse (1953):

$$t'' = \frac{D'}{D''} N t_0 = N^2 t_0 \tag{2.139}$$

Basically, he assumed that each random velocity is driven by the curvature of the configuration, as only set by the forces locally applied to each point of the chain. We assume here that each molecule escapes from the tube independently of any other, tackling the initial collective motion in terms of $N$ statistically independent random forces ($t' = Nt_0$). Note that, as in the length contraction rule, where a homogeneous unit of length ($l$) is assumed in each system, the step $t_0$ is regarded a common unit of time. Both reference frames detect their spatial and temporal intervals with the same units, and the former scaling relations are therefore unambiguous.

Actually, the calculation in Rouse's model would assign to the shape-like frame a different unit. The original result can be written in fact as $t''_R = N^2 t''_0$, where the friction constant ($\alpha$) in $t''_0 = l^2\alpha/(3\pi^2 k_B T)$ belongs to a chain segment. The definitions of single molecule in liquid and polymer systems may also be different, but universal laws in Brownian relativity cannot account for odd spatio-temporal units, in so far as special relativity could never relate reference systems with unspecified measuring rods and clocks. The point that counts here is the relationship among Brownian observers, expressed through their molecular numbers.

As stated above, these scaling results are insensitive to weak correlations. We are working in hydrodynamic and Gaussian regimes, and should be able to include the effect of short-range correlations rather easily. Note that the terms "short-range" and "long-range" should be referred to "chemical distances," along the so-called (sometimes improperly) polymer contour length. Referring to end-to-end distances, in space, would involve a larger number of units. Imagine thus to (slightly) enlarge the tube by a new diameter $\tilde{l}$ ($>l$). From the viewpoint of $O'$, this gives the liquid molecules some additional time to lose their correlation. In $O''$, this operation resets the ideal chain into another ideal system by a larger mean square length, grouping the short-range correlations among the first adjacent units, but affects the temporal step as well, increasing with $\tilde{l}^2$. Thereby, at constant monomer number ($N$), the linear mapping $l \to \tilde{l} = \sqrt{\tilde{c}_N} l$, rescales the previous walk by other internal states:

$$\overline{\mathbf{r}''^2} = \tilde{c}_N N l^2 \tag{2.140}$$

$$t'' = \tilde{c}_N N^2 t_0 \tag{2.141}$$

Such equations witness a finite-range memory, where the probability distribution is affected at most by a finite amount of the latest steps. Thus, the correlation factor $\tilde{c}_N$ brings to a "characteristic ratio", the limiting value ($\tilde{c}_\infty$) obtained upon a bond number tending to $N \to \infty$. In polymer chemistry, Flory's characteristic ratio is used to evaluate the influence of bond correlations on the intrachain dimension of (unperturbed) random chains, and is a measure of the polymer stiffness. In the time dilation rule, its presence is not very relevant, except to realize that $\overline{\mathbf{r}''^2}/t'' =$ const at fixed $N$, regardless of the (slight) perturbation the conformational statistics undergoes.

We should finally note that the diffusive interval is not stated as a quadratic expression of statistical coordinates. In the simplest way, coordinates and distances may be redefined by $\xi^\mu \equiv \{\tau = \sqrt{t}, \rho = \sqrt{\overline{\mathbf{r}^2}}\}$:

$$d\sigma^2 = -\bar{\eta}_{\alpha\beta}\, d\xi^\alpha\, d \ln \xi^\beta \tag{2.142}$$

here with $\bar{\eta}_{\alpha\beta} = \mathrm{diag}(-1, 1)$. However, when constant metric components are set at the hydrodynamic limit, in a flat spacetime without long-range correlations, any quadratic representation has no influence on the scaling results of the ideal chain.

## 2.4 Brownian Lorentz–Poincaré transformations

In the previous section, it was shown on an intuitive basis that the basic phenomenology of Brownian relativity can explain a simplest scaling picture for polymer solutions. Nonetheless, a general rule for coordinate transformations, bringing events from a reference frame to one other, has not been provided yet. In special relativity this task is accomplished by the Lorentz–Poincaré transformations, which are easily inverted upon reversing the relative velocity ($v \to -v$). Here, one is faced instead with the delicate concept of covariance. Starting from the previous 2-dimensional setting ($\xi^\mu$), the Brownian transformations could come at first sight from regarding $v \to \sqrt{{}''\Delta'}$ and $c \to \sqrt{\Delta'}$ in the original Lorentz–Poincaré's. Velocity reversals would so correspond to reverting the Brownian motion of the relative diffusive horizon ($\sqrt{{}''\Delta'} \to -\sqrt{{}''\Delta'}$). This analogy would present no formal problem, including covariance, has little significance.

Clearly, a full translation of the Lorentz–Poincaré transformations should deal with the initial, ballistic stage of motion, before it slows down as a consequence of friction forces. However, it is just in the long wavelength limit where the connection between polymer universality and Brownian relativity seems to establish in deep. The sought equations will have to preserve the invariance of diffusive intervals:

$$\Delta'\, dt' - d\overline{\mathbf{r}'^2} = \Delta'\, dt'' - d\overline{\mathbf{r}''^2} \tag{2.143}$$

and the rules of length contraction and time dilation. Consider so two reference frames, $O'(t', \overline{\mathbf{r}'^2};\, D')$ and $O''(t'', \overline{\mathbf{r}''^2};\, D'')$, and the linear transformation ($D_0 \equiv 0$):

$$\begin{aligned} t' &= \lambda^0{}_0 t'' + \lambda^0{}_R \overline{\mathbf{r}''^2} \\ \overline{\mathbf{r}'^2} &= \lambda^R{}_0 t'' + \lambda^R{}_R \overline{\mathbf{r}''^2} \end{aligned} \tag{2.144}$$

Preserving the law of length contraction gives us:

$$\lambda^R{}_R = \frac{D'}{D''} \tag{2.145}$$

whereas:

$$\Delta'\, dt' - d\overline{\mathbf{r}'^2} = \Delta'\, dt'' - d\overline{\mathbf{r}''^2} \tag{2.146}$$

produces two constraints, one in space and the other in time. The first is:

$$1 + \lambda^0{}_R D' = \lambda^R{}_R \tag{2.147}$$

or, exploiting the last but one:

$$\lambda^0{}_R = \frac{1}{D'}\left(\frac{D'}{D''} - 1\right) \tag{2.148}$$

while the temporal invariance equals:

$$D'\lambda^0{}_0 = \lambda^R{}_0 + D' \tag{2.149}$$

The time dilation rule provides the last condition:

$$\Delta t' = \left(\lambda^0{}_0 - \frac{\lambda^0{}_R \lambda^R{}_0}{\lambda^R{}_R}\right)\Delta t'' \tag{2.150}$$

which must be evaluated for $\frac{\Delta t'}{\Delta t''} = \frac{D''}{D'}$, returning:

$$\lambda^0{}_0 = \frac{D''}{D'} + \frac{\lambda^0{}_R \lambda^R{}_0}{\lambda^R{}_R} \tag{2.151}$$

Combining the last two temporal constraints, and replacing the components $\lambda^s{}_R$, finally results in:

$$\lambda^R{}_0 = D'\left(1 - \frac{D'}{D''}\right) \tag{2.152}$$

and:

$$\lambda^0{}_0 = 2 - \frac{D'}{D''} \tag{2.153}$$

completing the second couple of coefficients $\lambda^s{}_0$ in the Brownian transformation formulas. Their inverse representation obviously reads:

$$\begin{aligned} dt'' &= \left(1 + \frac{{}''\Delta'}{D'}\right) dt' + \frac{{}'\Delta''}{D'D''}\, d\overline{\mathbf{r}'^2} \\ d\overline{\mathbf{r}''^2} &= \frac{D''}{D'}\left({}''\Delta'\, dt' + d\overline{\mathbf{r}'^2}\right) \end{aligned} \tag{2.154}$$

or:

$$\begin{pmatrix} t'' \\ \mathbf{r}''^2 \end{pmatrix} = {}''\mathbf{L}' \begin{pmatrix} t' \\ \mathbf{r}'^2 \end{pmatrix} \tag{2.155}$$

where:

$${}''\mathbf{L}'\left(D', D''\right) = \mathbf{I} + \frac{{}''\Delta'}{D'}\, {}''\mathbf{P}' \tag{2.156}$$

takes the place, together with ${}'\mathbf{L}''$, of the Lorentz–Poincaré matrix transform $(\Lambda^{\mu}_{\alpha})$. The second term on the right involves a perturbation of the form:

$$ {}''\mathbf{P}'(D'') = \begin{pmatrix} 1 & -\frac{1}{D''} \\ D'' & -1 \end{pmatrix} \tag{2.157} $$

where superscripts still specify the direction of the transformation, here from time-like ($'$) to shape-like ($''$). We saw that changing frame equals to revert the spacetime scales at which the observations are conducted. The two molecular dimensions ($N \leftrightarrow 1$) and thus their diffusion coefficients ($D' \leftrightarrow D''$) are to be exchanged, getting:

$$ {}'\mathbf{L}''\big(D'', D'\big) = \mathbf{I} + \frac{{}'\Delta''}{D''}\,{}'\mathbf{P}'' \tag{2.158} $$

obviously with ${}'\mathbf{P}'' = {}''\mathbf{P}'(D')$. One may verify that the (same) length contraction and time dilation rules apply, while intervals are invariant under any horizon reversal ($\Delta' \rightarrow \Delta''$):

$$ \Delta''\, dt' - d\overline{\mathbf{r}'^2} = \Delta''\, dt'' - d\overline{\mathbf{r}''^2} \tag{2.159} $$

This symmetry results in the freedom to switch from a simple liquid to a polymeric fluid (and vice versa), and it is not surprising that the diffusion coefficient of each subsystem provides a well-posed horizon for the whole Brownian medium. In addition, from the invariance of the time dilation and length contraction laws, either frames will agree on observing the "universal" scaling in the shape-like system. The cost to be paid for these accords, as they stand, is naturally a matrix transform which is not invertible, breaking unavoidably covariance:

$$ {}'\mathbf{L}''\,{}''\mathbf{L}'\big(D', D''\big) = {}''\mathbf{L}'\,{}'\mathbf{L}''\big(D'', D'\big) \neq \mathbf{I} \tag{2.160} $$

An only exception is made for the trivial situation of a medium entirely homogeneous ($D' = D''$), where symmetry is recovered and the equations are set into a unitary transformation (${}'\mathbf{L}'' = {}''\mathbf{L}' = \mathbf{I}$). Otherwise, for $D' \neq D''$, should some observer ($O^*$) detect a time dilation and a length contraction relative to another frame, we would be allowed to conclude that $O^*$ is linked to the largest diffusion coefficient.

## 2.5 Fick's diffusion equation

To derive Fick's second law of diffusion from Brownian relativity, consider its probability density $W = W(\mathbf{O}')$, determined from the reference frame $O' = (t', \mathbf{r}')$, and its variation:

$$ \delta W_{ks} = W(\mathbf{O}') - W(\mathbf{O}'') + \mathrm{O}\big(|t|^k, |\mathbf{r}|^s\big) \tag{2.161} $$

to be evaluated from a "scratch" frame $O'' = (t'', \mathbf{r}'')$. Retaining for now all terms in Taylor's expansion:

$$ \begin{aligned} W(\mathbf{O}') = {} & W(\mathbf{O}'') + (\delta\mathbf{O} \cdot \vec{\nabla}_{\mathrm{O}'})W(\mathbf{O}')|_{\mathrm{O}''} \\ & + \frac{1}{2}\delta\mathbf{O} \cdot \big[\delta\mathbf{O} \cdot \vec{\nabla}_{\mathrm{O}'}\big(\vec{\nabla}_{\mathrm{O}'} W(\mathbf{O}')\big)\big]_{\mathrm{O}''} + \cdots \end{aligned} \tag{2.162} $$

and separating temporal from spatial $\mathbf{O}''$ components, at the second order in both coordinates one obtains:

$$\delta W_{22} = \left(\frac{\partial W}{\partial t''}\right)\delta t + \delta\mathbf{r}\cdot\vec{\nabla}W(\mathbf{O}'') + \frac{1}{2}\left(\frac{\partial^2 W}{\partial t''^2}\right)(\delta t)^2 + \frac{1}{2}\vec{\nabla}^2 W(\mathbf{O}'')(\delta\mathbf{r})^2 + \delta\mathbf{r}\cdot\vec{\nabla}\left(\frac{\partial W}{\partial t''}\right)\delta t \tag{2.163}$$

where $\delta\mathbf{O} = (\delta t, \delta\mathbf{r})$ is the increment vector, with $\delta t = t' - t''$ and $\delta\mathbf{r} = \mathbf{r}' - \mathbf{r}''$, and all derivatives on the right side are calculated in $O''$. As usual, the sum will be truncated to a couple of leading terms, one for each coordinate and, without additional criteria, the least orders should be adopted. This is certainly the case of the temporal contribution, for we set $k = 1$. The spatial terms, instead, can be discussed thermodynamically, in light of the entropy function ($S$). It is known that, if some constraints of an isolated system are removed, its parameters will readjust themselves so to allow the number of accessible states ($\Omega$) to get a maximum. This is why, from Boltzmann's relation, $S_\Omega = k_B \ln\Omega$, the entropy of a thermally isolated system can never decrease.

In our case, if all accessible states are fully unconstrained, they will be equally likely, and their number will be proportional to the probability distribution function, $\Omega(\mathbf{O}') \propto W(\mathbf{O}')$. At a fixed time $t' = t''$ ($\delta t = 0$), when the relevant parameters reduce to the spatial vector (components), the maximum entropy condition becomes:

$$0 = \delta S_\Omega(\mathbf{O}'') \propto \delta\mathbf{r}\cdot\vec{\nabla}\ln W(\mathbf{O}'') \quad (\delta^2 S_\Omega \leqslant 0) \tag{2.164}$$

Therefore, from the arbitrariness of both increments and scratch frames, one can set $\vec{\nabla}W(\mathbf{O}'') = 0$ and, regarding the second order in $\delta\mathbf{r}$ leads us to:

$$\delta W_{12} = \left(\frac{\partial W}{\partial t''}\right)\delta t + \frac{1}{2}\vec{\nabla}^2 W(\mathbf{O}'')(\delta\mathbf{r})^2 \tag{2.165}$$

Increments are taken independently of the scratch, thus, averaging over their probability density ($\mathsf{P}$) returns:

$$\overline{\delta^2 W} = \left(\frac{\partial W}{\partial t''}\right)\int \mathsf{P}(\delta t, \delta\mathbf{r})\delta t\, d(\delta\mathbf{r}) + \frac{1}{2}\vec{\nabla}^2 W(\mathbf{O}'')\int (\delta\mathbf{r})^2 \mathsf{P}(\delta t, \delta\mathbf{r})\, d(\delta\mathbf{r}) \tag{2.166}$$

with:

$$\overline{\delta^2 W} \equiv \int \mathsf{P}(\delta t, \delta\mathbf{r})\delta W_{12}\, d(\delta\mathbf{r}) \tag{2.167}$$

Supposing one only probability function ruling the phenomenon ($\mathsf{P} \equiv W$), with $\overline{\delta\mathbf{r}^2} = \delta\overline{\mathbf{r}^2}$ then:

$$\overline{\delta^2 W} = \left(\frac{\partial W}{\partial t''}\right)\delta t + \frac{1}{2}\vec{\nabla}^2 W(\mathbf{O}'')\delta\overline{\mathbf{r}^2} \tag{2.168}$$

that is what happens for the increments of a Bachelier–Wiener process, which are stationary, independent and described in terms of an only transition density.

Note that, from the Brownian Lorentz–Poincaré transformations, the short time interval $\delta t$ and the random displacement ($\delta\overline{\mathbf{r}^2}$) are not supposed here to vary independently. In the limit of small horizon perturbations ($\delta D$) around a given diffusion coefficient ("$D = 1$"):

$$D' \to 1 + \delta D, \qquad D'' \to 1 \tag{2.169}$$

they result from projecting the increment vector, defined as:

$$\delta\left(\frac{t}{\mathbf{r}^2}\right) = \delta\mathbf{L}\left(\frac{t'}{\mathbf{r}'^2}\right) \tag{2.170}$$

with:

$$\delta\mathbf{L} = {}'\mathbf{L}''\,{}''\mathbf{L}' - \mathbf{I} \tag{2.171}$$

onto the subspaces at $\overline{\mathbf{r}'^2} = 0$:

$$\delta t = \mathbf{e}_0 \cdot \delta\left(\frac{t}{\mathbf{r}^2}\right) \tag{2.172}$$

and $t' = 0$:

$$\delta\overline{\mathbf{r}^2} = \mathbf{e}_R \cdot \delta\left(\frac{t}{\mathbf{r}^2}\right) \tag{2.173}$$

with $\mathbf{e}_0 = (1, 0)$ and $\mathbf{e}_R = (0, 1)$. To work them out, remember:

$${}''\mathbf{L}'\big(D', D''\big) = \begin{pmatrix} 1 + \frac{{}''\Delta'}{D'} & \frac{{}'\Delta''}{D'D''} \\ \frac{{}''\Delta' D''}{D'} & \frac{D''}{D'} \end{pmatrix} \tag{2.174}$$

and, inversely, ${}'\mathbf{L}'' = {}''\mathbf{L}'(D'', D')$. Hence, their products read:

$${}''\mathbf{L}'\,{}'\mathbf{L}''\big(D', D''\big) = \begin{pmatrix} \frac{{}'\Delta''^2}{D''^2} + [1 + \frac{{}''\Delta'}{D'}][1 + \frac{{}'\Delta''}{D''}] & \frac{{}'\Delta''^3}{D'^2 D''^2} \\ -\frac{2\,{}'\Delta''^2}{D'} & 1 + \frac{{}''\Delta'^2}{D'^2} \end{pmatrix} \tag{2.175}$$

and ${}'\mathbf{L}''\,{}''\mathbf{L}' = {}''\mathbf{L}'\,{}'\mathbf{L}''(D'', D')$. Though such transformations are not invertible, their spatio-temporal increments can be defined unambiguously.

If one slightly perturbs the liquid diffusion coefficient by a small perturbation ($\delta D$), and expands the above matrix in Taylor's series, with variable $x = \frac{D''}{D'}$ and center $\bar{x} = 1$, then:

$$\delta\mathbf{L} = {}'\mathbf{L}''\,{}''\mathbf{L}'(1 + \delta D) - {}'\mathbf{L}''\,{}''\mathbf{L}'(1) \tag{2.176}$$

or, as the unperturbed term on the right is just the identity matrix ($\mathbf{I}$):

$$\delta\mathbf{L} = (x - 1)^2 \begin{pmatrix} -1 & x - 1 \\ -2 & 1 \end{pmatrix} + \mathrm{O}(x^4) \tag{2.177}$$

In this way, the couple of independent projections are:

$$\begin{pmatrix} \delta t' \\ \delta\overline{\mathbf{r}'^2} \end{pmatrix} = \begin{pmatrix} \mathbf{e}_0 \cdot \delta\mathbf{L} \\ \mathbf{e}_R \cdot \delta\mathbf{L} \end{pmatrix} = (x - 1)^2 \begin{pmatrix} -1 \\ 1 \end{pmatrix} \tag{2.178}$$

hence:

$$-\frac{\delta t}{t''} = \frac{\delta \overline{\mathbf{r}^2}}{\overline{\mathbf{r}''^2}} = (\delta D)^2 \tag{2.179}$$

The two variations have equal orders of magnitude and opposite signs, and are insensitive to exchanging frame ($\delta D \leftrightarrow -\delta D$ and so $'\mathbf{L}'' \leftrightarrow {}''\mathbf{L}'$). Clearly these increments, despite the connections to the Brownian motion theory, should not be identified with those of the Bachelier–Wiener process.

Using the former constraints and Einstein's law for relative diffusion, with twice coefficient ($\overline{\mathbf{r}''^2} = 2\Delta'' t''$), finally imply:

$$\left(\overline{\frac{\delta^2 W}{\delta D^2}}\right) = t''\left[-\left(\frac{\partial W}{\partial t''}\right) + \Delta''\vec{\nabla}^2 W(\mathbf{O}'')\right] \tag{2.180}$$

which regains the heat-diffusion equation (in "natural units"):

$$\left(\frac{\partial W}{\partial t''}\right) = \vec{\nabla}^2 W(t'', \mathbf{r}'') \tag{2.181}$$

provided the laboratory is still at rest ($\Delta'' = 1$) and $\frac{1}{t''}(\overline{\frac{\delta^2 W}{\delta D^2}}) \rightarrow 0$.

In summary, the Fick's second law for Brownian statistics is shown to come from the special-relativistic description of diffusive kinematics, and may be deemed as the stochastic analogue of an inertial state. It specifies a "probability gauge" condition, conciliating covariance of Brownian increments with the statistical description of molecules of arbitrary unit numbers.

## 2.6 Fluctuations, dissipation, and collisions

In special relativity the laws of Galilean kinematics are numerically corrected by Lorentz's factor, $\gamma_L = 1 + \frac{1}{2}\beta^2 + \frac{3}{8}\beta^4 + \cdots$. The equivalence $E = mc^2$ comes itself from expanding at the leading order in $\beta$ the point particle momentum, $p = mv\gamma_L$, in the energy function. In comparison with the current approach to diffusion, however, the implications of Brownian relativity are rather different from the special-relativistic corrections to kinematics, and mainly concerned with its formal aspects. Working in a diffusive spacetime, which is insensitive to interchanging static and dynamic random paths, has in fact deep consequences in modeling macromolecules and "universal" laws. As seen already, the latters consist of statistically equivalent observations, but cannot be fully compared to covariant laws of (special) relativity. There, the concept of absolute motion became totally meaningless. Here, distinguishing between paths in a random motion and random paths at rest becomes irrelevant in itself, but opens the search for new classes of statistical relations. For similar reasons, in the extended formulation of the next chapter, there will be no (particularly useful) analogue of the Parametrized Post-Newtonian metric, nor will the analysis of the diffusion coefficient, in terms of velocity self-correlation, give us further information.

It is helpful instead to comment on a fundamental application of statistics in light of Brownian relativity. Consider a sequence of $n$ independent random variables

$(\mathbf{X}_s)$, with equal mean values, $\overline{\mathbf{X}_s} = \mu$, and variances $\mathrm{Var}(\mathbf{X}_s) \equiv \overline{(\mathbf{X}_s - \overline{\mathbf{X}_s})^2} = \sigma^2$. Their average, a random variable defined as $\overline{\mathbf{X}}_n = \frac{1}{n}\sum_s \mathbf{X}_s$, will have $\overline{\overline{\mathbf{X}}_n} = \mu$ and $\mathrm{Var}(\overline{\mathbf{X}}_n) = \frac{\sigma^2}{n}$. In basic statistics, this example illustrates the difference between the distributions of $\mathbf{X}_n$, with constant standard deviation ($\sigma$), and $\overline{\mathbf{X}}_n$, with fluctuations around $\overline{\overline{\mathbf{X}}_n}$ tending to zero upon $n \to \infty$. In polymer statistics, it can be borrowed to formulate the size calculation of the static conformation of any (ideal) random walk chain. It is sufficient to choose $\mathbf{r}_s$ so to denote the random vector position of the $s$th monomer bond in a sequence of $n = N$ repeat units, with mean square length (of all bonds) $l^2 = \mathrm{Var}(\mathbf{r}_s)$ and $\mu = 0$. Each bond vector is oriented independently of, and does not interact with, any other random vector. In this simplest "freely jointed chain" model, the second central moment of the polymer vector, $n\bar{\mathbf{r}}_n$, thus reads:

$$\overline{(n\bar{\mathbf{r}}_n)^2} = \mathrm{Var}(n\bar{\mathbf{r}}_n) = nl^2 \tag{2.182}$$

that is, the trace of a correlation matrix with elements $C_{ss'} = \overline{\mathbf{r}_s \cdot \mathbf{r}_{s'}}$. This still agrees with the central limit theorem, which brings to a normal distribution of end-to-end distances with zero mean and mean square equal to $nl^2$. Furthermore, the previous arguments are independent of the space dimensionality ($\nu = \frac{1}{2}\ \forall d$), and the reason is to be found in the absence of any (long-ranged) interaction. Such a difference would be specially pronounced in $d = 1$, where the self-avoiding walk is fully "stretched out" ($\nu = 1$).

With (spatial) correlations, this "kinetic" calculation changes by virtue of non-null cross products ($C_{s \neq s'} \neq 0$) and, when they are short-ranged (enough), the former sum becomes again $\overline{(n\bar{\mathbf{r}}_n)^2} = c_n nl^2$, with:

$$c_n = 1 + \frac{2}{n}\overline{\sum_{i=1}^{n-1}\sum_{s=1}^{n-i}\cos\boldsymbol{\alpha}_{s,s+i}} \tag{2.183}$$

expliciting the ratio of perturbed and unperturbed paths in terms of the (discrete) stochastic process formed by the random angle $\boldsymbol{\alpha}_{s,s'} \equiv \widehat{ss'}$. When correlations propagate homogeneously along the contour length, $\overline{\cos\boldsymbol{\alpha}_{s,s+i}} = (\overline{\cos\boldsymbol{\alpha}_{s,s+1}})^i \equiv (\overline{\cos\boldsymbol{\alpha}})^i$ ($s' = s + i$), averaging over large ensembles and taking the limit $n \to \infty$ leads to a characteristic ratio of the form:

$$c_\infty = \frac{1 + \overline{\cos\boldsymbol{\alpha}}}{1 - \overline{\cos\boldsymbol{\alpha}}} \tag{2.184}$$

where the mean cosine may be negative or positive, according to the bias direction (backward or forward, respectively). In polymer theory this model is known as "freely rotating chain," but applies to any near random walk phenomenology. In crystal diffusion, $c_\infty$ is analogous to the "correlation factor" ($f$) for successive atomic jumps, expressible as the ratio of diffusion coefficients of tracer atoms and vacancies. What is important to remark is that the central limit theorem is still valid, as foreseen by its extension contemplating the presence of weak correlations, and the Gaussian model continues to hold, with second central moment rescaled by a new (Kuhn's) length ($\tilde{l} = \sqrt{\tilde{c}_n} l$, $\tilde{n} = n/\tilde{c}_n$). Both velocity and curvilinear length depend instead on the elementary walk step, and increase as $l$ decreases.

Basically, the ideal coil results base on the mathematical features of the variance, including the additivity property implied by the independence of the random monomer positions. The Lorentz–FitzGerald contraction for a diffusive spacetime, instead, is "physical" and comes from the Brownian–relativistic structure assigned to the host spacetime. We may go a little further and note that, in the standard calculation, fluctuations around $\overline{\overline{\mathbf{X}}_n}$ reduce with the sample dimension as $\sigma/\sqrt{n}$. In our case, the local mobility decrease ($D \rightarrow D/n$), contracting an initial rod-like dispersion ($nl$) into the random walk distance ($\sqrt{n}l$), suggests a rediscussion of the fluctuation–dissipation theorem (for Brownian movement).

The Einstein–Smoluchowski equation ($D = \mu_m k_B T$) depends in fact not only on the mobility coefficient, but also on absolute temperature and Boltzmann's constant. In principle, Brownian relativity would therefore lead to a common scaling picture for each of these quantities and the aspects related (e.g., the medium structure). Actually, it was just the search for universality in "critical" phenomena (e.g., phase transitions) that prompted the monomer–polymer transition to be a further example of "criticality." To approach both a critical temperature ($|1 - T/T_c|^{-1} \rightarrow \infty$) and an infinitely long chain molecule ($N \rightarrow \infty$) were conceived to be similar operations. In particular, $T > T_c$ corresponds to a symmetric (disordered) phase, tending to a "symmetry breaking" when $T < T_c$. The "entropic" picture, in $k_B$ (i.e., Avogadro's constant), would apply instead to a very different class of "molecular weights," such as those of chemical elements and substances. In this case, the clue would be to conceive molecules in any state of matter closely to monomers in a macromolecule, and think of any molecular assembly as some universal limit of its constituents. A picture like this, quite unexpected at present, would nevertheless bring to a more powerful scaling concept, by which relating the properties of matter at different scales. The author believes in such a possibility and will start to discuss a "geometrical scaling" in the conclusive chapter, on a possible "shape mechanics," hoping that this program could sooner or later be fully actualized.

A last concept to comment on would be that of collision. Nonetheless, having ascribed the length contraction and time dilation rules to the hydrodynamic limit, this point is not expected to be considerable, at least at this stage of research. Information on intermolecular collisions may be derived in fact (normally with some convergence problems) from the short-time expansion of the velocity autocorrelation function, whose coefficients reflect the dynamics of finite and progressively larger $n$-molecular clusters ($\sim t^n$). At any rate, a simple case lending itself to combine Brownian relativity and random walk at arbitrary scales is the motion of a (spherical) particle in a hard-sphere gas, where the ratio of Van der Waals's radii, of tracer and gas molecules, is kept fixed. The unperturbed system over which to define the special formalism would therefore be a gas, where "chains" of independent scattering events take place. They could be described for instance by (memoryless) Poisson's processes, in which the probability of an event happening in a small spacetime increment is proportional to the increment size (i.e., $P\{\boldsymbol{\sigma} > s + s'\} = P\{\boldsymbol{\sigma} > s\}P\{\boldsymbol{\sigma} > s'\}$). Whenever some class of collision sequences (e.g., binary or ring-like) is short-range correlated, one may expect the diffusion constant of a "scattering chain" to be of Enskog's type times a coefficient, identifying a Brownian–Lorentz factor, depending on gas and particle details. In principle, one might try a Brownian–relativistic formulation of the kinetic theory, and explain the features of scattering paths by a Brownian–Lorentz factor per single collision (or per collision cluster). To do so, however, another (kinetic) definition of invariant interval is required.

## 3. REAL POLYMER IN A MINKOWSKIAN FLUID

### 3.1 Intrinsic viscosity as a Brownian–Lorentz factor

The previous results can be grouped in a synthetic fashion by noting that:

$$\Delta\overline{\mathbf{r}^2}\Delta t = \text{const} \tag{2.185}$$

i.e., the chain conformation specified by:

$$\nu_{\mathrm{i}} = \frac{1}{2} \qquad \vartheta = 2 \quad \text{(ideal)} \tag{2.186}$$

fulfill the (constant) boundary value set by the rod-shaped system (or rigid-rod limit):

$$2\nu + \vartheta = 2\nu^* + \vartheta^* \equiv 3 \tag{2.187}$$

with maximum molecular repulsion, $\nu^* = \vartheta^* \equiv 1$. We could ascribe to this scheme a real chain, with radius given by Flory's theory (1949):

$$\nu = \frac{3}{5} \qquad \vartheta = \frac{9}{5} \quad \text{(real)} \tag{2.188}$$

endowed with excluded volume and therefore not expected to enter the predictions of the special formalism. It would correspond to a universal exponent $\delta = -\frac{4}{5}$ for the diffusion coefficient but, in principle, there is no reason to suppose this mobility scaling in $\gamma_B$. What happens is something similar to special relativity, for a relativistic point mechanics is proved successful without introducing general relativity. In this case, (longer-ranged) segment correlations and hydrodynamic interactions may equally come into play by a suitable analysis of a (single) "real chain" in a Minkowskian diffusive spacetime.

We start again from the equivalence of two Brownian intervals:

$$dt'' - d\overline{\mathbf{r}''^2} = dt' - d\overline{\mathbf{r}'^2} \tag{2.189}$$

implicitly defining a macromolecule in solution as a local perturbation that displaces the initial diffusive horizon of the host fluid. We continue to work in natural units ($D = 1$), employed throughout this section. An interesting issue to be discussed now is how this picture becomes when molecular mobility is perturbed by a real coil. Consider, accordingly, the time dilation rule:

$$\left(\frac{dt'}{dt''}\right) = \frac{1 - \left(\frac{d\overline{\mathbf{r}''^2}}{dt''}\right)}{1 - \left(\frac{d\overline{\mathbf{r}'^2}}{dt'}\right)} \tag{2.190}$$

and refer it to a pair of polymer frames, $O'$ and $O''$, diffusing across the medium. Owing to the significance of Brownian–Lorentz factor, times will run different by an overall mobility ratio, scaling now with two (local) exponents, $\delta' - \delta'' \equiv \iota$:

$$\left(\frac{dt'}{dt''}\right) = \frac{\gamma_B''}{\gamma_B'} \sim N^{-\iota} \tag{2.191}$$

The ideal chain analysis conducted in the previous section required the molecular mobility to be additive ($\iota = 1$). Wishing to give now an account of the real chain, the endpoint contraction and time dilation can be conceived as they directly experience the long-range segment interactions by a new factor $\gamma_B$. The simplest way is to set it so as to describe the viscous behavior of the polymer solution when the spacetime is slightly perturbed, in the limit of infinite dilution. Furthermore, on approaching the long-time fluctuation response, transport coefficients can yield a better characterization than (equilibrium) correlation functions. This suggests that we consider the concept of intrinsic viscosity ($[\eta]$), as introduced by Einstein (1906–1911) in his analysis of a dilute solution of structureless particles of volume fraction $\phi$:

$$[\eta] = \lim_{\phi \to 0^+} \eta_L(\phi) \tag{2.192}$$

for he obtained the famous result, $[\eta] = \frac{5}{2}$. It is easily extrapolated from "Huggins's equation":

$$\frac{\eta_L(\phi) - \eta_L}{\eta_L \phi} = [\eta]\big(1 + k_H[\eta]\phi + \cdots\big) \tag{2.193}$$

where the second-order coupling term ($k_H$) is said to be Huggins's coefficient. We underline that, contrarily to any higher order, the intrinsic viscosity is not affected by Brownian motion features. The main cause behind it is that, while Brownian motion tends to flatten uniformly the distribution function of the relative position, the liquid can favor some particle configuration. The $n$th term in the above expansion reflects thus the relative motion in an $n$-particle system (pairs, triplets and so on), but Brownian motion details do not take part in the calculation for $n = 1$. In reason of this, the analysis of higher orders led over the years to different conclusions, including on Huggins's coefficient for sticking particles. A last noteworthy contribution goes back to the continuum approach to a dispersion of impenetrable rigid particles, by Eligiusz Wajnryb and John S. Dahler (1997), who refined the value ($k_H \simeq 6.2$) carried out by Batchelor (1977) to $\simeq 5.9148$.

To recast the Brownian–Lorentz factor for an immaterial spacetime in terms of $[\eta]$, note that the (logarithmic) variations of viscosity ($\eta$) and diffusion coefficients are constrained by the Sutherland–Stokes–Einstein law, $\frac{\Delta D}{D} = -\frac{\Delta \eta}{\eta}$, thence we set:

$$\gamma_B = [\eta] \tag{2.194}$$

This definition is expected to preserve the scaling picture of the ideal coil into another flat-like model, regardless of specific Brownian motion properties, Minkowski's tensor still acting as a "base" background metric, and polymer hypersurfaces being nearly alike, devoid of physically significant history. We are going to show that this elementary rewriting can account consistently for some of the universal behavior shown by real macromolecules. Intuitively, a physical reason behind this agreement lies in the possibility of defining other measures of a chain size than the end-to-end distance (or gyration radius). These radii are $\rho_A \propto \sqrt[3]{A_2 N^2}$ (second virial coefficient), $\rho_H \propto T/(\eta_L D)$ (hydrodynamic) and $\rho_\eta \propto \sqrt[3]{[\eta]N}$ (viscosity). The latters are dynamic quantities coming from the hydrodynamic drag of an equivalent dispersion of spherical colloids described by the Sutherland–Stokes–Einstein relation. Spacetime perturbations can thus be detected by equivalent changes of thermodynamic or transport coefficients, and other expressions for $\gamma_B$ may be therefore attempted. Note also that, according to William W. Graessley (1980), the critical overlap concentration of polymer coils generally behaves as $c^* \sim 0.77/[\eta]$. This criterion is widely adopted to demark the boundary between dilute and semidilute solutions, provided the chains are not significantly deformed beyond their equilibrium conformation. Thus, the Brownian–Lorentz factor may also be connected with the polymer concentration regime.

## 3.2 Zimm's, Kirkwood's, and Flory's regimes

Consider thus the time dilation and length contraction rules taking place in a liquid in accord with:

$$\frac{\overline{\mathbf{r}'^2}}{\overline{\mathbf{r}''^2}} = \frac{t''}{t'} = \gamma_B \tag{2.195}$$

The Brownian–Lorentz factor can be described by one of the (four) empirical "Mark–Houwink–Kuhn–Sakurada" relations, $[\eta] = k_\mu N^\mu$, the others closely expressing the radius of gyration, the sedimentation and diffusion coefficients. It holds for monodisperse polymer solutions, and was first proposed as an empirical equation by Herman F. Mark (1938) and R. Houwink (1940). The exponent and, specially, the prefactor depend on the chain conformation, however, the former can be re-expressed by the Fox–Flory relation, or:

$$\mu = 3\nu - 1 \tag{2.196}$$

It yields a good agreement in the whole (physically meaningful) numerical range, going from the ideal Gaussian state, when the random coil is in $\Theta$ conditions ($\mu = \frac{1}{2}$), to an expanded chain with (very) high molecular weights ($\mu = \frac{4}{5}$). Here, working out the spatial constraint, still with $\overline{r'^2} \sim N^2$ and $\mu = \iota$, brings to the following relation:

$$\frac{\mu}{2} + \nu = 1 \tag{2.197}$$

which just intersects the intrinsic viscosity relation at Flory's chain radius ($\nu = \frac{3}{5}$). Furthermore, the $[\eta]$ exponent ($\mu = \frac{4}{5}$) identifies consistently the mobility value which was actually needed to ascribe Flory's coil to be part of Brownian special relativity.

Completing our picture now requires exploiting the last constraint in the time dilation rule. Accordingly, setting $t' \sim N$ yields:

$$\vartheta - \mu = 1 \tag{2.198}$$

well interpreting the involved universal exponents, either in a real chain model ($\vartheta = \frac{9}{5}, \mu = \frac{4}{5}$) or in the dynamic regime studied by Bruno H. Zimm (1956), when polymer relaxation modes are affected by long-range hydrodynamic interactions between monomers mediated by the liquid ($\vartheta = \frac{3}{2}, \mu = \frac{1}{2}$). Zimm's model in a "good solvent," when monomers experience their mutual repulsion and chain shapes spread out ("swell"), fulfills a variety of systems (including DNA molecules). Here, aside from thermal and entropic forces, a diffusing segment creates a long-range backflow coupling with the motion of the other segments. Note that, as endowing Newton's second law with the Lorentz–Poincaré symmetry can improve classical mechanics, here, by dealing with the intrinsic viscosity in place of mobility splits up the overall spacetime constraint into a pair of laws, combining geometry and chain interactions consistently. This can be summarized by a scheme, sketching out how a new universal exponent arises from the boundary value of the unperturbed rod-shaped system:

$$2\nu + \vartheta = 3 \rightarrow \begin{cases} 2\nu = 2\nu^* + \iota \\ \vartheta = \vartheta^* - \iota \end{cases} \tag{2.199}$$

with $\iota = \mu$. Joining the time dilation and Mark–Houwink equations returns the Kirkwood–Zimm formula (at constant $T$ and $\eta_S$):

$$\vartheta = 3\nu \tag{2.200}$$

It can be derived by expressing the diffusion coefficient under the approximation of John G. Kirkwood and Jacob Riseman (1948), when the velocity self-correlation function only refers to the host liquid, and does not account for polymer effects. In the end, the universal state solving the equation system summing up this analysis:

$$\nu = 1 - \frac{\mu}{2}, \qquad \mu = \vartheta - 1, \qquad \vartheta = 3\nu \quad \text{(real)} \tag{2.201}$$

deduces a Flory-like conformation state, $\nu = \frac{3}{5}$, $\mu = \frac{4}{5}$ and $\vartheta = \frac{9}{5}$, as argued at the beginning.

## 3.3 Characteristic function for diffusive intervals

The real polymer behavior can be better faced by generalizing the Brownian interval in the hydrodynamic regime to a time-dependent characteristic function for the position linking any two monomers in a chain at fixed molecular weight ($N$):

$$\varsigma_{\mathbf{r}_N}(\mathbf{q}, t) = \overline{e^{i\mathbf{q}\cdot\mathbf{r}(t)}} \tag{2.202}$$

where the average, taken with respect to the probability distribution function of the random chain vector:

$$\overline{\ldots} = \int W_N(\mathbf{r}, t) \ldots d\mathbf{r} \tag{2.203}$$

is clearly equivalent to Fourier transforming in the wavevector domain, yielding the response to single excitations of fixed $\mathbf{q}$. $\varphi_{\mathbf{r}_N}$ is (obviously) an "incoherent intermediate scattering function," as in the notation of neutron scattering theory, and means a transformed (van Hove's) self-correlation function. As usual, fluctuations can be discussed in Fourier's space, getting back to macroscopic quantities in the limit of $q = |\mathbf{q}| \to 0$.

We define at this point the functional displacement associated with the corresponding heat-diffusion equation, still in natural units, and dimension equal to a reciprocal of time:

$$\Sigma_N(\mathbf{q}, t) = \int \left( \frac{\partial W_N}{\partial t} - \vec{\nabla}^2 W_N \right) \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}\, d\mathbf{r} \tag{2.204}$$

Now, application of Green's theorem yields:

$$\Sigma_N(\mathbf{q}, t) = \left( \frac{\partial \varphi_{\mathbf{r}_N}}{\partial t} \right) + q^2 \varphi_{\mathbf{r}_N}(\mathbf{q}, t) \tag{2.205}$$

where a spherically symmetric distribution $(r(t) = |\mathbf{r}(t)|)$:

$$\varphi_{\mathbf{r}_N}(q, t) = \overline{\left( \frac{\sin qr}{qr} \right)} \tag{2.206}$$

expanded in a power series of $q$, gives us:

$$\varphi_{\mathbf{r}_N}(q, t) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)!} \overline{\mathbf{r}^{2n}} q^{2n} \tag{2.207}$$

with coefficients:

$$\left( \frac{\partial^{2i} \varphi_{\mathbf{r}_N}}{\partial q^{2i}} \right)_{q=0} = \frac{(-1)^i}{2i+1} \overline{\mathbf{r}^{2i}} \tag{2.208}$$

They depend on statistical moments, providing at any order ($2n$) a measure of the spatial spread for an ensemble of $N$ units. This means the extended diffusive interval (per unit time) can be expanded to:

$$\Sigma_N(q, t) = -\frac{q^2}{3!} \left( \frac{d\overline{\mathbf{r}^2}}{dt} \right) + \frac{q^4}{5!} \left( \frac{d\overline{\mathbf{r}^4}}{dt} \right) - \cdots + q^2 - \frac{q^4}{3!} \overline{\mathbf{r}^2} + \frac{q^6}{5!} \overline{\mathbf{r}^4} - \cdots \tag{2.209}$$

or:

$$\Sigma_N(q, t) = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{(2n-1)!} \sigma_{2n} q^{2n} = \sigma_2 q^2 - \frac{\sigma_4 q^4}{3!} + \frac{\sigma_6 q^6}{5!} - \cdots \tag{2.210}$$

where, for any $n \neq 1$, each generalized diffusion coefficient:

$$\sigma_{2n} = \overline{\mathbf{r}^{2n-2}} - \frac{(2n-1)!}{(2n+1)!}\left(\frac{d\overline{\mathbf{r}^{2n}}}{dt}\right) \tag{2.211}$$

couples a (separate) Brownian interval, for (complementary) non-Gaussian corrections at the $\mathrm{O}(q^{2n})$ scale. Such terms slow down the self-correlation decay, and do not contribute anymore when statistics turns back into Gaussian. When $n = 1$, the typical (fluctuation) wavelength accounted by $\sigma_2$ is much smaller than typical molecular step sizes or mean free paths, and the relative fluctuations of the spacetime scale are always of the order of unity. Thus, by truncating the series to the first (leading) term, one recovers Einstein's law for free-particle Brownian motion and the scaling picture of ideal coils, whose (Gaussian) statistical properties are determined only by the knowledge of the second moment (i.e., $d\sigma^2 \simeq \sigma_2\, dt$). Furthermore for a freely jointed chain, still of $N$ units with equal bond length ($|\mathbf{r}_s| = l$), then $W_N \to \overline{W}_N(\mathbf{r}; \{\mathbf{r}_s\}) = \delta(\mathbf{r} - \sum_s \mathbf{r}_s)$, so that:

$$\overline{\left(\frac{\sin qr}{qr}\right)} \to \left(\frac{\sin ql}{ql}\right)^N \tag{2.212}$$

and the expansion in powers of $q$ of the characteristic function on the right leads to $\mathrm{O}(\sigma_{2n}) \sim (Nl^2)^n$, as expected in this model for large (enough) molecular weights.

This central moment-generating scheme can be compared to (but not confused with) the "cumulant expansion," helpful to work with long-range correlations at arbitrary (time) scales in several statistical mechanics applications, as discussed by Kubo (1962) but first introduced by Kirkwood (1938) in the context of Ising's model and then applied to the classical virial expansion by Robert Brout (1959). Cumulants may be generated by taking the logarithm of the incoherent intermediate scattering function, $F_s = F_s(\mathbf{q}, t)$, returning the average value and variance at the first two orders. A noteworthy expression was given (for a liquid) by Aneesur Rahman et al. (1962):

$$\ln F_s(q,t) = \sum_{i\in 2\mathrm{N}} (-1)^{\frac{i}{2}} q^i \rho_i(t) = -q^2\rho_2 + q^4\rho_4 - q^6\rho_6 + \cdots \tag{2.213}$$

afterwards rewritten by B.R.A. Nijboer and Rahman (1966) by the same (time-dependent) coefficients used in statistics to characterize the deviation of a probability density from the Gaussian shape (third-order "skewness" factor for asymmetry, fourth-order "kurtosis" factor for tail persistence, and so on). Cumulant expansions might be questioned as being mathematical expedients rather than physical equations, but in principle there is no argument to mistrust about its convergence. Non-Gaussian corrections, however, are specially important at intermediate scales (e.g., in liquid Ar, $\sim 10^{-12}$ s). The functions $\rho_m$ are related to the spatial moments of the random particle displacement, generally taken as a function of time along the unit wavevector, e.g.:

$$2!\rho_2(t) = \overline{\Delta\mathbf{r}^2(t)}, \qquad 4!\rho_4(t) = \overline{\Delta\mathbf{r}^4(t)} - 3\overline{\Delta\mathbf{r}^2(t)}^2, \ldots \tag{2.214}$$

and the velocity autocorrelation functions. Thermally averaging Taylor's expansion of the plane wave in Fourier's transform, returns in fact:

$$F_s(q,t) = \sum_{k=0}^{\infty}(-q^2)^k \int_0^{t}\int_0^{t_1}\int_0^{t_{2k-1}} \overline{\mathbf{v}(t_1)\ldots\mathbf{v}(t_{2k})}\, dt_1\, dt_2 \ldots dt_{2k} \tag{2.215}$$

suggesting a natural identifications of spatial moments and velocity self-correlations at corresponding orders, i.e.:

$$\rho_2(t) = \int_0^{t}\int_0^{t_1} \overline{\mathbf{v}(t_1)\mathbf{v}(t_2)}\, dt_1\, dt_2 \ldots \tag{2.216}$$

which is still to be exploited in Brownian relativity.

In this respect, while the short-time power-law behavior is very sensitive ($i \geqslant 2$) to the nature of the molecular potential, if continuous or discrete (hard-sphere), the long-time regime (stably) obeys:

$$\rho_i(t) \simeq D_i(t)t + B_i(t) \tag{2.217}$$

that is, just the kinetic form that Brownian relativity relies on. Both coefficients on the right increase slower than $t^{\frac{i}{2}-1}$ and, for $i = 2$, one is left again with the ordinary diffusion coefficient, while:

$$B_2 = -\int_0^{\infty} t\overline{\mathbf{v}(0)\mathbf{v}(t)}\, dt \sim t^{\frac{1}{2}} \tag{2.218}$$

since, following the important contribution by Berni J. Alder and T.E. Wainwright (1970), the velocity autocorrelation function decreases asymptotically as $\sim t^{-\frac{3}{2}}$.

Provided $t \to N$ is replaced, the same representation applies as well to static macromolecules, as shown in the same years by Kazuo Nagai (1963) for sufficiently long chains:

$$S_N(q) = \mathrm{e}^{-\frac{\rho^*}{2}} \sum_{i=0}^{\infty} \mathrm{a}_{2i}\rho^{*i} \tag{2.219}$$

here with $\rho^* = q^2\rho_2/3$, $\mathrm{a}_0 = 1$, $\mathrm{a}_2 = 1$, and:

$$2^i \mathrm{a}_{2i} = \sum_{1<s\leqslant i} \frac{(-1)^{s-1}}{s!(i-s)!}\mathrm{A}_{2s} \tag{2.220}$$

The coefficients in the sum are useful to quantify the relative fluctuations of each (even) spatial moment of the chain vector distribution function:

$$\frac{\overline{\mathbf{r}^{2s}}}{\overline{\mathbf{r}^{2}}^{s}} = 3^{-s}(2s+1)!!(1-\mathrm{A}_{2s}) \tag{2.221}$$

and vanish whenever it is normal ($d = 3$):

$$W_N\big(|\mathbf{r}| = r\big) = \left(\frac{d}{2\pi N l^2}\right)^{\frac{d}{2}} \mathrm{e}^{-\frac{dr^2}{2Nl^2}} \tag{2.222}$$

They can be expressed by a recursive relation for our generalized diffusion coefficients and the second cumulant ($\rho_2$):

$$\left(\frac{2\rho_2}{3}\right)^{1-n} \frac{\sigma_{2n}}{(2n-1)!!} = 1 - \mathrm{A}_{2n-2} + \frac{1}{3n}\left[\rho_2\left(\frac{d\mathrm{A}_{2n}}{dt}\right) - n(1-\mathrm{A}_{2n})\left(\frac{d\rho_2}{dt}\right)\right] \tag{2.223}$$

where, from the above definition, it is meant $\mathrm{A}_{n\leqslant 2} \equiv 0$.

## 3.4 Real polymer size

In analogy with the previous extension, an expansion for the square end-to-end distance can be set to:

$$\overline{\mathbf{R}^2(q)} = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{(2n-1)!} q^{2n} \overline{\mathbf{R}^2_{2n}} \tag{2.224}$$

where each $\overline{\mathbf{R}^2_{2n}}$ possesses a Brownian–Lorentz factor scaling as:

$$\gamma^{-1}_{B,2n} \sim \frac{1}{\overline{\mathbf{r}^{2n-2}}}\left(\frac{d\overline{\mathbf{r}^{2n}}}{dt}\right) \tag{2.225}$$

If chains are ideal, any rod-like length ($\sim N^{2n}$) contracts evidently by the same factor ($\gamma_{B,2} \sim N$), yielding:

$$\overline{\mathbf{R}^2(q)} = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{(2n-1)!} q^{2n} N^{2-1/n} \tag{2.226}$$

Regarding the family of universal exponents in $\overline{R^2_n} \sim N^{2\nu_n}$, it may be observed they are bounded consistently from below by the Gaussian domain, and from above by the rod-like values, $2 - \frac{1}{n} = \nu_n \in [\nu_{\mathrm{i}}, 1)$. To get instead a simple evaluation of the real coil exponent ($\nu_{\mathrm{r}}$), let us start from the definition:

$$2\nu = \left(\frac{\partial \ln \overline{\mathbf{R}^2}}{\partial \ln N}\right) \tag{2.227}$$

and work out the leading contribution to the former series. It is useful, to this end, to consider the mathematical identity:

$$\nu Z N^{2\nu} = \lim_{q^{2n}N^{2-1/n} \to N^{2\nu}} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\chi_{2n}}{(2n-1)!} q^{2n} N^{2-1/n} \tag{2.228}$$

with $\chi_k = 1 - \frac{1}{k} + \frac{d\ln q^k}{d\ln N^2}$, where the normalization term, or "partition factor" ($Z$), is a sum over length scale weights:

$$Z = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{(2n-1)!} = \sin(1) \tag{2.229}$$

and equates the sine function of one radian ($= \frac{180}{\pi}$ degs).

To proceed, the simplest approximation is to get rid of wavenumber dependences ($q$) and focus on the neighborhood of $\bar{n} = \frac{1}{2(1-\nu)}$, near which the dominant contribution is envisaged to lie. Replacing its integer part $[\bar{n}]$ in the sum reduces the last but one equation into:

$$\nu_{\mathrm{r}} \sin(1) \simeq \frac{(-1)^{[\bar{n}]+1} \chi_{2[\bar{n}]}}{(2[\bar{n}]-1)!} \tag{2.230}$$

and note that any value $\nu \in [\nu_{\mathrm{i}}, \frac{3}{4})$ conducts to $[\bar{n}] = 1$. This sets the solution to be unique in the conformational domain ranging from the Gaussian state to polymer chains confined in two dimensions (e.g., adsorbed), for which $\nu = \frac{3}{4}$. Accordingly, as $1/(1!) - 1/(2!) = \frac{1}{2}$, the final result may be expressed by a simple and meaningful relationship:

$$\nu_{\mathrm{i}} \simeq \nu_{\mathrm{r}} \sin(1) \tag{2.231}$$

where, employing $\sin(1) \simeq 0.841$, returns $\nu_{\mathrm{r}} \simeq 0.594$. This 3-dimensional value is reasonably agreeing with the theory of critical phenomena applied to polymer systems, as pioneered by Pierre G. de Gennes (1972). After several refinements, the best value predicted by renormalization group techniques is considered to be $\nu_{\mathrm{r}} \simeq 0.588$.

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## CHAPTER THREE

# THE GENERAL THEORY OF BROWNIAN RELATIVITY

## Contents

## 1. GEOMETRIC APPROACH TO POLYMERS IN SOLUTION

### 1.1 Principle of equivalence for Brownian statistics and geometry

The special formalism should now be extended to a general–relativistic approach, accounting for particle correlations. When statistics is Gaussian, the former chapter taught us to deal with free Brownian particles and ideal chains as they were statistically equivalent. Just as “the laws of physics are the same in all inertial frames” (Einstein’s first postulate), time-like and shape-like observers could attain an equivalent (universal) description of the laws of statistics in ideal systems. In a spacetime modeled by the two Brownian postulates, to distinguish a molecular path (a random

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trajectory, in time) from a monomer path (a random polymer shape) is no longer meaningful. Gaussian chains form however a strongly idealized class of (Markovian) processes, with short-range (or null) segment correlations, well described in a "phantom" immaterial spacetime. In "real" macromolecules, not only the local interactions between adjacent units are important, but also those among segments which are far from each other (in the so-called "primary sequence"). As specific examples, this is the case of electrostatic repulsions, van der Waals's dispersion forces, excluded volumes and so on. More generally, long-range correlations (and density fluctuations) will have to be accounted for. In statistical terms, when liquid and polymer molecules are carriers of any form of interaction, the future evolution of their stochastic processes will be sensibly influenced by the past history. Geometrically, this means that the flat metric hypothesis is to be abandoned for a more realistic "massive" space, where any (local) measure of time and length intervals (e.g., $c_\infty$) now becomes meaningless.

Fortunately, including correlations in special Brownian relativity can be done in close analogy with the ordinary theory. There, when the vacuum is filled by matter and energy profiles, the equations are to be rewritten for a curved geometry. Here, any chain statistics will induce an equivalent geometry, ascribing the influence of correlations to a new metric tensor ($\eta_{\mu\nu} \rightarrow g_{\mu\nu}$). At that point, restating the equivalence principle in Brownian language will simply need to follow the logics of Einstein's formalism. We can look at any perturbation to the normal statistics as the analogue of a (gravity) field, but should care of a couple of differences.

Consider thus the (diffusive) worldlines in Fig. 3.1. They comprise random paths in the long wavelength regime, with different correlation strength, depicting the same rectangle as that in the translational case. The mean time to cross each side will tend to decrease with increasing correlations, and the deficit length (or angle) will be positive. Accordingly, a correspondence between field intensity and molecular disorder establishes, both for time-like and shape-like frames. For (single) linear macromolecules, the "ground" level is set to an ideal (Rouse's) chain, with its (relaxation) times $\tau_m$ (or modes $m$). They are the correlation times of chain portions of $N/m$ repeat units, the longest of which $\tau_1$ ($\sim N^2$) obviously dominating the uncorrelated dynamics. In this way, on varying the extent of correlations, one obtains the sample paths and characteristic times that are typical of other polymer models.

We can now enunciate a principle of equivalence for geometry and statistics:

> Correlated random paths in time, moving in a flat geometry, and unperturbed random shapes, evolving in a curved space, are equivalent,

Brownian relativity providing no way to discriminate between such circumstances. In so far as Einstein's equivalence principle was, for the first relativity postulate in the special formulation, this enunciate extends the first Brownian postulate to an arbitrarily correlated path. At first sight, it would appear to be obvious, at least qualitatively. Once any unperturbed system is set by embedding a background Minkowski's manifold, each worldline will have a metric tensor specified by the correlations with which it diffuses. However, just as the in the Einstein's relativity, this principle posits something more than a bare correspondence. It tells us in

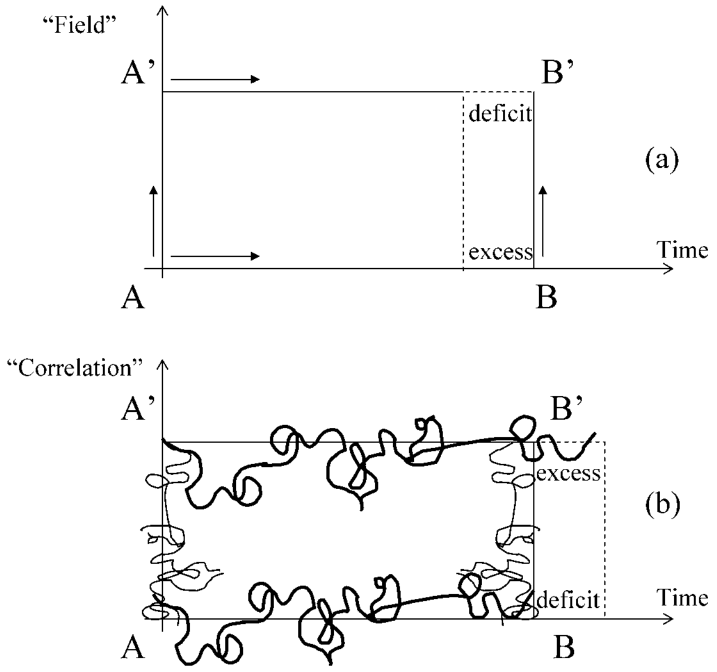

**Figure 3.1** Sketch of "geodesic rectangles" in Einstein's (a) and Brownian (b) relativities.

essence that the form of (ideal) universal laws maintains also in conditions of non-ideality.

Another consequence of the Brownian equivalence principle is that it implies in principle a multiplicity of spatio-temporal descriptions, where strictly unique definitions of finite times, distances and diffusion coefficients, can only be attained in the neighborhood of each event. It would be tough, if not impossible, to understand the topological properties of the space only from the knowledge of geometry (the metric tensor). We will begin to see to this aspect in the last chapter.

## 1.2 Statistical pseudo-coordinates

Before proceeding further, one happens to fall across the weakest point of Brownian relativity, consisting of certain restrictions to the general form of coordinate transformation laws. The special theory was considered originally for a particular class of frames, lying at the hydrodynamic limit, with radial symmetry and only detecting second central moments in $(1+1)$ Cartesian dimensions, a time and a space. The latter is the spatial coordinate which the relative movement establishes along. While in translational kinematics, it gives the uniform motion direction ($x^s = v^s t$), the spacetime of Brownian relativity is homogeneous and isotropic with respect to diffusion ($\overline{\mathbf{r}^2} \propto t$). Their spatial coordinates are related by $x^{s2} \to \overline{\mathbf{r}^2} = \sum \overline{\mathbf{x}^{s2}}$, and the radial position, $x^s \to \rho = \sqrt{\overline{\mathbf{r}^2}}$, may be employed, according to the involved probability density ($W_N$). Wishing to see $\rho$ as an independent variable, one may imagine varying it unconditionally, as a radial or Cartesian coordinate is used to be arbitrarily varied. Otherwise, any position displacement will be generally equivalent to a statistical perturbation. These remarks, though being elementary in themselves, are useful to recall that changing (spatial) coordinates induces a variational problem for the probability density. Furthermore, as being statistically representative of $N$-particle ensembles, they should rather be regarded as pseudo-coordinates. Several details are obviously lost if chain states are described by statistical moments instead of probability measures, by this means however Brownian relativity can let universal laws better emerge.

To get the gist, when the issue of changing coordinates through their probability functions (or functionals) is passed by, one enters the universality domain. In such a case, every statistical information is accessed through the behavior of the metric tensor components. Remember that not every transformation is feasible at this stage of research, but only those preserving the symmetry set by the long-wavelength regime. Otherwise, wishing to look into statistics, the Brownian equivalence principle requires developing the variational problem raised by conceiving coordinates as probability functionals. This issue does not cover a central role here, but will be initiated by this chapter. Hereinafter, the pseudo-coordinate basis in which polymer problems are carried out will be generally denoted by $\sigma^\mu$. In particular, polar and Cartesian:

$$\sigma^\mu \equiv \left\{\tau = \sqrt{t}, \rho = \sqrt{\overline{\mathbf{r}^2}}, \theta, \varphi\right\}, \qquad \sigma'^\mu \equiv \left\{x^0 = \tau, x^s = \sqrt{\overline{\mathbf{x}^{s2}}}\right\} \tag{3.1}$$

are suitable representations and transform consistently ($\sigma^\mu \to \sigma'^\mu$). It is worthwhile noting that the invariant interval is preserved by any constant "translation," $\mathbf{x}^s \to \mathbf{x}^s + l$, since for any random variable, $\mathrm{Var}(\mathbf{x} + l) = \mathrm{Var}(\mathbf{x})$. Again, one may easily realize that there is no way to (unlimitedly) outdistance the event in which rods and clocks are initially set.

## 1.3 Brownian metric tensor

Ascribing statistics to the geometry of worldlines, fluctuating along a curvilinear path of length $\sigma$:

$$d\sigma^2 = -\gamma_{\mu\nu}\, d\sigma^\mu\, d\sigma^\nu \tag{3.2}$$

now requires tackling the Brownian metric tensor ($\gamma_{\mu\nu}$). According to the Brownian equivalence principle, it will serve to define a "locally universal" frame, bringing the perturbed system back to unperturbed. To check how a change in the system statistics may alter geometry, one easily realizes that a connection between Brownian reference frames and kinematics of diffusion can be built in close analogy to Einstein's arguments.

Imagine thus laying down a random path, still in the long wavelength regime, and seeking the law for the average end-to-end displacement as a function of time, $\overline{[\mathbf{r}(\omega)]^2} \sim \omega^o$, in some evolutionary variable ($\omega$). The value $o = 1$ describes an ordinary diffusion, outside which the "anomalous" regimes of "subdiffusion"

($0 < o < 1$) or enhanced "superdiffusion" ($1 < o < 2$) will take place, regaining the special case of a ballistic (or wavelike) motion for $o = 2$. Examples of subdiffusive phenomena are random walks on percolation clusters, bead motions in a polymer network and diffusion in convective rolls. Enhanced cases are less frequent in nature and, probably, the most representative is Richardson's diffusion in a turbulent fluid. Subdiffusions are sometimes identified to (long memory) "fractional Brownian motions," with divergent temporal moments.

The complementary, superdiffusive scenario can be described by Lévy's symmetric (stable) densities, whose distribution of spatial increments is "heavy-tailed" (i.e., more variable than an exponential distribution). In spite of the divergent spatial moments, they are "stable under addition" and fulfill the generalized central limit theorem due to Lévy himself and Khinchin. These processes are still Markovian, but "Lévy's flights" fluctuate very differently from the Gaussian case. Their displacement is determined by the long, unfrequent steps (i.e., the "flights") arising from the power-tailed distribution. The (local) instantaneous fluctuations implied by stable laws are statistically independent, but large enough to alter the (macroscopic) state observed in a critical phenomenon.

In the general theory of Brownian relativity, resorting to such (modified) methods will no longer be necessary. We will be furthermore able to avoid the complicated diffusion equations in a curved space, at least at this stage. In our view, negative or positive deviations from linearity are well discriminated, and deficit or excess lengths emerge according to the sign of $o - 1$. Pushing the analogy further, one might also introduce a time-like "acceleration" (i.e., the velocity self-correlation function, $d^2\overline{\mathbf{r}^2}/dt^2$), and ascertain that the only "unaccelerated" frames are those evidently with $o = 1$. On mapping $t \rightarrow N$, the same reasoning would apply to the arise of deficit or excess angles in path configurations of correlated chains, leading to perfectly dual conclusions for shape-like frames.

In general, positive and negative deviations from the law of Brownian motion will take place, respectively, in hyperbolic and spherical frames of reference, of positive ($k_G > 0$) and negative ($k_G < 0$) Gaussian curvatures (Fig. 3.2). In particular, to say something more, some assumption should be made. Einstein, alongside the equivalence principle, supposed that curvature (i.e., the deficit angle) were to be ascribed to the mass ($M$) enclosed inside the space. His suggestive hypothesis, $k_G \propto M$, related for the first time matter to geometry, and opened a feasible experimental confirmation of his theory. Brownian relativity, on the other hand, relies on Einstein's law for Brownian motion, holding in the long-wavelength domain. This approach will be used to move "backwards," from such "events at infinity" back to the effect of correlations in the characteristic function at finite wavelengths. A notion of hyperbolic geometry which lends itself to exemplify a reference frame in the hydrodynamic regime is that of "horocycle." It yields a peculiar reference frame, having both the character of a ("straight") line and a circle with "center at infinity," whose simplicity is useful to illustrate the Brownian equivalence principle. To briefly sketch it out, let $A$, $B$ be points on a line $l$ and $c$ be a circle of radius $\overline{AB}$, centered at $B$. When, at $A$ fixed, $B$ moves to infinity along $l$, an Euclidean $c$ tends to the straight line perpendicular to $l$ that is passing to $A$. In a hyperbolic space, as $\overline{AB} \rightarrow \infty$, the circle does not converge to a line but to a horocycle.

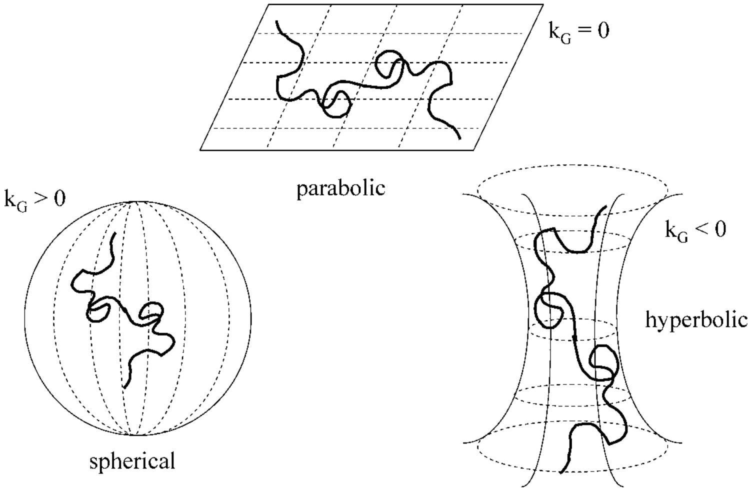

**Figure 3.2** Spaces of constant Gaussian curvature: positive (elliptic), zero (parabolic) and negative (hyperbolic).

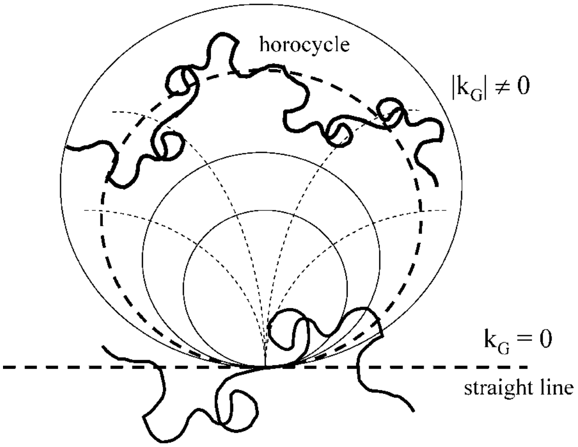

**Figure 3.3** Sketch of unperturbed and perturbed Brownian systems embedding a horocyclic (hyperbolic) frame.

To fix the ideas, consider the couple of schemes in Fig. 3.3. In (a), spacetime is taken to be flat and, when an unperturbed random path undergoes the effect of (positive) correlations, the random path interval will lengthen by a certain (positive) amount. Our principle of equivalence affirms that, on letting this path free to "devolve" in a curved spacetime, such an increment is preserved. We may come thus to (b), embedding perturbed ($p$) and unperturbed ($u$) paths from a horocyclic coordinate system in a space of constant curvature. It is known that the arclength ratio of two horocycles scales with their radial distance as $e^{\frac{r}{L}}$, where $L = \sqrt{2\pi/|k_G|}$ is

Lobačevskij's constant and $L \to \infty$ recovers the Euclidean limit. In this special case, a position translating the Brownian equivalence principle would be $\sigma_{\mathrm{p}}/\sigma_{\mathrm{u}} = \mathrm{e}^{\frac{r}{L}}$, $\sigma_k$ being the diffusive intervals for Gaussian (u) and (long-ranged) correlated (p) paths. As the parallelism angle ($\alpha$) follows from the Bolyai–Lobačevskij formula, the simple relation $\sigma_{\mathrm{u}}/\sigma_{\mathrm{p}} = \tan\frac{\bar{\alpha}}{2}$ would bridge in the simplest fashion the configuration of a correlated path to a mean $\bar{\alpha}$ value (b). In the Euclidean case, where paths are ideal and $\bar{\alpha} = \frac{\pi}{2}$ ($k_G = 0$), deficit (or excess) angles disappear. This exemplification, obviously, is hardly suitable to model situations of concrete interest, but already indicates that molecular trajectories and polymer conformations can be settled down in a variety of shapes, where geometry, to stress the words by Bernard Riemann in his 1854 dissertation, has a direct statistical meaning in its own right.

## 1.4 Postulate of geodesic Brownian motion

We learnt how Einstein's equivalence principle allows a description of a free falling system in terms of special relativity. It ensures the existence of a class of locally inertial observers, defined on a scale where spacetime can still be regarded unperturbed. Whatever the non-local form of the (curved) spacetime metric, there exists a free falling frame where the motion is still "geodesic." In macromolecular solutions, it is known that molecular hydrodynamics and polymer theory guarantee the existence of unperturbed regimes, in which statistics becomes (back) to normal. Close to ordinary relativity, this normally occurs for some (outer) long-wavelength scale, far distant apart from correlation and interaction sources, but does not mean that such frames will flatten geometry everywhere.

Consider thus the Brownian metric ($\gamma_{\mu\nu}$) for a given system of statistical coordinates ($\sigma^{\mu}$) and curvilinear path ($\sigma$). The Brownian principle of equivalence requires it be related to an ideal frame ($\iota^{\mu}$):

$$\left(\frac{d^2\iota^{\mu}}{d\sigma^2}\right) = 0 \tag{3.3}$$

and evolving with no correlation in a flat spacetime, with Minkowski's metric $\bar{\eta}_{\alpha\beta}$:

$$\gamma_{\mu\nu} = \left(\frac{\partial\iota^{\alpha}}{\partial\sigma^{\mu}}\right)\left(\frac{\partial\iota^{\beta}}{\partial\sigma^{\nu}}\right)\bar{\eta}_{\alpha\beta} \tag{3.4}$$

Proceeding as in Einstein's analysis, one arrives at:

$$\left(\frac{\partial\iota^{\mu}}{\partial\sigma^{\nu}}\right)\left(\frac{d^2\sigma^{\nu}}{d\sigma^2}\right) + \left(\frac{\partial^2\iota^{\mu}}{\partial\sigma^{\nu}\partial\sigma^{\lambda}}\right)\left(\frac{d\sigma^{\nu}}{d\sigma}\right)\left(\frac{d\sigma^{\lambda}}{d\sigma}\right) = 0 \tag{3.5}$$

of course, obtaining again:

$$\left(\frac{d^2\iota^{\tau}}{d\sigma^2}\right) + \bar{\Gamma}^{\tau}_{\nu\lambda}\left(\frac{d\iota^{\nu}}{d\sigma}\right)\left(\frac{d\iota^{\lambda}}{d\sigma}\right) = 0 \tag{3.6}$$

where it suffices to take the limit:

$$\bar{\Gamma}^{\tau}_{\nu\lambda} = \lim_{g_{\alpha\beta}\to\gamma_{\alpha\beta}} \Gamma^{\tau}_{\nu\lambda} \tag{3.7}$$

giving the Brownian analogue of the affine connection:

$$\overline{\Gamma}^{\lambda}_{\mu\nu} = \frac{\gamma^{\lambda\rho}}{2}(\gamma_{\rho\mu,\nu} + \gamma_{\rho\nu,\mu} - \gamma_{\mu\nu,\rho}) \tag{3.8}$$

The last but two is the Brownian–relativistic geodesic equation and states that, in a locally universal frame, each random path evolves as it were ideal. As already pointed out, this does not imply that the final scaling laws will be Gaussian too. Rather, it describes the variation of the ideal behavior, evaluated from a reference frame in which the Brownian equivalence principle applies.

## 1.5 Brownian–Einstein equations

We saw, in the first chapter, that the field equations of general relativity can be derived from the principle of stationary Einstein–Hilbert action. Here, with similar premises and notations, i.e.:

$$\delta \int \sqrt{-\gamma}\, \overline{R}\, d^4\sigma = -k' \int \sqrt{-\gamma}\, \overline{T}^{\mu\nu} \delta\gamma_{\mu\nu}\, d^4\sigma \tag{3.9}$$

the general equation of Brownian relativity can follow at once from setting again $g_{\mu\nu} \to \gamma_{\mu\nu}$, $\mathrm{g} \to \gamma = \det \gamma_{\mu\nu}$, and building all tensor quantities accordingly. We will continue to denote them by overscripting their symbols and write, in covariant form:

$$\overline{G}_{\mu\nu} = \overline{R}_{\mu\nu} - \frac{\gamma_{\mu\nu}\overline{R}}{2} = \overline{T}_{\mu\nu} \tag{3.10}$$

The left and right sides are respectively Einstein's ($\overline{G}_{\mu\nu}$) and the energy–momentum ($\overline{T}_{\mu\nu}$) Brownian tensors, the former depending on new Ricci's ($\overline{R}_{\mu\nu}$) and the curvature scalar ($\overline{R}$). The constant $k'$ is converted into another (unit) coefficient, which may be ignored in scaling calculations like the followings.

As a brief outline, the procedure that can be generally adopted to solve polymer problems comprises a characterization of mass and energy sources by their time-rates of change (i.e., $\overline{T}_{\mu\nu}$), a derivation of the Brownian metric from the field equations, and the calculation of a (test) polymer path as a Riemannian geodesics. Put more precisely, the second step starts from the spatial geometry and its rate of change at a given time, and determines the spacetime geometry at the same instant. From here on, the geometrodynamic equations predict at any time the 4-dimensional geometry and the mass–energy flowing throughout it. However, in taking advantage of the Brownian equivalence principle and the geodesic postulate, one should keep in mind the analysis by Einstein and Grommer, and should not regard them as strictly independent statements. Test polymers in fact take part of the total matter and energy distributions, though $\overline{T}_{\mu\nu}$ can represent diverse localization of them.

Another delicate point to remember in applying the Brownian–Einstein equations, is the impossibility of recognizing completely spacetime events. This is due to the constraint which they stem from, the stationarity of the action under arbitrary variations of the metric tensor components, which can take any value independently of pseudo-coordinates. Again, while geometry is measurable, Brownian metric is not, unless polymer correlations are detected from special classes of coordinates in the fluid, breaking what is technically known as "diffeomorphism invariance."

## 1.6 Energy–momentum and polymeric stress tensors

We need now to recast the energy–momentum tensor in light of Brownian–relativistic applications. The simplest thing to do is to discuss the stress tensor in polymer systems, and compare it with the viscous extra-term added to the perfect-fluid form, as seen in the first chapter. In polymeric networks (e.g., fluids and rubbers), the molecular origin of stress is mostly ascribed to intramolecular forces and, without significant concentration gradients, one normally works with:

$$\sigma_{ik}^{(\mathrm{n})} = \eta_S(\kappa_{ik} + \kappa_{ik}) + p_{\mathrm{i}}\delta_{ik} + \Pi_{ik} \tag{3.11}$$

as a function of time, $\sigma_{ik}^{(\mathrm{n})} = \sigma_{ik}^{(\mathrm{n})}(t)$. Here, $\eta_S$ and $\delta_{ik}$ are still the solvent viscosity and the covariant Krönecker symbol, $\kappa_{ik} = \frac{\partial v_i}{\partial x^k}$ is the (spatial) velocity gradient tensor, and:

$$\Pi_{ik} = \frac{\eta_P}{\tau_P \rho_{\mathrm{u}}^2}\pi_{ik} \tag{3.12}$$

is the polymer extra-stress term. It is proportional to a symmetric mean "configuration tensor," $\pi_{ik} = \overline{R_i R_k}$, averaged over all chain segments and giving a dynamic state variable for the intramolecular structure. Its physical significance is to account for the random vector orientation, $\mathbf{R}(s,t) = (\frac{\partial \mathbf{r}(t)}{\partial n})$, tangential to the macromolecule at segment $n$ at time $t$. The prefactor reports a (single) characteristic time ($\tau_P$), dominating the relaxation towards equilibrium, the polymer viscosity coefficient for infinitesimal shear ($\eta_P$), and the unperturbed root mean square extension ($\rho_{\mathrm{u}}$). $\Pi_{ik}$ had been essential in explaining the influence of polymer concentration on viscoelasticity. In the very dilute regime, viscoelastic effects are very small and the major contribution is viscous. With increasing concentrations, polymers get more and more entangled, and this term increases rather quickly.

To understand the way in which the previous expressions should be regarded, the experiences acquainted with polymer and relativity theories are to be recalled and compared with their main differences from Brownian relativity. The first descends from focusing on universal laws, intended here to be Brownianly covariant, and carrying the energy–momentum tensor into a spacetime defined differently ($x^\mu \to \sigma^\mu$). Secondly, the invariant quantity is no longer a velocity, but (dimensioned to) a diffusion coefficient. Because of the square root of the temporal coordinate in the unperturbed diffusive interval ($ct \to \sqrt{Dt}$), this will demand that our energy–momentum tensor be multiplied by some (characteristic) time.

Thus, provided the imperfect energy–momentum tensor is rewritten correctly, the large-wavelength phenomenological expression of $\overline{T}^{\alpha\beta}$ can be set to:

$$\overline{T}^{\alpha\beta} = \Upsilon^{\alpha\beta} \tag{3.13}$$

where $\Upsilon^{\alpha\beta}$ is identified as follows. On comparing the equations for polymer and relativistic hydrodynamics, the stress tensor can be separated again in (three) different contributions:

$$\bar{\sigma}_{\alpha\beta} = \bar{\sigma}_{\alpha\beta(\text{bulk})} + \bar{\sigma}_{\alpha\beta(\text{shear})} + \overline{\Pi}_{\alpha\beta} \tag{3.14}$$

where the last polymer term is added to generalize $\Pi_{\alpha\beta}$ to Brownian relativity. We will work, as usual, with incompressible liquids and inextensible chains, for which volume expansions and bulk (or "second") viscosity coefficients can be neglected, i.e.:

$$\Upsilon^{\alpha\beta} = -\bar{h}^{\alpha\mu}\bar{h}^{\beta\nu}\bar{\sigma}_{\mu\nu} \tag{3.15}$$

with $\bar{\sigma}_{\alpha\beta(\text{bulk})} = 0$. The tensor $\bar{h}^{\alpha\beta} = \gamma^{\alpha\beta} + (''\Delta')^{\alpha}(''\Delta')^{\beta}$ projects now on the rest (unperturbed) frame of the Brownian observer "codiffusing" with the liquid, and may be seen as the dynamic variant of Oseen's. At this point, one can take advantage of the Brownian equivalence principle and discuss the polymer problem in the time-like representation of an observer resting with the laboratory. It turns out that $\bar{\sigma}_{\alpha\beta(\text{shear})} = 0$, $(''\Delta')^{\alpha}(''\Delta')^{\beta} = \text{diag}(1, \mathbf{0})$, and:

$$-\Upsilon^{\alpha\beta} = \left(\gamma^{\alpha\lambda} + \delta^{\alpha 0}\delta^{\lambda 0}\right)\left(\gamma^{\beta\mu} + \delta^{\beta 0}\delta^{\mu 0}\right)\bar{\sigma}_{\lambda\mu} \tag{3.16}$$

or, expliciting each polymer term:

$$-\Upsilon^{\alpha\beta} = \overline{\Pi}^{\alpha\beta} + \delta^{\alpha 0}\overline{\Pi}^{\beta 0} + \overline{\Pi}^{\alpha 0}\delta^{\beta 0} + \delta^{\alpha 0}\delta^{\beta 0}\overline{\Pi}^{00} \tag{3.17}$$

Concerning the spatial components, a general expression matching the former requirements is:

$$\overline{\Pi}^{ik} = -\overline{E}^{ik}\bar{\pi}^{ik} \tag{3.18}$$

where $\overline{E}^{ik}$ depends on the adopted viscosity model, and the geometrical part $\bar{\pi}^{ik} = \overline{r^i r^k}$ is made for convenience non-dimensional by rescaling $R^s = \rho_{\text{u}} r^s$. Concerning the (pure) temporal component, it turns out $\Upsilon^{00} = -4\overline{\Pi}^{00}$. For equilibrium polymer solutions, the spatial matrix is diagonal, $\bar{\pi}^{ik} = \delta^{ik}$, while $\Upsilon^{00}$ is related to the thermal fluctuations of chain conformations. Working with one dominant relaxation process, $\overline{E}_{ik} = \eta_P\delta_{ik}$, the (phenomenological) relation $-\overline{\Pi}^{00} = \bar{\varrho}$ implies the traceless tensor condition:

$$\Upsilon^{\alpha}{}_{\alpha} = 0 = 4\overline{\Pi}^{0}{}_{0} - \overline{\Pi}^{i}{}_{i} \tag{3.19}$$

getting back, for $N \to 1$, to a result of the kinetic theory, $\eta_1 \propto \bar{\varrho}D'$ (in standard units). With this position, the influence of Brownianly–relativistic cooperative motions is neglected, but a dual analogy between Brownian movement and relativity (in covariant representation):

$$\Upsilon_{\mu\nu} = \text{diag}(\bar{\varrho}, \eta_P\mathbf{I}) \tag{3.20}$$

is attained, provided any transport coefficient be implicitly dependent on the repeat unit number of the Brownian frame moving across the fluid. Note that the fluctuation–dissipation theorem has taken the place of the state equation (i.e., coming from $T^{\alpha}_{\text{i}\alpha} = 0$). We could also set, in all generality, $\Upsilon^{\alpha}{}_{\alpha} = f(\bar{\varrho}, \eta_P)$, and observe that in the "pure" relativistic case (corresponding here to a simple liquid), the trace function $f \simeq 0$. Once the length scale is changed ($1 \to N$), this relation will vary according to the geometrodynamics induced by the polymer molecule. Verifying this point means to solve Einstein's equations, as shown by the forthcoming section for a relevant class of metric tensors.

## 1.7 "Static and isotropic" polymer solutions

Conformational and transport properties of a polymer solution of arbitrary concentration can be investigated by a general static isotropic metric ($\overline{\gamma}_{\mu\nu}$) in polar coordinates:

$$d\sigma^2 = b(\rho)\, d\tau^2 - a(\rho)\, d\rho^2 - \rho^2\, d\Omega^2 \tag{3.21}$$

with $-\overline{\gamma}_{00} = b$, $\overline{\gamma}_{\rho\rho} = a$, $\overline{\gamma}_{\theta\theta} = \rho^2$ and $\overline{\gamma}_{\varphi\varphi} = \rho^2 \sin^2\theta$. This metric "staticity," of course, does not prevent the system from having its own dynamics, just as statistical fluctuations do not prohibit attaining an equilibrium situation. Rather, it means that the diffusive interval (or proper time) won't be dependent upon time, but on space through the only rotational invariants, $\mathbf{r}^2$, $d\mathbf{r}^2$ and $\mathbf{r} \cdot d\mathbf{r}$. Furthermore, the spherical symmetry with respect to an arbitrary macromolecular "center," lying now in a non-Euclidean spacetime, promises a well-posed universality analysis. The metric $\overline{\gamma}_{\mu\nu}$ lends itself to a useful description of equilibrium polymer solutions, for which the Einstein–Brownian tensor is also diagonal, leading to field equations of the form:

$$\overline{G}_{\alpha\alpha} = \Upsilon_{\alpha\alpha} \tag{3.22}$$

and we are going to examine the results in some relevant cases.

## 1.8 Schwarzschild's single coil

Consider a real chain and a curved and empty portion of space around, to which:

$$\overline{R}_{\mu\nu} = 0 \tag{3.23}$$

applies, returning Schwarzschild's solution, $b(\rho) = 1 + c_S/\rho = 1/a(\rho)$. This behavior can characterize a (very) "heavy" polymer particle, diffusing in a medium perturbed by it. In the (scaling) limit, $N \to \infty$, the ($\rho\rho$) component should diverge, thus we set:

$$b(\rho) \sim D_N \tag{3.24}$$

obtaining $\rho D_N = c_S + \rho$. When the polymer particle moves across a medium that is nearly at rest, typical of a "Lorentz's gas," then $D_N \gg 1$ and:

$$\rho D_N \sim c_S \tag{3.25}$$

which essentially stands for a Sutherland–Stokes–Einstein law, provided $0 < c_S = k_B T/(6\pi\eta_S)$. This also needs that the scaling exponents for the chain gyration radius and diffusion coefficient are equal ($-\delta = \nu$), leading to a Kirkwood–Zimm relaxation time ($\sim\rho^3$).

Furthermore, the metric tensor change induced by replacing an ideal with a real chain, modifies the energy amount held in the 4-dimensional manifold. Space-like observers, with $d\tau = 0$, $d\theta = d\varphi = 0$, are generally linked by $d\rho^2 = g_{\rho\rho}\, d\rho'^2$, thence an elastic energy ratio can be defined to scale as $\sim g_{\rho\rho}$. It represents the strong entropic drive promoted by the flexibility, leading a chain in solution to take on the random polymer state or other disordered conformations. Reasoning in the variable time, an analogous configurational entropy can be identified to $\sim g_{00}^2$, thus the total energy ratio ($\varrho_\varepsilon$) for Schwarzschild's solution is:

$$\varrho_\varepsilon = g_{\rho\rho} + g_{\rho\rho}^{-2} \tag{3.26}$$

The radial metric element expresses the (actual) polymer size ($\rho$) divided by the ideal end-to-end distance ($\sqrt{N}\, l$), thus:

$$\varrho_\varepsilon(\rho, N) \sim \frac{\rho^2}{Nl^2} + \frac{N^2 l^4}{\rho^4} \tag{3.27}$$

we have the sum of an ideal elastic–entropic contribution (first term), quantifying the chain resistance to be fully stretched out by the square of the strain, with a repulsive term, giving the energy penalty coming from the spacetime perturbation caused by the self-intersections (the excluded volume). The first contribution alone would bring the molecule to an average size extremizing the amount of polymer microstates. In a Brownian–relativistic framework, the presence of time results into a self-exclusion opposing the entropic drive. The second is thus an intrinsic effect, uniform along the chain, and does not need of setting an excluded-volume parameter, as in Flory's mean-field theory. Their balance, evaluated by the usual stability condition, at constant $N$:

$$\varrho_{\varepsilon,\rho} = 0 \tag{3.28}$$

yields obviously the radius of Flory's (ideal) 4-dimensional chain, $\rho \sim \sqrt{N}\, l$. Here, it denotes the average distance over which the monomer density can be regarded constant and, for any conformation of $m$ units, proportional to $m\rho^{-4}$. Observe that this result comes again from an ideal polymer model, perturbed as in a "mean-metric field" theory, accounting for competing effects. The reason why any (Flory's) chain is ideal for $d \geqslant 4$ can be found intuitively in a geometrical analogy, clearly preserved in Brownian relativity. A Brownian movement, in fact, behaves more similarly to a surface than a curve. Surfaces, on the other hand, (almost) never meet when $d > 4$ and, if $d = 4$, (only) intersect at single points.

## 1.9 Concentrated polymer solutions

When the energy–momentum tensor is no longer neglected, the full solution of $\overline{G}_{\mu\nu} = \overline{T}_{\mu\nu}$ is required. To proceed, unless some specific potential field is known to have a strong motivation, it is simpler to posit the form of the metric components, and use the Brownian–Einstein equations to infer the matter and energy distributions. We can therefore start again from a general static isotropic metric, and use Einstein's tensor components in Appendix A to the first chapter. Note that, on tending to $N \to \infty$, the 00 (time–time) condition is proportional to the density times the diffusion coefficient, thus returning a relation for two vanishing quantities. Concerning instead the spatial conditions, we can regard a model with $\overline{E}_{ik} = \eta_P \delta_{\rho\rho}$. It comprises $\overline{G}_{\rho\rho} = \eta_P$ and two equivalent constraints, $\overline{G}_{\theta\theta} = \overline{G}_{\varphi\varphi} = 0$, holding at any fixed radial coordinate. In the present description, polymer and solvent molecules move together as a unique spherical body, "freely draining" with each other at a sphere of radius $\rho$. Recall that the free draining limit corresponds to Rouse's chain model, while in Kuhn's "impermeable sphere model," strong hydrodynamic interactions are assumed ("non-draining" limit).

In this framework, solving the Brownian–Einstein equations is equivalent to derive the (missing) metric components from:

$$\rho\psi_{\frac{db}{d\rho}} + 1 = \frac{\rho}{2}\psi_{ab} + \frac{\psi_a}{\psi_b} \tag{3.29}$$

with:

$$\psi_a = \frac{2\Upsilon_{\rho\rho} + \rho\Upsilon_{\rho\rho,\rho} + \frac{\psi_b}{\rho} + \psi_{b,\rho}}{\rho\Upsilon_{\rho\rho} + \frac{1}{\rho} + \psi_b} \tag{3.30}$$

The last but one simplifies upon introducing $z(\rho) = \psi_b$:

$$z_{,\rho} = \psi_a z - z^2 + \frac{2}{\rho}(\psi_a - z) \tag{3.31}$$

and regarding the limit of large $\rho$ values. In fact, if $z\xi_z \equiv 1$, then:

$$\xi_{z,\rho} \simeq \frac{1}{2}(1 - \psi_a \xi_z) \tag{3.32}$$

with:

$$\lim_{\rho\to\infty} \psi_a = \psi_{\Upsilon_{\rho\rho}} \tag{3.33}$$

and, let:

$$\mu(\rho) = \mathrm{e}^{\frac{1}{2}\int \psi_a \, d\rho} \tag{3.34}$$

it turns out:

$$\frac{z}{2} \simeq \frac{\mu}{\bar{c} + \int \mu(\rho')\, d\rho'} \tag{3.35}$$

where $\bar{c}$ is an arbitrary constant. Choosing $|\bar{c}| \gg |\int \mu \, d\rho'|$ implies:

$$\mu(\rho) \sim \sqrt{\Upsilon_{\rho\rho}} \tag{3.36}$$

and, let $n = 2/\bar{c}$:

$$b(\rho) \sim \mathrm{e}^{n\int\sqrt{\Upsilon_{\rho\rho}}\, d\rho'} \tag{3.37}$$

completing the sought metric components, together with:

$$a(\rho) \sim \Upsilon_{\rho\rho} \tag{3.38}$$

The Lorentz–Poincaré invariance for diffusive intervals was checked to be preserved by any diffusion coefficient change. We so use the Brownian equivalence principle under the following positions ($D = 1$):

$$1 \to D_N, \qquad D_N \to D^* \tag{3.39}$$

where $D^*$ is an overall diffusion coefficient. To represent it, consider Darken's generalized law, $D^* = 1 - (1 - D_N)\Phi$, where $\Phi = \Phi(\phi) \in [0, 1]$ is a (non-decreasing) function of the polymer fraction ($\phi$), with $\Phi(0) = 0$ and $\Phi(1) = 1$. Comparing Maclaurin's first-order expansion:

$$b(\rho) \sim 1 + n \int \sqrt{\Upsilon_{\rho\rho}}\, d\rho' \tag{3.40}$$

with:

$$b(\rho) \sim \frac{D^*}{D_N} = \Phi + \frac{1 - \Phi}{D_N} \tag{3.41}$$

implies, for any choice of $1 - \Phi = n \to 0^+$:

$$D_N^{-1} \sim \int \sqrt{\Upsilon_{\rho\rho}}\, d\rho' \tag{3.42}$$

This constraint may be conceived also as a new relationship, for tensor quantities and statistical coordinates, arising with increasing $N$ from the traceless tensor condition of the previous section ($\Upsilon^{\mu}{}_{\mu} = 0$).

Large segment numbers give a good approximation to a continuous space, and allow an (implicit) integration in the variable $N$, with $\Upsilon_{\rho\rho} \sim \eta_P$. Thus, since $\rho^2 \sim D_N \tau_P$, the universal law can be written as:

$$\delta + \nu = 3\nu - \vartheta = -\frac{\epsilon}{2} \tag{3.43}$$

with $\eta_P \sim N^{\epsilon}$ and $\tau_P \sim N^{\vartheta}$. It yields a new scaling behavior in the monomer number, essentially a modified Sutherland–Stokes–Einstein law and a different definition of hydrodynamic radius:

$$\rho D_N \sqrt{\eta_P} \sim N^0 \tag{3.44}$$

coupled to a chain relaxation time complying with:

$$\rho^3 \tau_P^{-1} \sqrt{\eta_P} \sim N^0 \tag{3.45}$$

In entangled dynamics, (stress) relaxation proceeds by a stochastic disorientation process of the polymer chain, diffusing out of the "tube" (tube "renewal") in which it is (initially) trapped. The time it takes to diffuse one length along the tube, so becoming trapped in another, independent tube, is the so-called "renewal time." The tube concept arose in the context of rubber elasticity, and is due to Sir Samuel

F. Edwards (1967), whereas the “reptation theory,” making a wide use of it, to de Gennes (1971).

With decreasing frequency ($\sim\tau_P^{-1}$), a progressively larger fraction of (individual) chains have enough time to re-entangle, and viscosity will increase here as the square of a mass density multiplied by a rescaled mobility coefficient. Nonetheless, due to the (weakly) covariance concept, introduced by Brownian relativity, these relations afford a satisfactory description of a solution of linear, homogeneous, neutral and flexible macromolecules, either in the unentangled or entangled regimes. In other words, they are fulfilled either for low or high molecular weights, above and below the “crossover” value ($N_c$) at which the scaling properties of transport coefficients change dramatically for the formation of entanglement points. This can be easily checked by using the theoretical values:

$$\epsilon = 1, \qquad \delta = -1, \qquad \vartheta = 2 \quad (N < N_c) \tag{3.46}$$

and:

$$\epsilon = 3, \qquad \delta = -2, \qquad \vartheta = 3 \quad (N > N_c) \tag{3.47}$$

where, as in Rouse’s model ($\vartheta = 2$), the reptation time ($\vartheta = 3$) is a rotational relaxation time, giving the “terminal” unit of time for the entangled dynamics (with large $M$). In fact, after setting $\nu = \frac{1}{2}$, our universal law is always satisfied.

The agreement continues to hold also for measured exponents, which raised a famous discrepancy with the theoretical (reptational) values. Experiments conducted on many species over a wide $M$-range returned $\epsilon \simeq (\vartheta \simeq)\ 3.4$. A diffused conviction about this disagreement is that it is not very important. Viscosity is difficult to be attained for large molecular weights, and the anomaly would be explained by the interplay of the reptation dynamics with related effects, in particular tube length fluctuations. Furthermore, the reptational motion adds a $t^{\frac{1}{4}}$ regime to Rouse’s dynamics in the tube. In our case, inserting this anomalous exponent into our universal law returns $\delta \simeq -2.27$ and $\nu \simeq 0.57$ ($N > N_c$), matching again realistic chain data. Note in fact that, unlike $D_N \sim N^{-2}$ and similarly to the viscosity coefficient, the diffusion constant exhibited over the years a range of actual values around $\delta \simeq -2.4$. Regarding the average size, observe that the realistic values of $\epsilon$ and $\delta$ are recovered by the value of a single real chain, ignoring the screening of the excluded volume interaction lying at the basis of the “Flory–de Gennes theorem” (polymers in a 3-dimensional melt are Gaussian). We conclude by emphasizing that one of the major Brownian relativity advantages is not the determination of single scaling exponents, but to establish (new) universal relations. Those above, being preserved in a number of regimes, provide a good example of Brownianly-covariant law. In this respect, it is interesting to remark that the influence of the solvent quality comes into play only indirectly.

## 1.10 Weak and stationary limit

Another relevant case is given by the weak and stationary regime, so to derive the universal behavior corresponding to the Newtonian limit. We know that, for nonrelativistic matter, the time-time metric component in ordinary relativity takes the form, $-g_{00} \simeq 1 + u(\mathbf{r})$, for some (Newtonian) potential function ($u$). Einstein's equations reduce in this case to $\vec{\nabla}^2 g_{00} = -8\pi G T_{00}$, with $T_{00} \simeq \bar{\varrho}$, stepping back to Poisson's equation for Newtonian gravity ($\vec{\nabla}^2 u = 8\pi G \bar{\varrho}$).

For a static isotropic Brownian metric, when $t \to \tau$ and $\bar{\gamma}_{00}$ depends on $\sqrt{\eta_P}$, a simple dimensional analysis gives the quantity $F \simeq (\vec{\nabla}^2 \bar{\gamma}_{00})^2$ the meaning of a (viscous) force. In particular, since:

$$\vec{\nabla}^2 \bar{\gamma}_{00} = \Upsilon_{00} \tag{3.48}$$

from a reference frame linked to an unperturbed portion of fluid, it obeys:

$$F \simeq \left[ -\vec{\nabla}^2 \int \sqrt{\Upsilon_{\rho\rho}}\, d\rho' \right]^2 \sim \left( \sqrt{\Upsilon_{\rho\rho}} \right)_{,\rho} = \bar{\varrho}^2 \tag{3.49}$$

Hence, if $x$ denotes the fluid density exponent, $\bar{\varrho} \sim N^x$, the scaling equation ($\Upsilon_{\rho\rho} \sim \eta_P$):

$$\frac{\epsilon}{2} = \nu + x \tag{3.50}$$

is expected to apply upon $x \to 0$ (fluid density independent of $N$). In fact, the law $\epsilon = 2\nu$ is satisfied in the unentangled regime by ($\nu = \frac{1}{2}$; $\epsilon = 1$) and, correspondingly:

$$F \sim \eta_P \rho^{-2} \tag{3.51}$$

will be the viscous force exerted by a polymer solution flowing in a cavity set by an ideal "phantom" chain size. The weak and stationary limit thus returns Brinkman's behavior, arising from colloid and polymer hydrodynamics as a special case of the Navier–Stokes equation.

## 1.11 Macromolecular continuity equation

The continuity equation, now carried out with respect to $\{\sigma^\alpha\}$:

$$\left( \bar{R}^{\mu\nu} - \frac{\gamma^{\mu\nu}\bar{R}}{2} \right)_{;\mu} = 0 = \bar{T}^{\mu\nu}_{\;;\mu} \tag{3.52}$$

i.e.:

$$\bar{T}^{\mu\nu}{}_{,\mu} = -\bar{\Gamma}^{\mu}_{\mu\alpha}\bar{T}^{\alpha\nu} - \bar{\Gamma}^{\nu}_{\mu\alpha}\bar{T}^{\mu\alpha} \tag{3.53}$$

is connected to Bianchi's identities for the Brownian curvature tensor, and expresses a closure relation for the whole geometrical structure, forbidding any energy–momentum exchange with the correlation sources. In the present context, this conservation law constrains any transport property to changing at the expense of a corresponding (geometrodynamic) perturbation of the conformational polymer statistics. Put differently, correlations can be neither created nor destroyed arbitrarily.

We work with no “spin-like” contributions (like torsions), and a symmetric energy–momentum tensor ($\varUpsilon^{\mu\nu}$) can be adopted. Thus, it simplifies into:

$$\varUpsilon^{\mu\nu}_{;\mu} = \frac{1}{\sqrt{-\bar{\gamma}}}\left(\sqrt{-\bar{\gamma}}\,\varUpsilon^{\mu\nu}\right)_{,\mu} + \bar{\varGamma}^{\nu}_{\mu\lambda}\varUpsilon^{\mu\lambda} = 0 \tag{3.54}$$

and, in addition, for a diagonal static isotropic metric:

$$\left(\sqrt{-\bar{\gamma}}\,\varUpsilon^{\nu\nu}\right)_{,\nu} = -\sqrt{-\bar{\gamma}}\,\bar{\varGamma}^{\nu}_{\mu\mu}\varUpsilon^{\mu\mu} \quad (\forall\nu) \tag{3.55}$$

where the affine connection coefficients are those reported in Appendix A, with $\bar{\gamma}^{2}_{\alpha\alpha}\varUpsilon^{\alpha\alpha} = \varUpsilon_{\alpha\alpha}$ and $\sqrt{-\bar{\gamma}} = \sqrt{ab}\,\rho^2\sin\theta$. Since $\bar{\varGamma}^{0}_{\alpha\alpha} = 0$, the temporal constraint ($\nu = 0$) returns:

$$\mathrm{T}_{0,0} \sim 0 \tag{3.56}$$

that is, the quantity $\mathrm{T}_0 = \rho^2\sin\theta\,\varUpsilon_{00}\sqrt{a/b^3}$ ($\sim\rho^2\bar{\varrho}\sin\theta\,\sqrt{\eta_P}$) does not depend explicitly on time ($\tau$). Also the azimuth equation ($\nu = \varphi$) points out a similar condition. Let $\mathrm{T}_\varphi = \varUpsilon_{\varphi\varphi}/(\rho^4\sin^2\theta)$, where $\varUpsilon_{\varphi\varphi} \simeq f_\varphi\eta_P$ and $f_\varphi$ is a strictly positive constant coefficient, then:

$$\mathrm{T}_{\varphi,\varphi} \sim 0 \tag{3.57}$$

The other two conservation laws need some more elaboration. In the second angular constraint ($\nu = \theta$), the only non-vanishing component of the affine connection is $\bar{\varGamma}^{\theta}_{\varphi\varphi}$, hence:

$$\varUpsilon^{\varphi\varphi}\left(\ln\sqrt{-\bar{\gamma}}\,\right)_{,\theta} + \varUpsilon^{\theta\theta}{}_{,\theta} = \frac{\sin 2\theta}{2}\varUpsilon^{\varphi\varphi} \tag{3.58}$$

from which, and the model assumption $\varUpsilon^{\varphi\varphi} = f_\theta\eta_P$, it turns out:

$$f_{\theta,\theta}\tan\theta\sin^2\theta = f_\varphi - f_\theta\sin^2\theta = 0 \tag{3.59}$$

since $f_\theta$ is a (positive) constant as well. Observe that the present equations aren’t well defined at the planes tangent to the surface that is bounding the polymer molecule. Here, in particular, $\theta \neq 0, \pi$ when $\rho \sim N^{\nu}l$. That said, relating the coefficients $f_\theta$, $f_\varphi$ and getting rid of angular dependences, the last equation can be averaged over the solid angle ($d\Omega = \sin\theta\,d\theta\,d\varphi$) by a uniform probability distribution function, $W(\Omega) = (4\pi)^{-1}$, obtaining in the end $f_\varphi = \frac{2}{3}f_\theta$.

The radial condition, with $\bar{\varGamma}^{\rho}_{00}$, $\bar{\varGamma}^{\rho}_{\rho\rho}$, $\bar{\varGamma}^{\rho}_{\theta\theta}$, $\bar{\varGamma}^{\rho}_{\varphi\varphi} \neq 0$, is the most meaningful:

$$a(\rho)\varUpsilon^{\rho\rho}(\ln\mathrm{T}_\rho)_{,\rho} = \rho^{-3}\left(\varUpsilon_{\theta\theta} + \csc^3\varUpsilon_{\varphi\varphi}\right) - \frac{1}{2}\left(\frac{\psi_b}{b}\varUpsilon_{00} + \frac{\psi_a}{a}\varUpsilon_{\rho\rho}\right) \tag{3.60}$$

with $\mathrm{T}_\rho = \rho^2\sin\theta\,\varUpsilon_{\rho\rho}\sqrt{b/a^3}$ ($\sim \rho^2\sin\theta/\sqrt{\eta_P}$). After working it out, one is left with:

$$\rho^{-3}\eta_P\left(f_\varphi + f_\theta\sin^3\theta\right) = \sin^3\theta\left[2\rho^{-1} + \frac{n}{2}\sqrt{\eta_P}\,(1 + \varUpsilon_{00})\right] \tag{3.61}$$

which, on averaging again over $\Omega$, reduces to:

$$\left(\frac{32}{9\pi}+1\right)f_\theta\rho^{-3}\eta_P = 2\rho^{-1}+\frac{n}{2}\sqrt{\eta_P}\,(1+\Upsilon_{00}) \quad (\forall f_\theta \neq 0) \tag{3.62}$$

$n$ being already introduced by the former section. As $\overline{G}_{00} \to 0$, on approaching $\rho \to \infty$, it turns out $\sqrt{\eta_P} \simeq \bar{c}\rho^3$, with constant prefactor $\bar{c} = \frac{9}{2}n\pi/(32+9\pi)$. Such a result requires $\eta_P \gg \rho^2 \gg \eta_P^{-1}$, a condition that normally applies to entangled polymer dynamics, and implies:

$$\frac{\sqrt{\eta_P}}{\rho^3} \sim N^0 \tag{3.63}$$

or:

$$\nu = \frac{\epsilon}{6} \tag{3.64}$$

In spite of coming from a closure relation, and being principally focused on entangled systems, this law also agrees with a number of regimes. For a concentrated polymer solution ($\nu = \frac{1}{2}$), one would obtain $\epsilon = 3$, which is just the viscosity exponent descending from the reptation theory. For a real chain molecule, with average size going from the renormalization group prediction to Flory's, $0.588 \leqslant \nu \leqslant \nu_F = 3/5$, Bianchi's identities would bound viscosity to $3.36 \leqslant \epsilon \leqslant 3.53$, matching nicely the most representative value ($\simeq 3.45$ against 3.4), the experimental and numerical ranges, $3.1 \lesssim \epsilon \lesssim 3.6$.

## 1.12 Scaling and polymer volume fraction

For investigating on the influence of polymer concentration, or volume fraction ($\phi$), it is useful to step back to the special theory, and reconsider the Brownian–Lorentz factor, $\gamma_B = 1 - \frac{''\Delta'}{\Delta'}$, bringing the local mobility change into the rules of length contraction and time dilation. We will begin from a low-concentrated solution at the $\Theta$ point, where the special Brownian relativity is expected to hold, and regard the general expression (in standard units):

$$\gamma_B = \frac{D'' - D_0}{D' - D_0} \tag{3.65}$$

i.e., with $\Delta' = D' - D_0$ and $''\Delta' = D' - D''$. Note that scaling behaviors in $N$ and $\phi$ are in Brownian relativity conceptually different. There, approaching universality requires bringing the chain molecule at rest ($D_0 = 0$). In the present case, where polymer chains spread throughout the liquid, this transformation ceases to be local, and $\gamma_B$ should be a function of $\phi$. Similarly, in a dynamic analysis of concentration fluctuations, the collective (relative) motion, between polymer and solvent molecules, is considered, while the effect of entanglements (or knots), for the relative motion of a chain and the solution, is not taken into account.

The most general way to do that is by introducing the cooperative (i.e., many-chain) diffusion coefficient, $D_c(\phi)$ and linking the laboratory frame to its value in the limit of infinite dilution, $D_c(\phi \to 0) = D_0''$. $D_c$ comes from the relaxation decay of concentration fluctuations, describing the cooperative diffusion of segments in each of the uncorrelated "blobs" partitioning the chains statistically, and is clearly a measure of the rapidity by which any heterogeneity propagates in the solution. It appears as the phenomenological coefficient in Fick's equation for the hydrodynamic description of monomer density fluctuations, and is expressible by a fluctuation–dissipation relation for the concentration ($c$) gradient of the osmotic pressure ($\Pi$) and the friction coefficient ($\alpha$), $D_c = \frac{1}{\alpha}(\frac{\partial \Pi}{\partial c})$. Moreover, $D_c \sim \phi^{\chi}$ increases with the volume fraction, the exponent $\chi$ ($> 0$) reflecting the solvent conditions (e.g., $\chi = 1$ at the $\Theta$ point) and, in dilute systems, equates the self-diffusion coefficient. Hence, we can work with:

$$\gamma_B(\phi) = \frac{D_c(\phi) - D_0''}{D'} \simeq w^* \frac{D_0''}{D'} \phi \tag{3.66}$$

where the condition $D' \gg D_0''$ and the first-order equation $D_c(\phi) \simeq D_0''(1 + w^* \phi)$ were exploited. Replacing $D$ with $D_c$ is what is normally done when the scattering function for dilute systems is rewritten for higher concentrations. Furthermore, (concentration) expansions are widely met in colloid science and of general validity. For hard-sphere fluids with stick particle boundaries it is known that expansions like $D = D_0(1 + a_d \phi)$ and $D_s = D_0(1 + a_s \phi)$ hold for certain values of $a_d$ ($\simeq -2.097$) and $a_s$ ($\simeq 1.454$). Here, the constant $w^*$ ($>0$ in most solutions) accounts for the 3-body contact interactions on which the osmotic pressure mainly depends at the $\Theta$ point, where the osmotic second virial coefficient is identified to vanish. This criterion is not rigorous, and can be improved, but leads here to rather simple developments. Again, for ideal chains, $D_0''/D' \sim N^{-1}$ (friction is additive), and one has synthetically:

$$\gamma_B \simeq \phi_P \tag{3.67}$$

namely, a linear dependence on the polymer number concentration $\phi_P = \frac{\phi}{N}$.

Aim is to find the scaling law for the polymer size (in three dimensions), thus we consider the "pervaded" volume ($\sim \rho^3$), the spherical domain enclosing a chain molecule of average size $\rho$. Because $\phi\rho^3$ gives the net amount of polymeric material, the universal quantity $F_v = (\phi\rho^3)^{\nu}$ stands in a direct relation with $\rho$, i.e.,

$$F_v(\rho, \phi) \sim l^{3\nu - 1} \rho(\phi) \tag{3.68}$$

Kuhn's size ($l$) playing the role in Brownian relativity of an invariant step length. Now, remember the general form of the length contraction law, for the Brownian frames of a polymer and a rod-shaped molecule (long $L$) obey:

$$\rho = \sqrt{\gamma_B}\, L \tag{3.69}$$

Combining the last two equations at $L \sim \rho$ yields the desired contraction rule, that is:

$$F_v(\rho, \phi) \sim \sqrt{\gamma_B}\, \rho(\phi) \tag{3.70}$$

which, being $\gamma_B \sim \phi$, gives us the first scaling result:

$$(\phi\rho^3)^{\nu} \sim \sqrt{\phi}\, \rho \tag{3.71}$$

i.e.,

$$\rho(\phi) \sim \phi^{\frac{1}{2}\left(\frac{1-2\nu}{3\nu-1}\right)} \tag{3.72}$$

The second behavior to be found should nearly express the dual relationship for time intervals, in which polymers diffuse out by a distance of the order of the contracted size ($\rho$). To proceed, we rewrite the first equation for $F_v$ by a single characteristic dimension, $F_v \equiv \ell_v^{3\nu}(\phi)$, and rearrange the second in light of the corresponding time dilation rule:

$$t = \gamma_B \tau \tag{3.73}$$

$t$ and $\tau$ still referring to a polymer and a rod-shaped molecule, respectively. Working in the time domain therefore requires the "unit changes" $\sqrt{\gamma_B} \to \gamma_B$ and $\ell_v \to t$, obtaining:

$$\frac{t^{3\nu}(\phi)}{\gamma_B} \sim t(\phi) \tag{3.74}$$

from which the time dilation rule constrains the chain relaxation time to:

$$\frac{(\phi\tau)^{3\nu}}{\phi} \sim \phi\tau \tag{3.75}$$

or:

$$\tau(\phi) \sim \phi^{\frac{2-3\nu}{3\nu-1}} \tag{3.76}$$

The diffusion coefficient comes from the derived laws of length contraction and time dilation, $(\phi\rho^3)^\nu \sim \sqrt{\phi}\,\rho'$ and $(\phi\tau)^{3\nu} \sim \phi^2\tau'$, rewritten for simplicity in two separate frames. In this way:

$$\phi^{-\nu} D^{3\nu} \sim \phi^{-1} D' \tag{3.77}$$

and again, at the common scale, $D' \to D$:

$$D(\phi) \sim \phi^{\frac{\nu-1}{3\nu-1}} \tag{3.78}$$

Before continuing, a couple of considerations are in order. The three scaling laws, for the average size, characteristic time and diffusion constant were determined by a special Brownian–relativistic analysis of cooperative diffusion. We envisage them to be Brownianly covariant for a number of regimes, particularly for those in which the role played by chain entanglements is not crucial. The above relation $\rho(\phi)$ applies in fact to solutions at the $\Theta$ temperature and any volume fraction, and to semidilute solutions in a good solvent, where the average size decreases more weakly as $\rho \sim \phi^{-0.12}$ ($\nu \simeq 0.588$). At higher concentrations, excluded volumes are screened out and chain conformations get back to be (nearly) ideal ($\nu = \frac{1}{2}$). The relationships for $\tau(\phi)$ and $D(\phi)$ equally describe the semidilute chain relaxation times and (Zimm's) diffusion coefficients, either in $\Theta$ or good solvents.

The last law we are interested in, for the viscosity scaling, is more difficult to achieve from simple considerations, but let us remember the former universal relations, $\delta + \nu = 3\nu - \vartheta = -\frac{\epsilon}{2}$. We wrote them in the variable $N$, but the generalized

Lorentz's factor accounting for the polymer concentration is written here in the number of chain molecules per unit volume ($\phi_P$). Thereby, one can work with a chain ensemble where $N$ is fixed and $\phi$ is free to vary. By doing so, using the exponents for $\rho(\phi)$, $\tau(\phi)$ and $D(\phi)$, viscosity is predicted to scale as:

$$\eta(\phi) \sim \phi^{\frac{1}{3\nu-1}} \tag{3.79}$$

This, however, is just the expected scaling result, giving the polymer contribution to (i.e., the specific) viscosity for unentangled semidilute solutions in $\Theta$ and good solvents.

We come thus to the important conclusion that all these quantities fulfill the same covariant equations, previously derived in $N$, also in the scaling variable $\phi$. In formula, let:

$$\rho \sim N^{\nu}\phi^{\nu'}, \qquad \tau \sim N^{\vartheta}\phi^{\vartheta'} \tag{3.80}$$

and:

$$D \sim N^{\delta}\phi^{\delta'}, \qquad \eta \sim N^{\epsilon}\phi^{\epsilon'} \tag{3.81}$$

it turns out that:

$$\delta + \nu = 3\nu - \vartheta = -\frac{\epsilon}{2} \tag{3.82}$$

and, equally:

$$\delta' + \nu' = 3\nu' - \vartheta' = -\frac{\epsilon'}{2} \tag{3.83}$$

Within the present discussion, it is legitimate to wonder whether the available exponents for entangled polymer solutions satisfy again this scaling scheme. Remarkably, the values established by the reptation theory at the $\Theta$ point and in extremely good (i.e., "athermal") solvents:

$$\vartheta' = \frac{3(1-\nu)}{3\nu-1}, \qquad \delta' = \frac{\nu-2}{3\nu-1}, \qquad \epsilon' = \frac{3}{3\nu-1} \quad \text{(athermal)} \tag{3.84}$$

$$\vartheta' = \frac{7}{3}, \qquad \delta' = -\frac{7}{3}, \qquad \epsilon' = \frac{14}{3} \quad (\Theta \text{ point}) \tag{3.85}$$

solve again the same universal equations, still with $\nu'(\nu = \frac{1}{2}) = 0$, that is, $2\delta' = -2\vartheta' = -\epsilon'$. These exponents cover a range of excluded volumes ($v$) going from zero ($v = 0$, $T = \Theta$) to their maximum values (athermal), when $v$ becomes independent of temperature.

## 1.13 Fluctuating–deflecting entanglement points

So far, a Brownian–relativistic analysis of "entanglement effects" and the related (entangled) dynamics has not been presented yet. To model the polymer self-diffusion, de Gennes exploited Edwards's tube and his reptation theory is a masterpiece of deepness and simplicity. In Brownian relativity, this will be done by the postulate of geodesic motion, implying an equation of the form:

$$\left(\frac{d^2\sigma^\alpha}{du^2}\right)+\overline{\Gamma}^{\alpha}_{\nu\lambda}\left(\frac{d\sigma^\nu}{du}\right)\left(\frac{d\sigma^\lambda}{du}\right)=0 \tag{3.86}$$

that is, rewritten upon $s \to u$, $x^\alpha \to \sigma^\alpha$, $g_{\mu\nu} \to \overline{\gamma}_{\mu\nu}$, and generally parametrized by $u = u(\sigma)$. We have now to interpret the former integrals of motion in Brownian relativity. Apart from the obvious $\theta = \frac{\pi}{2}$, the condition:

$$\rho^2\left(\frac{d\varphi}{du}\right)=\ell_\varphi \tag{3.87}$$

settles, in orbits at fixed $\rho = \bar{\rho}$, a constant ratio between curvilinear abscissas of pure time-like ($u$) and shape-like ($w = \rho\varphi$) paths ($\frac{dw}{du} = \frac{\ell_\varphi}{\bar{\rho}}$). The third descends from the reparametrization:

$$\left(\frac{du}{d\tau}\right)=b(\rho) \tag{3.88}$$

so that, if $b$ is nearly unperturbed then $u$ approximates the Brownian time, and again, from the geodesic equation:

$$a(\rho)\left(\frac{d\rho}{d\sigma}\right)^2-\frac{1}{b(\rho)}+\left(\frac{\ell_\varphi}{\rho}\right)^2=-\varepsilon \tag{3.89}$$

In relativistic mechanics, $\sqrt{\varepsilon}$ ($=\frac{d\sigma}{du} \geqslant 0$) stands for a constant (dimensionless) energy per unit mass, equal to zero for light rays only. In Brownian relativity, it reparametrizes the invariant interval, and (only) vanishes over the long-wavelength diffusions of a single liquid molecule and of a monomer unit in a chain conformation, when their proper times can be normalized independently. Now, to pass from the orbit time history to its shape, recall:

$$\varphi=\pm\ell_\varphi\int\sqrt{\frac{a(\rho)}{\frac{\rho^2}{b(\rho)}-\varepsilon\rho^2-\ell_\varphi^2}}\,d\ln\rho \tag{3.90}$$

exploited in Einstein's theory to show that light rays bend toward massive objects, deflecting by $\frac{\Delta\varphi}{2} = |\varphi(r_m) - \varphi_\infty| - \frac{\pi}{2}$, where $\varphi_\infty$ is the incident direction and $r_m$ is the distance of closest approach to the mass. Here, it will model the influence of entanglements in a polymer solution.

To do so, consider the "scattering" phenomenon depicted in Fig. 3.4, compared with a light deflection experiment. A liquid molecule ($\varepsilon = 0$) self-diffuses, from a point at infinity where the Brownian metric is Minkowskian, to the vicinity of a polymer chain. When these reference systems, one time-like and the other shape-like, do not interact at all, the single molecule will proceed its Brownian motion undisturbed, returning again to infinity by the opposite direction. Otherwise, any correlation will have the effect to "distorce" (or "deflect") the unperturbed free particle trajectory, and the result will evidently be a random path, bending toward (or away) the correlation source. In concrete terms, one first sets an entanglement point

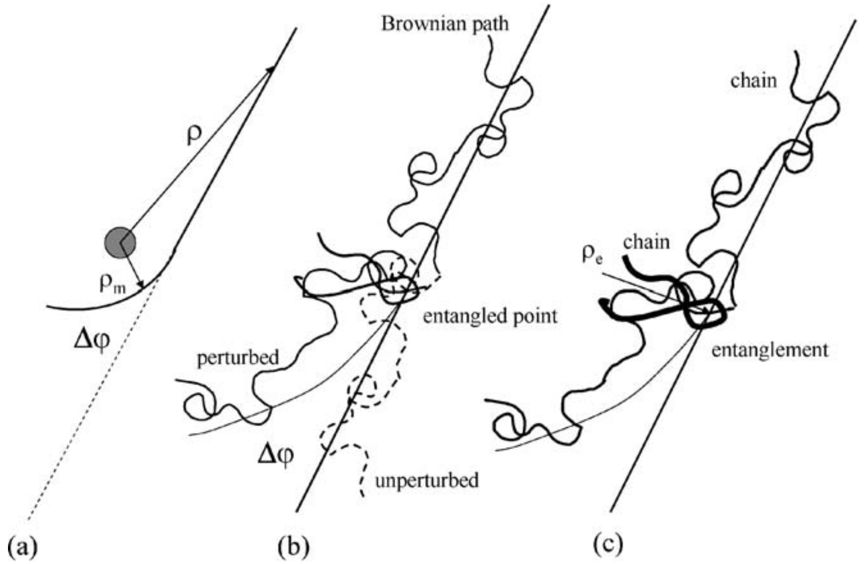

**Figure 3.4** Comparing the roles of mass (in light deflection) and entanglement points (in polymer dynamics).

(or event) along the path, and then calculates the azimuth angles, before and after it, by the difference $\Delta\varphi$ as a function of $\rho$. From the Brownian equivalence principle, this ("flat") molecular trajectory possesses the same statistics as a ("curved") macromolecular shape, the long-range correlations of which affecting the value of $\Delta\varphi = \varphi(\rho) - \varphi_\infty$. The last step is expliciting the azimuth difference (under $\varepsilon = 0$). As $(d\rho/d\varphi)_{\rho_m} = 0$, it turns out $\ell_\varphi = \rho_m/\sqrt{b(\rho_m)}$, thence:

$$\Delta\varphi(\rho) = \int_\rho^\infty \sqrt{\frac{a(r)}{B(r)}}\, d\ln r \tag{3.91}$$

with $B(r) = B[b(r), r; \rho_m] \equiv \frac{r^2}{\rho_m^2}\frac{b(\rho_m)}{b(r)} - 1$. For Minkowski's metric ($a = b = 1$), configuration paths return to be ideal, with constant azimuth angle ($\Delta\varphi = 0$).

Finally, the sketch in the last figure depicts an entanglement point, but could be equally referred to the formation of a polymer knot. The analogy with a light deflection experiment seems thus to be suitable also in view to combine knot theory with Brownian relativity.

## 1.14 Scaling behavior in semidilute solutions

At the origin and detection points of the previous scattering experiment, $\overline{\gamma}_{\mu\nu}$ is unperturbed and $\varphi$ is unambiguously defined. Hence, $\Delta\varphi$ should be connected to some measurable properties, as we are going to show. To check it, recall the expression for the time-time metric component, generally derived for a concentrated polymer solution, and set for brevity $\Upsilon_{\rho\rho} \sim \rho^{\beta}$ ($\beta = \frac{\epsilon}{\nu}$). From:

$$\frac{b(\rho_e)}{b(\rho)} = \exp\left(-n \int_{\rho_e}^{\rho} \sqrt{\Upsilon_{\rho\rho}}\, d\rho\right) \tag{3.92}$$

one gets:

$$B\big[\rho(k)\big] = k^2 \mathrm{e}^{-k_e(k^{\zeta+1}-1)} - 1 \tag{3.93}$$

$\rho_e$ being the distance of closest approach to the Brownian path, while $k \equiv \rho/\rho_e$, $\zeta \equiv \beta/2$ and $k_e \equiv n\rho_e^{\zeta+1}/(\zeta+1)$. We should sum over $[\rho_e, \infty)$ and, as $k_e \ll 1$, can approximate the integral to:

$$\int_{\rho_e}^{\infty} \sqrt{\frac{a(\rho)}{B(\rho)}}\, d\ln\rho \simeq \mathrm{e}^{-k_e}\rho_e^{\zeta} \int_{1}^{\infty} \frac{k^{\zeta-1}}{\sqrt{k^2-1}}\, dk \tag{3.94}$$

which, if $\zeta < 1$, converges to:

$$\Delta\varphi \simeq \frac{1}{2}\mathrm{B}_{\frac{1}{2}(1-\zeta),\frac{1}{2}}\, \mathrm{e}^{-k_e}\rho_e^{\zeta} \tag{3.95}$$

where (the constant term) $\mathrm{B}_{s,s'}$ indicates the Beta function, evaluated in $s$ and $s'$. The stretched exponential in $k_e$ plays the role of a scaling correction, preventing $\varphi$ from increasing indefinitely. Notwithstanding, for $n \ll 1$, the bound it sets lies far away from the entanglement point and may be ignored.

The last equation yields the azimuth deviation of the polymer path, derived by summing all contributions from the entangled point ($\rho_e \equiv \rho_m$) to the point at infinity in a static isotropic Brownian space, and can be approximated to:

$$\Delta\varphi \sim \rho_e^{\frac{\epsilon}{2\nu}} \tag{3.96}$$

Actually, $\rho_e$ is meant to be a (dimensionless) length scale, increasing with the entanglement correlation. Convergence reasons impose $\epsilon < 2\nu$, a condition which certainly applies in a Zimm-like limit ($\epsilon = 3\nu - 1$; $\nu < 1$), when monomer–solvent (in the chain pervaded volume) and monomer–monomer hydrodynamic interactions coupling distant units are strong enough. Actually, it also holds on approaching Rouse's limit ($\frac{\epsilon}{2} \lesssim \nu$), where hydrodynamic (as well as excluded volume) interactions are screened out. The scaling equations in the previous section were able to model concentrated (Gaussian) systems. We will examine here a semidilute entangled solution, and focus on the universal regime at the scale of a chain portion of size somewhat proportional to the (static) correlation length ($\xi$). This quantity, separating small-scale single-chain from large-scale many-chain conformational statistics, is expected in turn to be proportional to the hydrodynamic screening length ($\xi_H \sim \xi$), discriminating between Zimm's and Rouse's limits. With increasing polymer excluded volume or volume fraction, the segment concentration tends to distribute uniformly, and $\xi$ decreases. Again, a suitable reference framework is provided by Edwards's tube and de Gennes's reptation concepts. Accordingly, the topological constraints produced by molecular entanglements would bound the polymer motion to proceed curvilinearly, across a tube-shaped region of given diameter (d) and contour length ($L_P$) of its "primitive path" (i.e., the shortest "curvilinear axis" of the tube). In a Gaussian system, they are connected by the random walk statistics of $\frac{N}{N_e}$ entanglement strands, each with segment number $N_e \simeq N\mathrm{d}/L_P \simeq (\mathrm{d}/l)^2$. At the $\Theta$ point and in athermal solvents, the relationship $\mathrm{d} \sim \xi$ is also expected.

On this basis, consider $\rho_e \sim N_e^{-z}$. The exponent $z$ ($\geqslant$0) may be discussed in light of the mean square azimuth deviation, $\sigma_\varphi^2 \equiv \overline{(\Delta\varphi)^2}$, collecting positive and negative deflection contributions together. The equation for $\Delta\varphi$ is in fact of local nature, referring to a single entangled point. To get a scaling behavior for $\sigma_\varphi^2$, we divide its squared value first by the "overlap" volume fraction ($\phi^*$), at which the solution enters the semidilute regime, and then by another statistical factor, weighting the entanglement formation. We know that the whole concentration domain is organized in four regions (dilute, semidilute unentangled, semidilute entangled, concentrated) by the overlap, entanglement and semidilute-concentrated crossover volume fractions ($0 \lesssim \phi^* \lesssim \phi_e \lesssim \phi_c \lesssim 1$, respectively). The latter is a constant value that, in athermal solvents, is $\phi_c \simeq 1$, makes highly concentrated systems to remain semidilute. Thus, the other statistical weight can be set to the reciprocal of the concentration ratio giving the width of the semidilute unentangled domain, which is:

$$\frac{\phi_e}{\phi^*} \sim \begin{cases} \text{const} & \text{(athermal)} \\ N^{-\frac{1}{4}} & (\Theta \text{ point}) \end{cases} \tag{3.97}$$

and, after recalling $\phi^* \sim N^{1-3\nu}$:

$$\sigma_\varphi^2 \sim \phi_e {\phi^*}^{-2} (\Delta\varphi)^2 \tag{3.98}$$

In athermal solvents $\sigma_\varphi^2 \sim N_e^{-\frac{z\epsilon}{\nu}} N^{3\nu-1}$ and, since $\epsilon = 3\nu - 1$:

$$\sigma_\varphi^2 \sim \left(\frac{N}{N_e^{\frac{z}{\nu}}}\right)^{3\nu-1} \tag{3.99}$$

we may require no other scale to come into play (i.e., a scale homogeneity), and set ($z = \nu$):

$$\rho_e \sim N_e^{-\nu} \tag{3.100}$$

Observe that, on approaching Rouse's limit, a random walk statistics given by $\rho_e^{-1} \sim \sqrt{N_e} \sim \mathrm{d}$ would establish. Alongside, azimuth deflection and tube length fluctuations would scale simultaneously as:

$$\sigma_\varphi \sim \sqrt{\overline{(\Delta L_P)^2}} \sim \sqrt{\frac{N}{N_e}} \tag{3.101}$$

going to zero with $d/L_P \rightarrow 0$. To face instead $\Theta$ solutions, the above $-1/4$ scaling behavior should be accounted for. Precisely, when $\phi_e/\phi^* \sim N^{-\frac{1}{4}}$, scale homogeneity requires a new $z$ value, $z/\nu \to z'(\nu)/\nu = 1 - [4(3\nu - 1)]^{-1}$, which is $z'(\frac{1}{2}) = \frac{1}{4}$.

Let us turn now to a dynamic, time-like description. We want to express the chain time by the shape-like, conformational properties ($\rho_e$, $\rho$, $\sigma_\varphi$), and this can be done by a relation stemming from the geodesic theory:

$$\rho^2\left(\frac{d\varphi}{d\tau}\right) = \ell_\varphi b(\rho) \tag{3.102}$$

It produces $\rho_e \tau \simeq \sigma_\varphi \rho^2$, bringing to:

$$\rho_e \sim \sigma_\varphi D_e \tag{3.103}$$

with diffusion coefficient $D_e \sim \frac{\rho^2}{\tau}$. When $\sigma_\varphi \simeq$ const, the last equation identifies two universal regimes, in $N$ and $\phi$. The former corresponds again to the (high dilution) limit $\mathrm{d}/L_P \to 0$, for $\sigma_\varphi \sim N^0$ and $D_e \sim \rho_e(N_e \to N) \sim N^{-\nu}$ scales as Zimm's diffusion coefficient. Correspondingly, when $\sigma_\varphi \sim \phi^0$:

$$\tau_e(\phi) \sim N_e^z(\phi)\xi_e^2(\phi) \tag{3.104}$$

i.e., a scaling law for quantities defined at the entanglement spacetime scale ($\tau = \tau_e$ and $\rho = \xi_e$). In particular, if $\rho \equiv \xi$ and $z = \nu$, then $\tau \sim \xi^2\mathrm{d}$ and $N_e^\nu \simeq \mathrm{d} \sim \xi$, identifying the strand relaxation time in each correlation volume to $\tau_\xi \sim \xi^3$, as it has to be. Nevertheless, we can go a little further, over larger length scales $\simeq(\xi, \mathrm{d}]$. Let $\tau_e \sim \phi^{\sigma_e}$ denote the entanglement relaxation time of a strand, provided with $N_e \sim \phi^{\nu_e}$, at the tube diameter scale $\mathrm{d} \sim \phi^{\nu_d}$. The last constraint, i.e.:

$$\vartheta_e = 2\nu_d + z\nu_e \tag{3.105}$$

is satisfied in both limits, characterized by:

$$\vartheta_e = -\frac{3\nu}{3\nu - 1}, \qquad \nu_d = -\frac{\nu}{3\nu - 1}, \qquad \nu_e = -\frac{1}{3\nu - 1} \quad (\text{athermal},\ z = \nu) \tag{3.106}$$

$$\vartheta_e = -\frac{5}{3}, \qquad \nu_d = -\frac{2}{3}, \qquad \nu_e = -\frac{4}{3} \quad \left(\Theta \text{ point},\ z = \frac{1}{4}\right) \tag{3.107}$$

The equations for $\tau_e(\phi)$ and $\vartheta_e$ equally holds at the correlation length scale ($\xi \sim \mathrm{d}$), when strand relaxation time ($\tau_\xi \sim \tau_e$) and repeat unit number ($g \sim N_e$) are referred to a correlation volume ($\sim\xi^3$).

## 2. STATISTICAL GAUGE AND ELECTROMAGNETIC ANALOGY

### 2.1 Extended heat-diffusion equation

As the coordinate transformation rule, between two frames $O$ and $O'$, is:

$$\gamma'_{\mu\nu} = \left(\frac{\partial\sigma^\varepsilon}{\partial\sigma'^\mu}\right)\left(\frac{\partial\sigma^\omega}{\partial\sigma'^\nu}\right)\gamma_{\varepsilon\omega} \tag{3.108}$$

we may address the simplest case in which one of the two lies in Minkowski's spacetime, $O' = \{\xi^\mu, \eta_{\alpha\nu}\}$, and the other is a Brownian system, $O = \{\sigma^\mu, \gamma_{\alpha\nu}\}$:

$$\eta_{\alpha\beta} = \gamma_{\mu\nu}\left(\frac{\partial\sigma^\mu}{\partial\xi^\alpha}\right)\left(\frac{\partial\sigma^\nu}{\partial\xi^\beta}\right) \tag{3.109}$$

Here we will not take into consideration the specific form to be assigned the probability density (or Green's function), by which coordinates are defined. It only matters that a set of real- or complex-valued statistical distribution functions, $\mathrm{P}^\alpha = \mathrm{P}^\alpha(\xi^\omega)$, generally exists to well-pose the following definition:

$$\sigma^\alpha\left[\mathrm{P}^\alpha(\xi^\omega)\right] = \left[\int \mathrm{P}^\alpha(\xi^\omega)\, d^4\xi\right]^{\frac{1}{2}} \tag{3.110}$$

Consider thus a molecule in the local frame $O'$, endowed with (small) intrinsic fluctuations. The hunch is that particles, in a way, "build" their own frames by performing random walks under Brownian–relativistic constraints. We set out thus to focus on a coordinate change in $O'$, as detected by $O$, by the only variations of $\mathrm{P}^\alpha$. Each $\sigma^\alpha$ will vary by the change of P that is consequent, at given $\gamma_{\mu\nu}$, upon $\xi^\mu \to \xi^\mu + \delta\xi^\mu$:

$$\delta\sigma^{\alpha^2}\left[\mathrm{P}^\alpha(\xi^\omega)\right] \equiv \int \delta\mathrm{P}^\alpha(\xi^\omega)\, d^4\xi \tag{3.111}$$

Accordingly, the variation observed by $O$ turns out to be:

$$\delta\eta_{\alpha\rho} = \frac{\gamma_{\mu\nu}}{2\sigma^\mu\sigma^\nu}\left(\frac{\partial\sigma^{\mu^2}}{\partial\xi^\alpha}\right)\left[\left(\frac{\partial\delta\sigma^{\nu^2}}{\partial\xi^\rho}\right) - \left(\frac{\partial\sigma^{\nu^2}}{\partial\xi^\rho}\right)\frac{\delta\sigma^{\nu^2}}{2\sigma^{\nu^2}}\right] \tag{3.112}$$

that, after expanding $\delta\mathrm{P}^\alpha = \mathrm{P}^\alpha_{,\kappa}\delta\xi^\kappa$, implies:

$$\left(\frac{\delta\eta_{\alpha\rho}}{\delta\xi^\kappa}\right) = \frac{\gamma_{\mu\nu}}{2\sigma^\mu\sigma^\nu}\left(\frac{\partial\sigma^{\mu^2}}{\partial\xi^\alpha}\right)\left[\left(\frac{\partial^2\sigma^{\nu^2}}{\partial\xi^\rho\partial\xi^\kappa}\right) - \frac{1}{2\sigma^{\nu^2}}\left(\frac{\partial\sigma^{\nu^2}}{\partial\xi^\rho}\right)\left(\frac{\partial\sigma^{\nu^2}}{\partial\xi^\kappa}\right)\right] \tag{3.113}$$

Any metric variation will produce an energy–momentum perturbation (say, $t_{\mu\nu} \sim \delta\eta_{\mu\nu}$), whose conservation law ($t^\mu{}_{\nu,\mu} = 0$) fixes the additional constraint:

$$\left(\frac{\delta\eta^\kappa{}_\alpha}{\delta\xi^\kappa}\right) = 0 \tag{3.114}$$

from which:

$$0 = \eta^{\rho\kappa}\left(\frac{\delta\eta^\kappa{}_\alpha}{\delta\xi^\kappa}\right) = \frac{2\gamma_{\mu\nu}}{\sigma^\nu}\left(\frac{\partial\sigma^\mu}{\partial\xi^\alpha}\right)\eta^{\rho\kappa}\left[\frac{1}{2}\left(\frac{\partial^2\sigma^{\nu^2}}{\partial\xi^\rho\partial\xi^\kappa}\right) - \left(\frac{\partial\sigma^\nu}{\partial\xi^\rho}\right)\left(\frac{\partial\sigma^\nu}{\partial\xi^\kappa}\right)\right] \tag{3.115}$$

or:

$$\gamma_{\mu\nu}\sigma^\mu{}_{,\alpha}\Box\sigma^\nu = 0 \tag{3.116}$$

where $\Box = \vec{\nabla}^2 - v_c^{-2} \frac{\partial^2}{\partial^2 t}$ still denotes the (Cartesian) d'Alembertian, left indicated for some velocity $v_c$.

A first point to note is on the arbitrariness in the last equation, of the same nature of that in Maxwell's and Einstein's, which can be eliminated by fixing a particular "gauge." In fact, while Lorentz's condition is employed in electrodynamics for the 4-vector potential, the ambiguity in the metric tensor of ordinary relativity can be removed by some special reference system. We saw that a suitable choice may be given by the harmonic coordinates ($\Box x^\mu = 0$), hence the analogy with the previous equation is rather evident. It denotes a "statistical gauge" invariance that would seem to widen the class of probability equations for Brownian statistics.

To look more closely into this point, we address the concrete case of an experimentalist, who measured the "scattering law" of a system, $S = S(\mathbf{q}, \omega)$. It is a double-Fourier-transformed (van Hove's) distribution function ($G$), containing all information about temporal and spatial correlations in the wavevector ($\mathbf{q}$) and frequency ($\omega$) domains. The experimentalist can thus proceed with defining a generalized coordinate system (e.g., $\Sigma^\alpha = f(\Sigma)$), from which recovering the second-order statistical description ($\sigma^\alpha$), i.e.:

$$\Sigma^2 = \int \mathrm{e}^{\mathrm{i}q_\mu \xi^\mu} G\big(\xi^\omega\big)\, d^4\xi \tag{3.117}$$

with $q_\mu \xi^\mu \equiv \omega t - \mathbf{q} \cdot \mathbf{r}$ and $d^4\xi \equiv d\mathbf{r}\, dt$. Accordingly, $\mathrm{P}^\alpha$ becomes the product of a plane wave, solving a hyperbolic differential equation, times a typical solution of the parabolic heat-diffusion equation. To meet the constraint in the last but one equation, a restricted gauge transformation may be thereby adopted in the form:

$$\Box\big[G(\xi^\omega)\mathrm{e}^{\mathrm{i}q_\alpha \xi^\alpha}\big] = 0 \tag{3.118}$$

and coupled to a Lorenz-like condition, i.e.:

$$G^{\alpha}_{,} = 0 \tag{3.119}$$

They may be easily joined together for a non-dispersive wave ($q_\mu q^\mu = 0$):

$$\Box G = \frac{4\mathrm{i}q}{v_c} G_{,0} \tag{3.120}$$

$q$ denoting the wavevector magnitude. We introduce now an intrinsic diffusion coefficient, $D^* = \omega/(4q^2)$, a heat-diffusion operator, $\Box_{\mathrm{D}^*} = \vec{\nabla}^2 - \frac{1}{D^*}\frac{\partial}{\partial t}$, and rotate $t$ into an imaginary direction, $t \to \mathrm{i}t$. This analytic continuation in time is named "Wick's rotation," after Guglielmo C. Wick (1954), switching from a Minkowski's to a 4-dimensional Euclidean space. It is frequently used in field theory and statistical mechanics, and here is motivated by the complex-valued coordinate definition, implying:

$$\big(\Box_{\mathrm{D}^*} - \Box + \vec{\nabla}^2\big)G = 0 \tag{3.121}$$

We adopt now the same procedure regaining the classical Hamilton–Jacobi equation from its relativistic form. Under the non-relativistic limit $v_c \equiv c \to \infty$, then $\Box \to \nabla^2$, and the above reduces to a Fickian equation, $\Box_{\mathrm{D}} G = 0$, with $D^* \to D$.

We end this subsection by noting that a statistical gauge invariance like this would assign the spacetime stochasticity the role of a necessary condition for the establishment of universal laws. Conversely, merely "deterministic" processes could never be characterized by "universality," at least according to the meaning assigned by Brownian relativity. Another point opened by such an interpretation, concerns the relationship between locality and globality in this gauge transformation concept.

## 2.2 Lagrangian theory and Klein–Gordon field

Sir Edwards (1965) was the first to write a probability functional for self-avoiding polymers, inventing a self-consistent field description for the interaction of the chain with itself. In his continuous Hamiltonian theory, a first contribution accounts for the chain connectivity as a Bachelier–Wiener process, and the second introduces a non-local pseudo-potential for the monomeric repulsion. This "base" model stated the basis for many further investigations, and is surely one of the milestones of polymer physics.

We discuss here the two postulates of Brownian relativity in light of a scalar field ($\phi$), implicitly defined for simplicity through a 2-dimensional invariant interval. This will give our "minimum" model to be adopted in any future development. An event in our coordinate basis will write $\boldsymbol{\sigma} \equiv (\tau, \rho)$, by which:

$$d\sigma^2 = D\,dt\,d\ln t - d\overline{\mathbf{r}^2}\,d\ln\overline{\mathbf{r}^2} \tag{3.122}$$

gets back to a quadratic form, upon $dt \to (d\sqrt{Dt}\,)^2$ and $d\overline{\mathbf{r}^2} \to (d\sqrt{\overline{\mathbf{r}^2}}\,)^2$. While coordinates have depended so far on time and (implicitly) on the molecular weight, $\phi$ will stand here for a continuous function of $(d-1)$ space variables, specifying a $1+1$-dimensional field theory. Thus, some differential calculus can prove that the quantity:

$$\phi_{(\sigma^\alpha)} = \frac{(\phi^2)_{,\alpha,\alpha}}{2\phi} - \phi_{,\alpha,\alpha} \tag{3.123}$$

allows a useful representation of the following derivative product:

$$\left(\frac{\partial\overline{\mathbf{r}^2}}{\partial t}\right)\left(\frac{\partial\ln\overline{\mathbf{r}^2}}{\partial\ln t}\right) = \frac{\phi_{(\tau)}}{\phi_{(\rho)}} \tag{3.124}$$

and thus of the second postulate of Brownian relativity. We may ask that, for any coordinate change, the diffusion coefficient invariance should correspond to ($D = 1$):

$$\frac{\phi_{(\tau)}}{\phi_{(\rho)}} = 1 \tag{3.125}$$

promptly rearranged by a d'Alembertian in $\rho$ and $\tau$ as:

$$\frac{1}{2}\Box\phi^2 - \phi\Box\phi = \phi_{,}^{\alpha}\phi_{,\alpha} = \text{invar.} \tag{3.126}$$

Let $\phi$ to be a free and massless scalar field, defined in Minkowski's space, the first postulate translates into the Lorentz–Poincaré invariance of the free Lagrangian density, comprising an only kinetic term ($\mathsf{K}$):

$$\mathsf{L}_0(\phi) \equiv \mathsf{K}(\phi) = -\bar{\eta}^{\alpha\beta}\phi_{,\alpha}\phi_{,\beta} \tag{3.127}$$

to which the principle of stationary action obviously relates a standard wave equation:

$$\Box\phi(\boldsymbol{\sigma}) = 0 \tag{3.128}$$

We know it is not form-invariant under any Galilean-like transformation, $\rho' = \rho - \sqrt{\Delta'}\,\tau$ and $\tau' = \tau$:

$$\Box'\phi = \sqrt{\Delta'}\left(\sqrt{\Delta'}\right)_{,\rho'}\phi_{,\rho'} + 2\phi_{,\rho',\tau'} \tag{3.129}$$

unless the spurious term, on the right side, vanishes. With constant diffusive shift ($\Delta'$), this would correspond to ask $\phi_{,\rho',\tau'} = 0$, introducing an unphysical spacetime asymmetry.

To understand the constraint due to the presence of mass, real macromolecules can be modeled like strings vibrating in a Brownian spacetime. We know that, in Einstein's theory, matter is curving the portion of space it occupies. Here, after introducing the Brownian metric ($\gamma_{\mu\nu}$), Lagrange's former function extends to:

$$\mathsf{L}(\phi) = -\gamma^{\alpha\beta}\phi_{,\alpha}\phi_{,\beta} \tag{3.130}$$

It corresponds to the same Lorentz–Poincaré invariance ($\mathsf{L}_0$), where measuring a diffusion coefficient is altered by a metric ratio:

$$\frac{-\gamma^{00}}{\gamma^{\rho\rho}}\frac{\phi_{(\tau)}}{\phi_{(\rho)}} = 1 \tag{3.131}$$

which, for a diagonal metric, preserves upon $\frac{\gamma^{00}}{\gamma^{\rho\rho}} \to \frac{\gamma_{\rho\rho}}{\gamma_{00}}$. This means we can focus on:

$$L(\phi) = \gamma_{00}(\phi_{,\rho})^2 + \gamma_{\rho\rho}(\phi_{,0})^2 \tag{3.132}$$

still returning the Euclidean formulation upon $\gamma_{\alpha\beta} \to \bar{\eta}_{\alpha\beta}$. This invariance, on exchanging covariant with contravariant components, reminds us of a spacetime structure with a Lorentz–Poincaré symmetry which is totally equivalent with respect to any coordinate. We have already met this aspect, in the equivalence of molecular dynamics and macromolecular statics, and will get back to this indifference, of polymer time and space, in the fifth chapter. The guess is the same, the possibility of working with another mechanical formalism.

To proceed, we expand the metric tensor around an arbitrary origin ($\delta\sigma^\mu = \sigma^\mu - 0$):

$$\gamma_{\mu\nu} = \bar{\eta}_{\mu\nu} + \gamma_{\mu\nu,\lambda}\delta\sigma^\lambda + \frac{\gamma_{\mu\nu,\lambda\kappa}}{2}\delta\sigma^\lambda\delta\sigma^\kappa + \mathrm{O}(3) \tag{3.133}$$

and use Riemann's normal coordinates $(\widehat{...})$, giving a simple realization of a locally Gaussian frame:

$$\begin{aligned} \widehat{\gamma}_{\mu\nu,\lambda} &= 0 \\ \frac{1}{2}\widehat{\gamma}_{\mu\nu,\lambda\kappa} &= -\frac{1}{3}\widehat{\overline{R}}_{\mu\lambda\nu\kappa} \end{aligned} \tag{3.134}$$

We saw that the first derivative reflects the vanishing of the affine connection and the second behaves as the Riemann–Christoffel tensor, i.e.:

$$\widehat{\gamma}_{\mu\nu} \simeq \bar{\eta}_{\mu\nu} - \frac{\widehat{\overline{R}}_{\mu\lambda\nu\kappa}}{3}\left(\frac{\delta\phi}{\delta\sigma^{\lambda}}\right)^{-1}\left(\frac{\delta\phi}{\delta\sigma^{\kappa}}\right)^{-1}\delta\phi_{\lambda}\delta\phi_{\kappa} \tag{3.135}$$

In two dimensions, it has only one independent component (e.g., $\widehat{\overline{R}}_{0\rho0\rho} = -\widehat{\gamma}k_G$):

$$\widehat{\overline{R}}_{\mu\alpha\nu\rho} = k_G(\widehat{\gamma}_{\mu\nu}\widehat{\gamma}_{\alpha\rho} - \widehat{\gamma}_{\mu\rho}\widehat{\gamma}_{\nu\alpha}) \tag{3.136}$$

so that, in terms of the curvature scalar ($\overline{R} \equiv -2k_G$):

$$\begin{aligned} \widehat{\overline{R}}_{0000} = \widehat{\overline{R}}_{\rho\rho\rho\rho} = \widehat{\overline{R}}_{\rho\rho00} = \widehat{\overline{R}}_{00\rho\rho} &= 0 \\ \widehat{\overline{R}}_{0\rho0\rho} = \widehat{\overline{R}}_{\rho0\rho0} = -\widehat{\overline{R}}_{\rho00\rho} = -\widehat{\overline{R}}_{0\rho\rho0} &\simeq \frac{\bar{\eta}\overline{R}}{2} \end{aligned} \tag{3.137}$$

with metric tensor determinant $\widehat{\gamma} \simeq \bar{\eta}$. After observing:

$$\begin{aligned} -\widehat{\gamma}_{00} &\simeq 1 - \frac{\bar{\eta}\overline{R}}{6}\left(\frac{\delta\phi}{\delta\rho}\right)^{-2}\delta\phi_{\rho}^{2} \\ \widehat{\gamma}_{\rho\rho} &\simeq 1 - \frac{\bar{\eta}\overline{R}}{6}\left(\frac{\delta\phi}{\delta\tau}\right)^{-2}\delta\phi_{0}^{2} \end{aligned} \tag{3.138}$$

the perturbed Lagrangian density finally reads:

$$\begin{cases} \mathsf{L}(\phi) = -\bar{\eta}^{\alpha\beta}\mathsf{L}_{\alpha\beta} \\ \mathsf{L}_{\mu\nu}(\phi) = \phi_{,\mu}\phi_{,\nu} - \frac{\bar{\eta}\overline{R}}{6}\delta\phi_{\mu}\delta\phi_{\nu} \end{cases} \tag{3.139}$$

Consider now an infinitesimal Brownian transformation like:

$$\delta\phi_{\kappa} = \delta\mu_{\kappa}\phi \tag{3.140}$$

where the perturbation term on the right can be expressed by the involved generator (group), whose form is not essential here. As curvature scalar and Gaussian curvature are related by $\overline{R} = -2k_G$, the Lagrange's function can be rearranged into:

$$\mathsf{L}_{\alpha\beta}(\phi) = \phi_{,\alpha}\phi_{,\beta} - \frac{k_G}{3}\phi^{2}\delta\mu_{\alpha}\delta\mu_{\beta} \tag{3.141}$$

the (Cartesian) value $\bar{\eta} = -1$ being replaced. The principle of stationary action now results in the wave equation carrying the names of Walter Gordon (1926) and

Oskar Klein (1927):

$$\left(\Box + k_M^2\right)\phi(\boldsymbol{\sigma}) = 0 \tag{3.142}$$

where:

$$k_M^2 = -\frac{1}{3} k_G \bar{\eta}^{\alpha\beta} \delta\mu_\alpha \delta\mu_\beta \tag{3.143}$$

denotes a curvature-induced (mass) perturbation and $\mathsf{U}(\phi) = k_M^2 \phi^2$ is the associated potential, so that $\mathsf{L}(\phi) = \mathsf{K}(\phi) - \mathsf{U}(\phi)$.

The first who actually ran into the Klein–Gordon equation was Erwin Schrödinger when, before arriving at his equation, replaced the quantum operators ($E \rightarrow \mathrm{i}\frac{\partial}{\partial t}$ and $\mathbf{p} \rightarrow -\mathrm{i}\vec{\nabla}$) into the squared energy relation of relativistic mechanics ($E^2 = m^2 + \mathbf{p}^2$). The main problem with it is the occurrence of negative probabilities and energy solutions, afterwards reinterpreted by Paul A.M. Dirac (1928), with his quantum-relativistic equation, and finally by Richard P. Feynman (1962) in terms of his famous prescription (negative-energy particles backward in time correspond to positive energy antiparticles forward in time).

Here, we can solve it by the trial function $\phi \sim \mathrm{e}^{\mathrm{i}(\omega\tau - q\rho)}$, with "dispersion relation" ($\omega(q)$) given by $\omega^2 = q^2 + m^2$ (in natural units). Therefore, if $\delta\mu_0 = \mathrm{i}\omega$ and $\delta\mu_\rho = -\mathrm{i}q$, then the mass square is identified with $m^2 = -3k_M^2/k_G$. For small enough metric perturbations, our statistical description of curvature is thus equivalent to the rise of mass in a flat space. In other words, macromolecular scaling and mass concepts turn out to have the same statistical significance. They "shape" the Brownian disorder by merely geometrical means, in the framework of which, curving spacetime, lowering diffusivity and increasing mass share the same universal behavior. We should only require a large number of degrees of freedom ($N \gg 1$), which is the condition to represent a (relativistic) field as a dynamic system, as is ours at the beginning. Finally, the limiting end-to-end chain distribution can be recovered from a suitable "path integral" description, as in the formulation due to Feynman (1948), summing over all configurations that the fluctuating worldlines can take on at a constant length (e.g., $L_c$). The statistical weight of each contribution follows from setting a Wiener's measure in the integral, and the final result, evaluated over small separation distances ($|\boldsymbol{\sigma}| \ll L_c l$), is still a Gaussian function with variance $L_c l$.

## 3. OUTLOOK AND NOTES

Relativity and field theories are nowadays well established, and it is stimulating to think that, behind the various solutions of Einstein's equations, there may emerge a better understanding of polymer science and its facets. Different geometries or interactions can be coped with by using new metric and energy–momentum tensors. This should be the case, for instance, of the Robertson–Walker solution, suitable at first sight to describe the kinetics of polymer collapse in poor solvent conditions ($T < \Theta$).

An analysis of chain flexibility is expected, instead, to be more complicated, and a reason for this may be immediately argued from the expression of the second central moment in the Kratky–Porod "worm-like chain" model. It represents the limiting (continuous) case of a freely-rotating chain, with bond length and angle tending to zero and an infinite number of repeating units, under the restriction that contour length ($L_c$) and "persistence length" ($l_p$) remain constant. In brief, for a 3-dimensional molecule, one obtains a formula matching the flexible and rigid-rod limit:

$$\overline{\mathbf{r}^2} = 2l_p L_c\left[1 - \frac{l_p}{L_c}\left(1 - \mathrm{e}^{-\frac{L_c}{l_p}}\right)\right] \tag{3.144}$$

where Kuhn's step size equals twice the persistence length, $2l_p = \rho^2/L_c$ ($L_c \to \infty$). The latter estimates the minimum length of two neighboring segments with unrestricted relative orientations and can be used (whenever appropriate) as a stiffness parameter. Thus, in a Brownian relativistic-analysis, passing from flexible to stiffer macromolecules will (probably) require reconsidering the (quadratic) form of the invariant interval, and restarting from the exact solution of Langevin's equation. A close observation could also be made on the rotational diffusion, where a quadratic interval is appropriate at most for the transient regime.

Concerning the insights that Brownian relativity might suggest about classical gravity and field theories, we are unable at present to give an answer. However, it is interesting to note that the transition density of a Brownian movement points out the following equation ($d = 3$):

$$2\pi w_s\left(x', x\right) = |x' - x|^{-1} \tag{3.145}$$

with ($\delta t = t' - t$):

$$w_s\left(x', x\right) = \int_0^\infty W_s(x, t; x', t')\, d\delta t \tag{3.146}$$

It interprets Newton's potential by (an angle built on) the Gaussian distribution integrated over time. A similar relation will also be met in the last chapter, where the (average) dimension of a polymer conformation is derived from the torsional rotation of the monomeric units.

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CHAPTER FOUR

# THE COVARIANT SCALING OF PROBABILITY

## Contents

In a Brownian–relativistic interpretation of a polymer solution, the two characteristic (spacetime) scales, of macromolecules and liquid molecules, are related by the invariance of diffusive intervals between Brownian events, which here are no longer separated. This symmetry set together space, time and, because of the mobility scaling, the chain unit number as well. By the diffusive Lorentz–Poincaré transformations, any movement slowdown was thus regarded as a spacetime contraction–dilation, amounting to an equivalent diffusion coefficient decrease in a phantom chain molecule. We were afterwards able to make more "physical" the "formal" equivalence in polymer problems for time and molecular weight, and afford universality in both Gaussian and non-Gaussian systems by what we called the Brownian equivalence principle.

Close arguments will now be presented about some more probabilistic issues. Again, our thesis will be that the scaling picture displayed by macromolecules encloses the statistical properties of the liquid which they embed, and vice versa. The stochastic process modeling how a cluster of liquid molecules decorrelates with time will be traceable in the fluctuations of an identical conformation of a line-like (polymer) object, diffusing across the same liquid phase. The aim be-

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comes so to comprehend how (molecular) distribution functions, closely to coordinate transformations between Brownian observers, are constrained so to be connected at different scales. We will introduce a further criterion of probability conservation for subsystems sharing a common Brownian medium, and get a form-preserving statistical function that will be expoited in a couple of relevant situations. In the first, the distribution function of a (single) "true self-avoiding walk polymer" is rebuilt by the total correlation function of the liquid units. We will secondly address the (tough) problem of turbulence in liquids, suggesting that intermittency phenomena in "passive scalar advection" have close roots to the excluded volume problem in polymer chains. The basic idea, put forward in either cases, is to start from the simplest molecular microstructure and get to that antagonistic by Brownian–relativistic means. So to suggest a conceptual image, Brownian relativity would act as an "Archimedean lever" for statistics, the "fulcrum" being given by the full statistical knowledge of some spacetime scale.

## 1. VINEYARD'S VAN HOVE DISTRIBUTION FUNCTION

We have already extended the second-order diffusive interval to any length scale, and applied it to obtain an approximate closed-form equation for the size exponent of the real chain. There, emphasis was given to the (static) molecular weight domain ($N$). When $N = 1$, we were concerned with the spatial moments of the self-correlation function that, in the (hydrodynamic) limit of long wavelength fluctuations, is ruled by simple diffusion. For a large molecule of $N$ units, such an extended treatation referred instead to the chain vector statistics. Here, the attention will mostly be given to the dynamical aspects, and the generalized diffusion coefficients used to define an overall interval ($\Sigma_N \, dt$), serving basically as a total normalization term. In this way, still for a spherically symmetric system, one arrives at a condition for the incoherent intermediate scattering function:

$$d \ln F_N(q,t) + Dq^2 \, dt = \text{invar} \tag{4.1}$$

or:

$$\frac{F_N(q,t)}{F_{\text{eq}}(q,t)} = \text{invar} \tag{4.2}$$

equilibrium being clearly described by a normal statistics:

$$F_{\text{eq}}(q,t) = \mathrm{e}^{-Dq^2 t} \tag{4.3}$$

This invariance must be averaged over the involved molecular ensembles, and this can be done by recalling that Brownian relativity connects time and space intervals of liquid and chain molecules. If $\Delta_{nm}$ is used to specify any finite displacement, evaluated between a couple of sites $(n, m)$, we have:

$$D\big(\Delta_{nm}t' - \Delta_{nm}t\big) = \Delta_{nm}\overline{\mathbf{r}'^2} - \Delta_{nm}\overline{\mathbf{r}^2} \tag{4.4}$$

and thus:

$$F_N\big(q, \Delta_{nm}t'\big) = \exp\big\{q^2\big(\Delta_{nm}\overline{\mathbf{r}^2} - \Delta_{nm}\overline{\mathbf{r}'^2}\big)\big\}F_N(q, \Delta_{nm}t) \tag{4.5}$$

or:

$$\exp\big(q^2\Delta_{nm}\overline{\mathbf{r}^2}\big)F_N(q, \Delta_{nm}t) = \text{invar} \tag{4.6}$$

where, conventionally, each time interval will take on positive values. Again, the quantity $\Delta_{nm}\overline{\mathbf{r}^2}$ can either refer to the average distance that a single tagged particle travels within $\Delta_{nm}t$ or to the endpoint contraction of a polymer path passing through $n$ and $m$. Furthermore, as $\Delta_{nm}\overline{\mathbf{r}^2} = (n-m)l^2$, a "self-diffusion propagator" can be identified for $m < n$ with:

$$\mathrm{e}^{-\frac{1}{6}q^2l^2|n-m|} = \overline{\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot(\mathbf{r}_n-\mathbf{r}_m)}} \tag{4.7}$$

and write:

$$\overline{\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot(\mathbf{r}_n-\mathbf{r}_m)}}F_N(q, t_n - t_m) = \text{invar} \tag{4.8}$$

Summing this equation over distinct molecular domains will be influenced by the polymer concentration regime. We start here by working in the limit of high dilutions and large chain molecules ($N \gg 1$), in which the contributions of time and space intervals in macromolecular and molecular subsystems can, to some reasonable extent, be regarded independent and thus separated. Hence, on restricting the sum to the spatial positions occupied by each ensemble at a fixed time origin, it turns out:

$$\frac{1}{N}\sum_{\{\mathbf{r}_m,\mathbf{r}_n\}}^{N} F_N(q, \Delta_{0N}t)\overline{\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot(\mathbf{r}_n-\mathbf{r}_m)}} = F_N(q,t)S_N(q) \tag{4.9}$$

where $\Delta_{0N}t$ converges to the actual time elapsed, and the static structure factor evaluates the initial behavior, $S_N(q) = F_N(q, 0)$. Observe that each term $(n, m)$ can be replaced in the sum by an equally invariant "reversed" contribution, $(m, n)$, preserving in this way its convergence to the above expression. We can turn finally to Fourier's inverse transform, and recall the relation between structure factor and total correlation function ($h_N$), describing the wandering of a particle away from some arbitrary position:

$$S_N(\mathbf{q}) = 1 + \bar{\varrho}_N\int h_N(\mathbf{r})\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}\,d\mathbf{r} \tag{4.10}$$

Accordingly, the covariant probability expression reads:

$$G_{S,N}(r,t) + \bar{\varrho}_N h_N(r) \otimes G_{S,N}(r,t) = \text{invar} \tag{4.11}$$

$\bar{\varrho}_N$ being the average equilibrium density of a $N$-particle system and the symbol $\otimes$ denoting a spatial convolution product. $G_{S,N}$ is the (Van Hove) self-correlation function, giving the probability per unit volume to find a (tagged) molecule at $(r, t)$, given that it was initially located at the origin. The previous result can also be rewritten in compact form as:

$$G_N(r,t) = G_{F,N}(r) \otimes G_{S,N}(r,t) = \text{invar} \tag{4.12}$$

where $G_N$ is now Van Hove's total function, and:

$$\bar{\varrho}_N G_{F,N}(r) = \bar{\varrho}_N \delta(\mathbf{r}) + \bar{\varrho}_N^2 h_N(r) \tag{4.13}$$

is a correlation function for density fluctuations around $\bar{\varrho}_N$, involving a pointwise "singlet" autocorrelation and the affinity between homogeneous fluid constituents. The translational invariance conveyed by the convolution form prompts the idea that a covariant constraint can also be developed both in terms of characteristic and intermediate scattering functions of the (two) Brownian systems.

Van Hove's total function is an important tool to model particle (pair) correlations, and was proposed by Léon Van Hove (1954) as a time-dependent extension for the pair correlation function (or radial distribution function), $g(\mathbf{r}) = 1 + h(\mathbf{r})$, of an interacting particle system. It means the conditional probability of finding a molecule $(n)$ in some infinitesimal volume around the point $\mathbf{r}$ at time $t$, given that another molecule $(m)$ was set at the spacetime origin ($t = 0$ and $\mathbf{r} = \mathbf{0}$). We will see that, in our formulation, Van Hove's total function acts also as an extension of the correlation function for the monomer concentration. In general, by the two complementary circumstances, $n = m$ or $n \neq m$, it can be separated into a couple of terms, termed in fact the self ($S$) and distinct ($D$) parts:

$$G(\mathbf{r},t) = G_S(\mathbf{r},t) + G_D(\mathbf{r},t) \tag{4.14}$$

with initial conditions set by $G_S(\mathbf{r},0) = \delta(\mathbf{r})$ and $G_D(\mathbf{r},0) = g(\mathbf{r})$. The self-correlation function has already been seen to be a tagged particle density (different from the fluid density), and is surely simpler to be evaluated than $G_D$. At short times (free particle), it comes from Maxwell's momentum distribution, and is normal with variance proportional to $(v_0 t)^2$. At long wavelength fluctuations (diffusing particle), the Gaussian takes the Einstein–Smoluchowski form. Intuitively, as the particle is wandering away from the origin by $\boldsymbol{\rho}(t)$, its autocorrelation will progressively weaken and, when $t$ exceeds the characteristic relaxation time:

$$\bar{\varrho} G_N\big(|\mathbf{r} - \mathbf{r}'|, t\big) \to \overline{\delta\big(\mathbf{r} - \boldsymbol{\rho}(t)\big)}\,\overline{\delta\big(\mathbf{r}' - \boldsymbol{\rho}(0)\big)} = \bar{\varrho}^2 \tag{4.15}$$

Concerning $G_D$, to yield a closed-form expression for it is a tough task, and nowadays the convolution approximation due to George H. Vineyard (1958) remains the simplest and best known model. In short, starting from a direct term set to a linear superposition like:

$$G_D(\mathbf{r},t) = \int g(\mathbf{r}',t)\,\Gamma(\mathbf{r} - \mathbf{r}',t)\,d\mathbf{r}' \tag{4.16}$$

he assumed the unknown distribution $\Gamma$ to behave as the self-correlation:

$$G(\mathbf{r},t) = G_S(\mathbf{r},t) + \int g(\mathbf{r}',t)G_S(\mathbf{r}-\mathbf{r}',t)\,d\mathbf{r}' \tag{4.17}$$

that, to within a density shift, has just the form of our covariant function. It can be rewritten in fact as:

$$G(\mathbf{r},t) - g_0 = G_S(\mathbf{r},t) + \int \big[g(\mathbf{r}',t) - g_0\big]G_S(\mathbf{r}-\mathbf{r}',t)\,d\mathbf{r}' \tag{4.18}$$

with constant mean number density at infinity ($g_0$). Accordingly, in any homogeneous medium ($N \to 1$), the found covariant constraint will reduce to an identity relation, complying Vineyard's ordinary approximation.

In the "ideal" case, with vanishing or negligible total correlations, it simplifies into the scaling property of Brownian motion ($h \to 0$):

$$G_N(r,t) = \text{invar} \tag{4.19}$$

and the normal distribution function becomes statistically invariant. This better translates the equivalence for time and monomer number in Brownian relativity, often exploited in polymer problems as a formal analogy ($t \leftrightarrow N$). In immaterial spacetimes, where either excluded volumes or self-avoiding walks fail to take place, (chain) statistics is equally Gaussian or, otherwise said, the macromolecular system "physically" corresponding to uncorrelated Brownian–relativistic media (perfect or non-interacting gases) is the ideal polymer. More generally, one will have a covariant reinterpretation of the standard Gaussian model to correlated media (i.e., liquid and interacting systems) or, otherwise said, of the central limit theorem for a family of random variables observed from two Brownian frames and not independent. For these reasons, the found covariant constraint can be exploited to study the equivalence for statics and dynamics, and carried into some static relation for molecular and macromolecular systems applying at a common scale. We will have to deal with one of the two specular inverse problems, "from molecule to macromolecule" and "from macromolecule to molecule," arising from extending the diffusive interval to any order.

A last noteworthy point to underline is that Vineyard's convolution law has not been conjectured or assumed here, but deduced from Brownian relativity. Consistent with the supposed separation, of spatial and temporal contributions, it states that any assembly, regardless of its molecular weight, moves in a given time over a length $r'$, independently of any other particle system located at $r' - r$. Nevertheless, as 2-particle motions cannot be uncorrelated for arbitrarily small $|r' - r|$ displacements, one is left with the major problem with the Vineyard's law. Though fairly agreeing with experimental data, the convolution approximation suffers in fact from the disadvantage of neglecting the correlations inhibiting the liquid structure breakdown, at the initial stages of motion.

# 2. FROM MOLECULE TO MACROMOLECULE: TRUE SELF-AVOIDING WALK POLYMER

## 2.1 Self-correlation functions of chain and liquid molecules

Polymer dynamics is normally described by the stochastic and collective monomer motion that develops under those connectivity constraints fixed and propagated by the chain molecule. Brownian relativity, on the other hand, encourages pursuing a somewhat opposite view, the analysis of chain conformations by the (only) liquid correlation "sea" that macromolecules embed and diffuse across. When large unit numbers are approached, $N \rightarrow \infty$, Van Hove's covariant function gives rise in fact to a static relation, suitable to obtain the statistics of a real polymer chain from correlation functions of the liquid. In this line, the equation:

$$G_{F,N} \otimes G_{S,N} = G_{F,1} \otimes G_{S,1} \tag{4.20}$$

will be inverted ($1 \rightarrow N$) when the convolution product, which is defined for two arbitrary functions as:

$$f_1 \otimes f_2 = \int_0^R f_1(R-r)\, f_2(r)\, dr = f_2 \otimes f_1 \tag{4.21}$$

is shared at some common scale ($R$), assumed for simplicity dimensionless. To write an analytic solution, one may employ a theorem relying on the "regularization procedure" acknowledged to Andrey N. Tikhonov (1943). Accordingly, the functional:

$$L_\alpha\big[G_{S,N}(R)\big] = \|G_{D,N} \otimes G_{S,N} - G_1\|^2 + \alpha\|G_{S,N}\|^2 \tag{4.22}$$

will have to be minimized in the polymer autocorrelation function ($G_{S,N}$). We see here that optimizing the (standard) error, the (first) norm of the difference on the left, is enforced by the second extra-constraint, selecting the solutions which are stable with respect to small initial data perturbations. The approximation strategy for the "regularization parameter" $\alpha$ (>0) controls the functional convergence, and fixes the best approximation by minimizing $L_\alpha$. In brief, for integral equations like:

$$\int_0^z w(s)\, ds = y(z) \tag{4.23}$$

with $z \in [0,1]$ and $y(0) = 0$, it can be proved that the solution $w_\alpha \equiv w(z,\alpha)$ fulfills the following differential equation in $z \in (0,1)$:

$$-\alpha w''(z) + w(z) = y'(z) \tag{4.24}$$

with primes abbreviating the symbols of derivatives with respect to the independent variable (here $z$) and boundary conditions:

$$\lim_{z\to 1} w(z) = \lim_{z\to 0} w'(z) = 0 \tag{4.25}$$

The assumptions and calculations, bringing back our radial problem to this framework, are rather tedious and with numerous details. They may take our attention away from the central physical aspects, and are referred to elsewhere (Mezzasalma, 2006). What matters instead is stressing that polymer and liquid systems are, in the end, statistically related by:

$$G'_{S,N}(R) + \alpha_N G_{S,N}(R) = F(R) \tag{4.26}$$

being:

$$F(r) = G'_{S,1}(r) + X_{0\alpha}\widetilde{h}_1(r) + X_{2\alpha}\widetilde{h}_1''(r) \tag{4.27}$$

where $\alpha_N = 8\pi\alpha\bar{\varrho}_N$, $X_{s\alpha}$ are constant model coefficients and $\widetilde{\ldots(r)} = 4\pi r^2 \ldots$. Recall that real, self-avoiding polymers possess non-negligible excluded volumes, originating microscopically from the steric self-repulsion among monomers, and resulting in their distribution functions by a sharp decrease at small distances. In other words, it is highly unlikely that their conformations return arbitrarily close to the origin, thence $G_{S,N}(0) = 0$. Regarding the liquid, long wavelength fluctuations can be accounted for in $G_{S,1}(s)$ by a Gaussian function with some (heuristic) root mean square length ($\sigma$). By integrating the above differential equation, one is led to the following general solution in $R \in (0, 1)$:

$$G_{S,N}(R) = \mathrm{e}^{-\alpha_N R}\left\{\int_0^R F(r)\mathrm{e}^{\alpha_N r}\,dr + \text{const.}\right\} \tag{4.28}$$

the first contribution ($\mathcal{G}$) being Gaussian-like and the second ($\mathcal{H}$) identifying a perturbation that alters the ideal chain statistics:

$$G_{S,N}(R) = \mathcal{G}(R) + \mathcal{H}(R) \tag{4.29}$$

As to the first, a simple integration by parts leads to:

$$\mathcal{G}(R) = G_{S,1}(R) + S\mathrm{e}^{-\alpha_N R}\left\{\Phi\left(\frac{R}{\sqrt{2}\sigma} - \frac{\alpha_N\sigma}{\sqrt{2}}\right) - \mathrm{c}\right\} \tag{4.30}$$

$\Phi$ denoting the probability error integral, $S \equiv \alpha_N(4\pi\sigma^2)^{-1}\mathrm{e}^{\alpha_N^2\sigma^2/2}$ and c a normalization factor. The perturbation term depends instead on the total correlation function of the liquid molecules ($h_1$) as:

$$\mathcal{H}(R) = X_{2\alpha}\left[\widetilde{h}_1'(R) - \alpha_N\widetilde{h}_1(R)\right] + \left(\alpha_N^2 X_{2\alpha} + X_{0\alpha}\right)\mathrm{e}^{-\alpha_N R}\int h_1(r)\mathrm{e}^{\alpha_N r}\,d\mathbf{r} \tag{4.31}$$

## 2.2 Ornstein–Uhlenbeck spatial process

It may be noteworthy to briefly remark that the differential equation for $G_{S,N}$ is formally similar to the initial value problem arising from Langevin's formalism:

$$d\mathbf{v}(t) = -\nu_S\mathbf{v}(t)\,dt + d\mathbf{W}_B(t) \tag{4.32}$$

where $\mathbf{v}(t)$ is (still) a stochastic Brownian velocity in continuous time, $\mathbf{W}_B(t)$ is a Bachelier–Wiener process and $\nu_S$ is still a (constant) characteristic frequency (typically, $\nu_S \simeq 10^8$ s). When $\mathbf{v}(0) = 0$, the solution is in fact an adapted integral modification in the stochastic calculus formulated by Kiyosi Itô (1942):

$$\mathbf{v}(t) = \varsigma(t) \int_0^t \varsigma(-t)\, d\mathbf{W}_B(t) \tag{4.33}$$

again, with $\varsigma(t) = \mathrm{e}^{-\nu_S t}$. This defines the Ornstein–Uhlenbeck process, defined on phase space, and normally acknowledged as the first actual dynamic theory of Brownian movement.

Evidently, on mapping $t \to R$, $\nu_S \to \alpha_N$ and $d\mathbf{W}_B(s) \to F(s)\, ds$, the above description is equivalent to ours. After developing $F$, one may note that the stochastic process for the spatial conformations of a real polymer consists of a linear superposition ($\mathcal{L}$) of Bachelier–Wiener's, with three other contributions ascribed to the liquid phase:

$$\mathbf{W}_B(s) \to \mathcal{L}\big\{\mathbf{W}_B(s), \delta\overline{(\Delta N)^2}, \delta p, h_1(s)\big\} \tag{4.34}$$

That in the molecular unit number ($N$) is linked to the fluctuation equation of state and the integral of the total correlation function:

$$\bar{\varrho}_1 \int \widetilde{h}_1(r)\, dr = \frac{\overline{(\Delta N)^2}}{N} - 1 \equiv \frac{\delta\overline{(\Delta N)^2}}{N} \tag{4.35}$$

Those further originate from $\widetilde{h}_1{}'(s)$. One is the total correlation of the liquid molecules ($h_1(s)$), the second ($sh_1'(s)$) can be better understood if the virial equation of state for a dilute system is written as:

$$p = \bar{\varrho}_1 k_B T\left(1 - \frac{\bar{\varrho}_1}{6} \int r h_1'(r)\, d\mathbf{r}\right) \equiv p_{\text{ideal}} + \delta p \tag{4.36}$$

where $p_{\text{ideal}} = \bar{\varrho}_1 k_B T$, $k_B T h_1'(r) \simeq -g_1(r)(du_1/dr)$, $g_1(r)$ is the pair correlation function and $u_1(r)$ ($\simeq -k_B T \ln g_1(r)$) is the pairwise potential.

These remarks still suggest that molecular correlations can be dealt with here within a generalized normal statistics. When they vanish, the (relative) unit number fluctuation, the total correlation and pressure functions are retrieved to the ideal gas behavior. We are left again with the free particle case, for which Einstein's theory is known to nicely approximate Ornstein–Unlenbeck's (i.e., the variance of the random coordinates differs from $2Dt$ by at most $3D/\nu_S$). In the presence of fields of force, a good approximation can be given by Markov's process due to Smoluchowski. For a harmonic potential with characteristic frequency $\omega$, it has as well the same form of a free Ornstein–Unhlembeck (velocity) process:

$$\nu_S\, d\mathbf{x}(t) = -\omega^2 \mathbf{x}(t)\, dt + \nu_S\, d\mathbf{W}_B(t) \tag{4.37}$$

and is expected to be satisfactory for $\nu_S \Delta t \gg 1$ and $\nu_S/(2\omega) \gg 1$ (slow force variations).

## 2.3 Percus–Yevick–Wertheim scaling hypothesis

Imagine working out a computer-assisted investigation, one should first be able to access the specific correlation functions, case by case involved, and then rebuild up numerically the conformational statistics from the implied equations. The inversion of Van Hove's covariant function would benefit itself from using numerical techniques. Nevertheless, wishing to find an (approximated) analytical solution, one may seek a scaling hypothesis making the model less complicated and evidencing physics better. There are two points that can be reasonably adopted, (i) a small (enough) regularization parameter ($\alpha \ll 1$) with a polymer length scale defined by $\alpha_N R \to \rho$; (ii) a functional form for the total correlation function of the liquid molecules relying on the Percus–Yevick solution for a hard-sphere fluid.

The first point renders the general form of the polymer self-correlation function independent of the macroscopic density. Formally, it would require working with a medium homogeneous in space in the thermodynamic limit. This sort of constraint on the translational invariance of the system rearranges the Gaussian-like term into:

$$\mathcal{G}_0(\rho) = G_{S,1}\big(\alpha_N^{-1}\rho\big) + x_0 \mathrm{e}^{-\rho} \tag{4.38}$$

and simplifies its perturbation as:

$$\mathcal{H}(\rho) = x_1 \mathrm{e}^{-\rho} \int h_1(\rho)\mathrm{e}^{\rho}\, d\boldsymbol{\rho} \tag{4.39}$$

$\alpha_N$, $x_0$, and $x_1 = (2\pi\sigma)^{-\frac{3}{2}}$ playing the role of three heuristic coefficients. The simple exponential in $\mathcal{G}_0$ modifies the normal statistics and may be used to require the self-avoidance, $\mathcal{G}_0(\rho \to 0^+) = 0$ ($x_0 = -x_1$). Once the polymer path turns from the origin, the second contribution ($\mathcal{H}$) begins to account for the liquid correlations at the chain molecule scale.

Concerning the second point, Jerome J. Percus and George J. Yevick (1957) gave the simplest and best known integral equation for the radial distribution function of a classical fluid, i.e.:

$$u(r) = -k_B T \ln\big[g(r) - c(r)\big] \tag{4.40}$$

where $u$ is the interparticle potential and $c$ is the "direct correlation function," earlier introduced by Ornstein and Frederik Zernike (1914). On the basis of the effect that a molecule can exert on any other unit, they distinguished between a "direct" from an "indirect" contribution to the total correlation:

$$h(r) = c(r) + \bar{\varrho} h(r) \otimes c(r) \tag{4.41}$$

The Percus–Yevick equation is an exact equation, accurate at low density, but needs to be complemented by a second relation. It was solved exactly by M.S. Wertheim (1963) and E. Thiele (1963) for hard spheres with fixed particle diameter $D$ and packing parameter ($=\pi\bar{\varrho}D^3/6$). Remember that, due to the singular nature of the potential, Boltzmann's factor for hard spheres is either zero or unity, according to the interparticle radial distance, and this family of pair correlation functions cannot take temperature changes into account. However, as density increases, the medium screens out the long-range interactions and it becomes more accurate than expected.

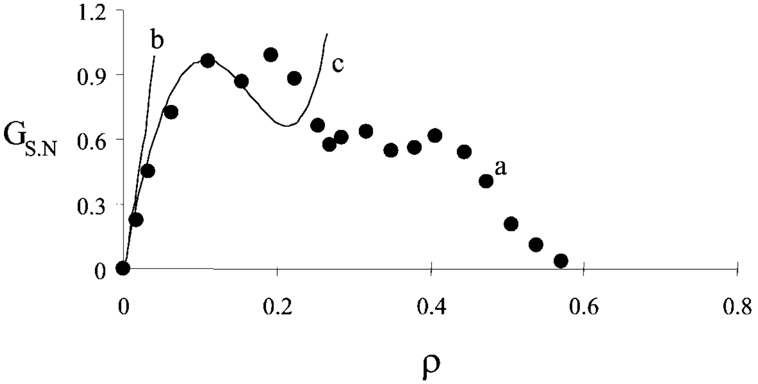

**Figure 4.1** Numerical (Pearson and Anderson, 1993) (a) and theoretical (Mezzasalma, 2006) (b–c) results for a true self-avoiding-walk polymer. Curves depict the (b) Gaussian-like and (c) repulsive hard-sphere behaviors at small scales ($x_0 = 18.90$ and $\alpha_N = 0.35$).

When $r < D$, the direct correlation function writes as a cubic polynomial with quadratic term absent, while it equates zero elsewhere ($r \geqslant D$), thence:

$$rg(r) = \begin{cases} 0 & (0 \leqslant \frac{r}{D} < 1) \\ G_M(r) & (M \leqslant \frac{r}{D} < M + 1) \end{cases} \tag{4.42}$$

where the behavior inside any shell ($M$) is written by polynomials $P_{KM} = P_{KM}(r/D)$ of order $M - 1$ and the complex roots of a third-order equation ($\tau_K \in \mathrm{C}$):

$$G_M(r) = \sum_{K=0}^{2} P_{KM}(r)\mathrm{e}^{\tau_K r} \tag{4.43}$$

Thus, the simplest expression to make use of is:

$$G_M(\rho) = P_M(\rho)\mathrm{e}^{-\rho}\big[1 + \cos(q_M\rho)\big] \tag{4.44}$$

that, after recalling $\widetilde{h_M} = 4\pi\rho^2 h_M(\rho)$, suggests the $M$th shell contribution:

$$\widetilde{h_M}(\rho) \sim p_M(\rho)\mathrm{e}^{-\rho}\big[1 + \cos(q_M\rho)\big] \tag{4.45}$$

$q_M$ being a heuristic wavenumber and $\frac{1}{4\pi}p_M(\rho) = x_M\rho^M + \cdots + x_1\rho$ denoting a polynomial of order $M \geqslant 1$ with constant coefficient absent.

## 2.4 “True” self-avoidance from molecular correlations

The derived equations are employed here to model a case of a certain difficulty. Solid points in Fig. 4.1 are taken from the autocorrelation function of a “true self-avoiding walk polymer” plotted against the end-to-end distance (in molecular size unit) for a computer-grown ensemble of 18.500 monomers. Details can be found elsewhere (Mezzasalma, 2006; Pearson and Anderson, 1993), where a thorough analysis is reported in terms of the main current polymer models and our interpretation. Gaussian, exponential and power laws provide best fits that are often satisfactory, from which quantities such as the gyration radius or the Hausdorff–Besicovitch (fractal) dimension may be extrapolated correctly. In this case, however, none of them are good candidates for reproducing the so-called Guinier's region (small wavenumbers) or the mild oscillations in the structure factor. As suggested by the relative minima in Fig. 4.1, they arise from a certain number of chain loops, where the walk performed by the monomeric segment reverses direction. Their irregularity indicates that monomers in the neighborhood of a given loop will be equally distant from some other monomer, belonging to another loop.

As a short digression, remember that the shapes of true self-avoiding polymers are obtained from random walks which avoid visiting a given site with probability proportional to the number of "visits." Ordinary self-avoiding (or self-repelling) chains are more representative instead of the excluded volume problem (in dilute solution). In this case, the probability of meeting a given segment comes from the Maxwell–Boltzmann weight that is set from the beginning to account for the total amount of self-intersecting configurations, where all permitted walks of equal length possess the same probability. Among the first papers on the subject are those by Gilbert W. King (1949–1951), John M. Hammersley and (K.W.) Bill Morton (1954), in their pioneering applications of the Monte Carlo method, but also William J.C. Orr (1946–1947) and Elliott W. Montroll (1950), who developed a random walk analysis with finite memory. Nevertheless, it was Flory (1949) who guessed that the average size of a self-avoiding chain increases with the molecular weight more steeply than linearly. His heuristic thermodynamic arguments were taken further by Michael E. Fisher (1966) to conclude that $\nu(d \leqslant 4) = \frac{3}{d+2}$ and $\nu(d > 4) = \frac{1}{2}$. This "Fisher–Flory formula" is exact for $d = 2$ and $d \geqslant 4$ but, as already seen, for $d = 3$ slightly exceeds the renormalization group result (0.6 against $\simeq 0.588$). Despite this remarkable agreement, Flory's model was never fully justified, sometimes commented to be fortuitous and bringing to wrong free energy contributions. In addition, for any conformation, the excluded volume parameter in Flory's theory is of deterministic nature and uniform along the chain, which are too idealized assumptions fully ignoring the conformational structure.

In summary, a true self-avoiding walk brings to a lower excluded volume interaction, and is less expanded than a self-repelling conformation. Their prototype molecules refer moreover to different polydispersed solutions. The former behaves as a chain with given weight-average molecular weight, whose excluded volume is screened by the surrounding molecules. A self-repelling walk identifies instead an isolated and long macromolecule, interacting only with itself in the (good) solvent formed by all the surrounding ($m$-mer) units. Another interesting case, intermediate between free random walks and strongly non-Markovian chains, is that with conformational (energy) states built on the configurations of some "Pólya's walk," for instance, the "weakly self-avoiding walk" by Cyril Domb and Geoffrey S. Joyce (1972).

Applying now the equation for $G_{S,N}$ requires to derive each perturbation term for a Percus–Yevick hard-sphere fluid, and it turns out:

$$\mathrm{e}^{\rho}\mathcal{H}_M(\rho) = I_M(\rho) + \frac{\rho^{M+1}}{M+1} \tag{4.46}$$

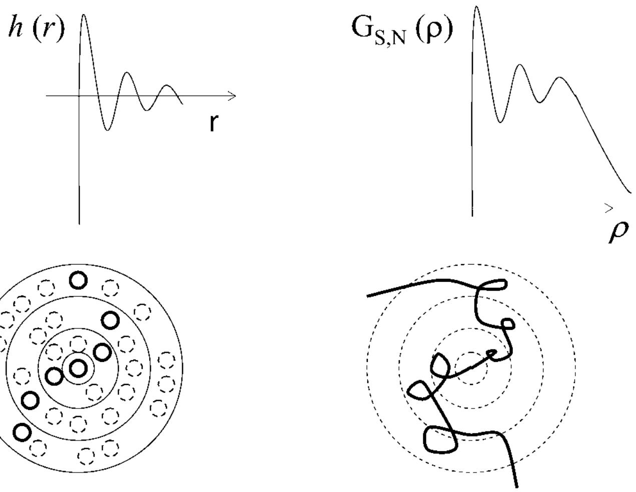

**Figure 4.2** Rebuilding polymer conformations by solvent density fluctuations.

where, for the first three shells:

$$I_M(\rho) = \int_0^{\rho} \rho'^M \cos\left(q_M \rho'\right) d\rho'$$

$$= \begin{cases} \dfrac{\cos(q_1\rho)}{q_1^2} + \dfrac{\rho \sin(q_1\rho)}{q_1} - q_1^{-2} \\ \dfrac{2\rho\cos(q_2\rho)}{q_2^2} + \dfrac{\rho^2 \sin(q_2\rho)}{q_2} - \dfrac{2\sin(q_2\rho)}{q_2^3} \\ \dfrac{\rho^3 \sin(q_3\rho)}{q_3} + \dfrac{3\rho^2\cos(q_3\rho)}{q_3^2} - \dfrac{6\cos(q_3\rho)}{q_3^4} - \dfrac{6\rho\sin(q_3\rho)}{q_3^3} + 6q_3^{-4} \\ \ldots \end{cases} \tag{4.47}$$

The innermost behavior obviously involves a zero pair correlation function, or $h_0(r) = -1$ $(r < d)$, for the corresponding perturbation reads:

$$\mathcal{H}_0(\rho) = 8\pi x_1 \left(\mathrm{e}^{-\rho} - \rho^2/2 + \rho - 1\right) \tag{4.48}$$

To understand the significance of this relation, one may look at the scheme of Fig. 4.2, sketching out how chain statistics rebuilds in Brownian relativity. Owing to Van Hove's covariant function, the polymer self-repulsion is described by a statistical convolution, combining the liquid wavelength contributions at the macromolecular scale. Thus, while the innermost correlation profile witnesses the small-scale repulsion among liquid molecules, the last equation similarly reflects the impossibility for a real polymer path to return arbitrarily near the initial point (i.e., $R \gtrsim 0$). The final result is thus a smoother repulsion term, depending on the chain hindrance as $\mathcal{H}_0(\rho) = -\frac{1}{3}\sqrt{2/\pi}(\rho/\sigma)^3 + \mathrm{O}(\rho^4)$. A close mechanism is then expected to take place then for the irregular oscillations in Fig. 4.1, reflecting the typical wiggles and peaks in radial distribution functions of fluids. Monomer density fluctuations, with its higher loops concentrations, and liquid density fluctuations, with its shell corre-

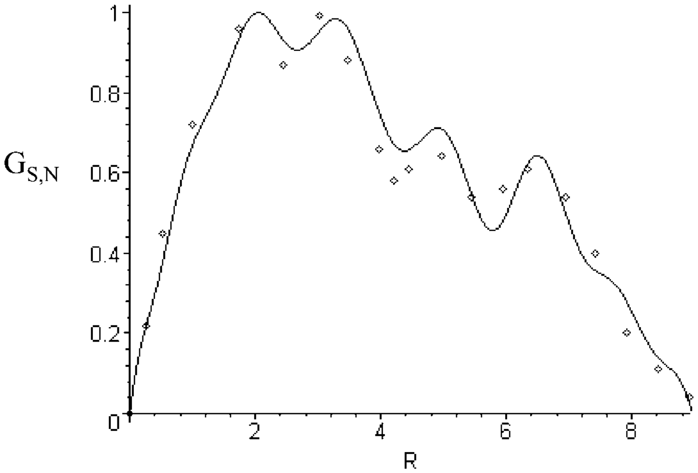

**Figure 4.3** Numerical (Pearson and Anderson, 1993) and theoretical results in the whole spatial domain. ($x_0 = 1.36$, $\alpha_N = 4.15$, $M = 10$, $q_M \equiv 4$). Further details are shown elsewhere (Mezzasalma, 2006).

lation peaks, should thus correspond. On this basis, the self-correlation function:

$$G_{S,N}(\rho, M) = \mathcal{G}_0(\rho) + \mathcal{H}_M(\rho) \tag{4.49}$$

was applied to a true self-avoiding walk polymer at different scales, and the results are shown by Fig. 4.1 ($\rho = 0.64\, r/l$) and Fig. 4.3 ($\rho = 10\, r/l$). The former shows that the Gaussian term ($G_{S,N} \simeq \mathcal{G}_0$) can reconstruct the real chain behavior near the origin ($< 2.5{\cdot}10^{-2}$) and the ground perturbation $G_{S,N}(\rho, 0)$ can reproduce the first oscillation ($< 1.6{\cdot}10^{-1}$). The latter shows the best fit in the whole spatial domain, rescaling the first $M = 10$ molecular shells and using an even polynomial ($p_M$) with linear term retained.

We conclude this section by a couple of general considerations, useful in view of future developments. First remember that, in interacting and concentrated systems, an error source may come from the neglect of time and wavevector dependences in the diffusion coefficient. Close to the retardation kernel in Langevin's generalized formalism, a (dynamic) self-diffusion propagator should generally obey a memory function equation, and describe the departure from the free Brownian motion. Also, the distinction between short-time and long-time self-diffusion regimes can be exploited. The former is known to be indicative of the time required to cross two adjacent minima of the energy function, "felt" by the tracer, and determined by the (host) liquid molecules. With an increasing number of potential barriers, before the asymptotic regime, the self-diffusion coefficient may generally evolve with time. As to the fluctuations of liquid molecules, their collective diffusion indicates another "interaction scale," over which the energy function fluctuates too. Among the other aspects, which an enlarged analysis should account for, are then the connections with statistical thermodynamics. For example, the initial slope of a time-dependent diffusion coefficient is related to the spring constant of the (harmonic) potential felt by the Brownian particle at short times, resulting into a further constraint for the pairwise potential and the radial distribution function.

In a second remark, we note that inverting Vineyard's convolution approximation possesses some analogies with the so-called "scattering inverse problem," where a scattered radiation is used to study the scatterers (and the radiation before scattering). Since different distributions of scattering centers (microstructures) can produce identical patterns (e.g., radial distribution functions), the solution is not generally unique. The knowledge of additional information becomes mandatory to select among a multiplicity of possible models (here, the chain self-avoidance and the long wavelength fluctuations). These remarks get our problem close to a scattering experiment, the liquid density giving itself the radiation source in the form of "correlation waves," scattered geometrically by the macromolecule.

# 3. FROM MACROMOLECULE TO MOLECULE: TURBULENCE IN LIQUIDS

## 3.1 Fluid turbulence and Brownian relativity

The field of (developed) turbulence should not be confused with the time-dependent ("non-deterministic") chaos in dynamic systems. It arises in spatially extended systems, in which an infinite number of degrees of freedom come into play. This situation is suitable for Brownian relativity, where the random molecular motion in a turbulent fluid should be regained from a simpler statistical mechanics analysis of chain conformations. Our thesis is going to be supported by dealing with a turbulently advected passive scalar in terms of the partition function of a polymer network of a given topology.

A correspondence between Alexandre J. Chorin and Robert H. Kraichnan (1988) shows that the effectiveness of polymer representations in the statistical theory of fluid turbulence has already been argued. The major problem, however, is that such analogies would mostly consist of technical expedients, not so much involved and sometimes conflicting with the physical model. For instance, in the 3-dimensional and incompressible fluid turbulence, a universal relation between fractal dimension ($D_H$) and the inertial exponent ($\gamma_i$), characterizing the energy spectrum in the "inertial range," $E(q) \sim q^{-\gamma_i}$, has been proposed. This domain is formed by values ($\sim q^{-1}$) which are small in comparison to those on which the fluid is stirred ($\ell$), but large compared to typical dissipation scales ($\ell_d$). Vortex stretching produces an energy cascade from large to small scales, the so-called inertial-range cascade pioneered by Kolmogorov (1941). Polymers were thought here as being analogous to vortex tubes, and their critical exponents at thermal equilibrium compared to inertial exponents in the turbulence of fluids. It was noted, however, that this analogy had the effect of restricting the support of the "vorticity" ($\vec{\nabla} \wedge \mathbf{v}$), making it possible, in principle, to state relations outside the Navier–Stokes dynamics. Suitable counter-examples can prove in fact that $\gamma_i$ and $D_H$ are independent under kinematic constraints, and their relationship is actually undetermined. On this ground, it was also conjectured that the equality of Kolmogorov's exponent with the reciprocal of Flory's ($\gamma_K = 1/\nu_F = 5/3$), for the average size of a self-avoiding walk polymer, would not be a coincidence. The (heuristic) argument relied in this case on the conservation of a quantity known as "helicity" ($\int \mathbf{v} \cdot (\vec{\nabla} \wedge \mathbf{v})\, d\mathbf{r}$), which in fluids is the formal analogue of self-avoidance in polymers. This constraint, completing the conditions of energy conservation and Kelvin's circulation theorem, would set the vortex tubes to be significantly correlated on Flory's radius scale.

With the aim of proposing an alternative, more "physical" prospect to research on turbulence in liquids by polymer scaling and conformational statistics, consider a homogeneous and isotropic simple liquid at thermal equilibrium, with Van Hove's function $G_1 = G_1(\mathbf{r}', t')$. When a single coil is immersed in the liquid, a dilute polymer solution is formed, and the covariant Van Hove's function applies. We expect that, for some common scale ($\mathbf{R}$) and large $N$ values:

$$G_N(\mathbf{R}) \sim G_1\big(\mathbf{R}, t'(N)\big) \tag{4.50}$$

the polymer chain would act as a scale transformation, "collecting" all correlations of the liquid molecules into itself. It may be worth expliciting the simplest, unperturbed case, where Van Hove's function of an ideal chain stems from the hydrodynamic limit of a free Brownian particle:

$$G_N\big(\mathbf{r}'' = \mathbf{R}\big) = G_1\big(\mathbf{r}' = \mathbf{R},\ t' = N\big) \tag{4.51}$$

with $\frac{r''}{l\sqrt{N}} = \frac{r'}{\sqrt{6Dt'}}$ ($h_1(\mathbf{r}') = h_N(\mathbf{r}'') \equiv 0$). The normal distribution is here statistically preserved, i.e.:

$$\left(\frac{\partial G_1}{\partial t'}\right) = D\vec{\nabla}^2 G_1\big(\mathbf{r}', t'\big) \tag{4.52}$$

and, specularly, for the random conformation developed in space by an ideal chain:

$$\left(\frac{\partial G_N}{\partial t''}\right) = \frac{l^2}{6}\vec{\nabla}^2 G_N\big(\mathbf{r}'', t''\big) \tag{4.53}$$

where the "monomer diffusion coefficient" ($l^2/6$) ensures that Einstein's two laws correspond ($\overline{\mathbf{r}'^2(t)} = 6Dt'$ and $\overline{\mathbf{r}''^2(N)} = Nl^2$).

In the presence of correlations, Vineyard's covariant approximation implies a "gauge-like" extension of the form:

$$G_K \to G_K + h_K \otimes G_K \tag{4.54}$$

that we have seen to preserve the statistics of correlated ensembles, simplifying their description to a certain extent. Now, imagine that the host liquid ceases to be in thermo-mechanical equilibrium. When the onset of turbulence is reached, and a polymer chain is put subsequently in the turbulent flow, the above covariant scheme should not modify. If the fluid is modeled as a Brownian–relativistic medium, being at rest, in motion or turbulent, is not expected to have any influence on the statistical constraint implied by the diffusive Lorentz–Poincaré symmetry. Brownian relativity, and so as the covariant probability conservations, should hold regardless of the velocity field which the macromolecule diffuses across. This suggests an important working hypothesis to be examined at least in the simplest case of homogeneous and isotropic velocity fields, whose dynamics is kept decoupled from the statistical quantity of interest. It belongs to the study of passive scalar advection, briefly outlined in the next paragraph.

## 3.2 Passive scalar advection and intermittency (Notes)

The model introduced by Kraichnan (1994), for a turbulently advected scalar, involves a stochastic advection-diffusion equation for a scalar fluctuation field $\phi = \phi(\mathbf{r}, t)$:

$$\left(\frac{D\phi}{Dt}\right) = \kappa \vec{\nabla}^2 \phi(\mathbf{r}, t) \tag{4.55}$$

where $\kappa$ is a molecular diffusivity, $\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}(\mathbf{r}, t) \cdot \vec{\nabla}$ is the Lagrangian derivative and the stochastic velocity models a solenoidal flow, obeying the incompressible fluid condition ($\vec{\nabla} \cdot \mathbf{v} = 0$). In principle, the scalar field may either refer to the concentration of a contaminant (a solute) or temperature. However, while the former would affect velocity through the buoyancy forces, and be an active scalar, the latter is a passive scalar, meaning that $\phi$ does not couple to the dynamics of $\mathbf{v}$ and the last equation is linear in it. Kraichnan's starting point was the theory of Batchelor (1959) for a convected scalar field, in which the advecting velocity represents a "synthetic turbulence." It is a Gaussian random field that, again, is homogeneous, isotropic, stationary, white-in-time, with zero mean and covariance $\overline{v_s(\mathbf{r}, t) v_{s'}(\mathbf{r}', t')} = D_{ss'}(\mathbf{r} - \mathbf{r}')\delta(t - t')$. Furthermore, an external fluctuation source can be added to keep the system in a statistically steady state. It is the "forcing" and, in Kraichnan's theory, still consists of a white and Gaussian random field with zero mean. Its covariance acts only on the largest scales of the outer length ($\ell$) and is negligible in the inertial domain.

This model is exactly solvable. Closed equations exist for any $n$-point correlation function at equal times, $\Phi_n(\mathbf{r}_1, \dots, \mathbf{r}_n; t) = \overline{\phi(\mathbf{r}_1, t) \dots \phi(\mathbf{r}_n, t)}$, the average being performed over the homogeneous and isotropic statistics of both the advecting and forcing fields. Another remarkable property is its "anomalous scaling" behavior. Anomalous means here, unpredictable from dimensional (or mean-field) arguments, such as those pioneered by Kolmogorov. In the special case of stationary forcing, multipoint correlators are time-independent, and anomalous scaling laws equal to ask that the exponents ($z_n$) taking part in the transformation, $\Phi_n(\lambda\mathbf{r}_1, \dots, \lambda\mathbf{r}_n) = \lambda^{z_n}\Phi_n(\mathbf{r}_1, \dots, \mathbf{r}_n)$, are non-trivially depending on $n$.

Kraichnan's approach became thus the subject of extensive studies, especially focused on the inertial-convective range. It concerns very small molecular diffusivities and power-law correlations for velocity increments:

$$D_{ss'}(\mathbf{r}) - D_{ss'}(\mathbf{0}) \propto r^{\xi}\left[\delta_{ss'} + \frac{\xi}{d-1}\left(\delta_{ss'} - \frac{r_s r_{s'}}{r^2}\right)\right] + \mathrm{O}\left(\frac{r}{\ell}\right)^2 \tag{4.56}$$

where $\xi \in (0,2)$ is the velocity scaling exponent and $\ell$ ($\gg r$) is the "injection scale." Kraichnan derived the scaling exponents ($\zeta_n$) of the structure function ($\mathrm{S}_{n\phi}$) for a passive scalar:

$$\mathrm{S}_{n\phi}(r) \doteq \left\langle \left| \phi(\mathbf{r}+\mathbf{r}',t) - \phi(\mathbf{r}',t) \right|^n \right\rangle \tag{4.57}$$

at any integer order ($n$), for any space dimensionality ($d$) and velocity scaling exponent ($\xi$). He resorted to a "linear ansatz" for dissipation terms in the starting motion equation, approximating the molecular diffusivity contributions. In short, if one assumes a power-law inertial-range scaling of the form:

$$\mathrm{S}_{n\phi}(r) \sim \left(\frac{r}{\ell}\right)^{\zeta_n} \tag{4.58}$$

with $\ell \gg r \gg \ell_d$ (dissipation scale), then the scaling exponents ($\zeta_n$) turn out to fulfill the inequality $n\zeta_2 > \zeta_{2n}$ ($n > 2$) where $\zeta_n \sim \sqrt{n\, d\zeta_2}$ as $n \to \infty$. This violates the normal behavior expected from mean-field arguments (remember Hölder's relation, $n\zeta_2 = \zeta_{2n}$) and brought to conjecture an intrinsic "intermittency." Formally, when a system is intermittent, the flatness factor of scalar increments is scale-dependent, and growing as:

$$\mathrm{F}_{n\phi}(r) \sim \left(\frac{r}{\ell}\right)^{-\sigma_{2n}} \tag{4.59}$$

with $\sigma_{2n} = \zeta_{2n} - n\zeta_2$. Flows thus become more and more spotty with decreasing scale ($r \to 0$). Particularly, in Kraichnan's ansatz, intermittencies are supposed not to cumulate during the energy cascade, but to fully relax through the spatial smearing driven by diffusion. Here, we set out to explain the last two relationships on a Brownian relativity basis.

## 3.3 Polymer topology and turbulence statistics

Before dealing with passive scalar advection, a couple of considerations are in order. The first concerns the relationship between Eulerian and Lagrangian points of view. The former describes the motion at fixed position in the fluid, and considers the time-dependent velocity field, while the latter describes it along the trajectories followed by each fluid particle. The Eulerian time derivative is so a particular case ($\mathbf{v} = \mathbf{0}$) of Lagrangian's ($\frac{D}{Dt} = \frac{\partial}{\partial t}$). The additional, non-linear operator ($\mathbf{v} \cdot \nabla$) denotes the advective part of the total time differentiation, and is responsible for the richness and complexity of the fluid motion. Besides the equivalence of these views, and that the geometric approach by Vladimir I. Arnol'd (1966) could shed new light on that Lagrangian, different equation forms and notions of instability are implied.

In a Brownian–relativistic spacetime, the statistical description linked to Eulerian and Lagrangian frames will be equivalent as well, and left invariant upon changing flow. Due to the strict relation set in Brownian relativity between liquid and polymer scales, the random velocity will act nearly as a gauge field. This (apparent) freedom comes from the relativistic view on Brownian movement, and obviously disappears with it. We know, to mention an example, that interactions-at-a-distance are not allowed in special relativity by the second postulate for the constancy of the light speed. This restriction, on the other hand, connects space and time more in depth, giving rise to new kinematic relationships. Something similar happens in Brownian relativity, where the effect of velocity is not neglected in itself, but only relative to different (Brownian) observers.

Again, this equivalence must be regarded in light of the other, among static and dynamic random paths, and of the Brownian equivalence principle for geometry and statistics. Accordingly, the statistics of molecular paths in a turbulent flow will be described here by the "statistical mechanics of polymer networks of any topology." In inverted commas, the title of a famous work by Bertrand Duplantier (1989) is reported, some results of which being exploited in the following in support of the central insight advanced in this study, "seeking which polymer topology is statistically equivalent to turbulence statistics."

That said, our calculation will consist of (i) choosing the simplest "gauge" ($\mathbf{v} \to \mathbf{0}$), working out (ii) the structure function ($\mathrm{S}_{nN}$) for a chain long $N$ and (iii) the equality $\mathrm{S}_{n1} = \mathrm{S}_{nN}$, shared at some common scale upon $N \to \infty$. Concerning the first point, the elementary condition $\mathbf{v} = \mathbf{0}$ restricts in Brownian relativity the class of solenoidal velocity fields ($\vec{\nabla} \cdot \mathbf{v} = 0$) to a "static" problem, linearizing the motion equation. In the second step, one translates $\phi$ into some polymer distribution (or partition) function, and calculates the structure function thereof by including segment correlations. The third step follows from identifying the liquid and chain structure functions in the thermodynamic limit, where equal (Brownian–relativistic) times ($t'$) will correspond to equal segment numbers ($N$). Averaging will be performed over a polymer network of given "shape" (or topology) and "extension" (or length scale), as next shown in the general case of star polymers.

## 3.4 Brownian–relativistic anomalous exponents

In cases like these, the simplest assumption is often the most general, and one can choose the topology generated by star polymers. They have an idealized structure, far simpler than in almost all branched polymers, and are formed by linear chain molecules (the arms or branches), attached with one end to the common branch point, near which stars form a melt-like common core region. Obviously, once the unit number $N$ (here, per chain) is large enough, cores become negligibly smaller than the whole chain size. Another relevant quantity is the functionality ($f$), specifying the number of arms departing from the branch point. When they possess the same chemical length, star polymers are said to be uniform.

We will therefore translate the structure function, for a uniform star polymer network, in Brownian relativity. The idea goes similarly to a convenient change of reference frames, from a pair of moving point-like liquid units, to a static star-like chain. It will only be necessary to recall the universal quantities involved in our calculation, that is, the average chain size and, specially, the partition function ($\mathcal{Z}$), providing the chain configuration numbers. As to the solvent quality, we will refer to the general situation of a real chain, swelling in a good solvent up to one Flory's radius (i.e., a factor of order unity). What matters, however, is mostly the existence of well defined critical exponents, and this is guaranteed by the polymer scaling theory and its relation, unveiled by de Gennes (1972), with the $n$-component spin model for magnetic systems in the (unphysical) $n \to 0$ limit. When no pair of chain portions intersect the same spatial point, linear polymer models ($f = 2$) are recovered upon $n \to 0$. By removing this constraint, a random walk chain is regained in the $n = -2$ limit. In the original formulation, by H.E. Stanley (1968–1974), every site ($m$) of a lattice brings a spin vector ($\mathbf{s}$) in $n$ dimensions, defining an isotropic distribution of independent random variables with $\mathbf{s}^2(m) = n$. The Hamiltonian for this model formally resembles Heisemberg's, for the ferromagnetism, or more popular Ising's, after which one can easily write the partition function and proceed with deriving the scaling laws for the critical exponents (e.g., Fisher's, Rushbrooke's, Josephson's or Widom's) from opportune scaling arguments.

In the $n \to 0$ limit, the trick is taking the "analytic continuations" (from natural to positive real $n$) of suitable thermodynamic functions. Despite this conjecture is more formal than rigorous, the analogy between spin vector ensembles and monomer vectors in a polymer conformation are rather evident. They are entropic systems driven by local random movements of each component. Furthermore, the magnetic analogy has been strikingly productive. For non-zero applied (magnetic) fields, the $n$-vector model corresponds in de Gennes's limit to a chain performing a simultaneous random walk in a solution at finite concentration. This analogy, between semidilute polymer solutions and ferromagnets under external fields was discovered by Jacques des Cloizeaux (1975), explaining why such systems strongly deviate from mean-field predictions. It is worth to stress that these advancements were made possible by parallel experimental progresses, as the labeling technique devised by Jean P. Cotton (1973). He replaced chain hydrogen with deuterium atoms and could focus on single polymers in solution by small-angle neutron scattering experiments.

The partition sum for a linear chain of length $L \sim N$ scales as $\mathcal{Z}_1 \sim z^N N^{\gamma-1}$, that is, by a geometrical fugacity constant ($z$) and a non-trivial "enhancement" exponent ($\gamma - 1$). The former, non-universal, accounts for the number of ways of adding one more segment to the chain (with lattice-dependent chemical potential $\ln z$). The latter, universal, includes the (long-range) self-avoidance interactions along the chain. For a lattice of sites with no excluded volume, it turns out in fact that $\mathcal{Z}_1 = \sum_{\{\mathbf{r}\}} Z_N(\mathbf{r}) = z^N$, where $Z_N(\mathbf{r})$ denotes the number of walks connecting the origin to $\mathbf{r}$ in $N$ steps, and the sum is over sites of coordination number $z$. In the language of Van Hove's covariant function, the annulments of the enhancement exponent and the total correlation function correspond here as:

$$G_N(h_N = 0) = \frac{Z_N(\mathbf{r})}{\mathcal{Z}_1} = W_N(\mathbf{r}) \tag{4.60}$$

otherwise, with long-range correlations, one gets back to the "statistical gauge" transformation and the enhancing contribution ($N^{\gamma-1}$) in $\mathcal{Z}_1$.

In an arbitrary topological system of branched, self-avoiding walk polymers, it is known that new "anomalous" critical exponents arise. They follow from the physical branching of all polymers tied together, and are usually evaluated by numerical computations and perturbative techniques. For star polymers, the configuration number may be written by two families of exponents, $\gamma_f$ and $\eta_f$:

$$\mathcal{Z}_f \sim z^{Nf} N^{\gamma_f - 1} \sim \left(\frac{R_F}{\ell}\right)^{\eta_f - f\eta_2} \tag{4.61}$$

where the power law for Flory's chain size is unchanged. The family $\eta_f$ is introduced by requiring $\gamma_f - 1 = \nu(\eta_f - f\eta_2)$ and that the stars with $f = 1, 2$ are linear chains ($\gamma_1 = \gamma_2 = \gamma$, or $\eta_1 = 0$, $\eta_2 = \frac{1-\gamma}{\nu}$). Passive structure and star polymer scaling behaviors ($\zeta_n$ and $\eta_f$) will now be described as a couple of Brownianly covariant laws. Each of the two will be intended to be the counterpart of the other, coming across as the same physical phenomenon at different scales.

## 3.5 Passive structure exponents and (star) polymer configurations

The first similarity between intermittency and polymer problems lies into a close decomposition of their anomalous exponents. We have seen in fact that the two deviations from ideality are expressed by a similar violation of a normal scaling condition. In the former section, polymer excluded volume and short-scale repulsion of liquid molecules were already proposed to stand for a unique phenomenon, "split" into a pair of (seemingly) distinct phenomenologies by distinct Brownian-like observations. Alongside, the short-scale behavior of structure functions would come across as having the same topological roots of self-avoiding star configurations. For the scaling behavior of passive structure exponents to be non-anomalous, self-contacting star polymers should (ideally) be non-repelling. If intermittency in passive scalar advection arises with close necessity to the excluded volume in real polymer systems, its properties should be regained from a Brownian–relativistic treatation of macromolecular conformations and internal molecular motions at Flory's radius scale. We have not yet reached a formalism for arbitrary correlations but may anyway afford a semiheuristic analysis under the special gauge of a vanishing velocity field.

The starting point is that the polymer partition sum will generalize into that induced by the structure function ($\mathcal{Z}_f \to \mathrm{S}_{mf}$) and, to this end, one may consider a probability distribution scaling as $dP(\lambda' = \frac{r}{\ell}; f) \sim d[\lambda'^{\mu_f}]$. It gives the number density of configurations in any domain $L_F \subseteq [l_\ell, \Lambda_F]$, bounded from below by Kuhn's statistical segment $l_\ell$ ($=l/\ell$) and from above by Flory's size $\Lambda_F$ ($=R_F/\ell$). The lowermost acts here as a statistical cutoff, negligibly contributing to the following scaling analysis. Thus, one is left with:

$$\mathrm{S}_{mf} = \overline{\left|\left(\lambda' + \Lambda\right)^{\mu_f} - \lambda'^{\mu_f}\right|^m}^{(P,L)} \tag{4.62}$$

where $\mathrm{S}_{mf} = \mathrm{S}_{mf}(\lambda, \Lambda)$ and $\overline{\cdots}^{(P,L)} = \int_{\mathrm{L}} \ldots dP(\lambda'; f)$ and any length is in the outer length unit. In particular, $\Lambda$ stands for a common scale, while $\mathrm{L} = [l_\ell, \lambda]$, with $\lambda \in (l_\ell, \Lambda_F]$ and $0 < l_\ell \ll \lambda$, $\Lambda \ll \Lambda_F \ll 1$. When $\mu_f > 0$, the last equation lends itself to a suitable approximation. Expanding the integrand in Newton's binomial series, gives us:

$$\mathrm{S}_{mf} = \sum_{i=0}^{m} (-1)^i \binom{m}{i} \overline{\lambda'^{\mu_f i} \left(\lambda' + \Lambda\right)^{\mu_f (m-i)}}^{(P,L)} \tag{4.63}$$

which can be rewritten in compact form as:

$$\mathrm{S}_{mf} = \left(\Lambda^m \lambda\right)^{\mu_f} \Xi_m(f,u) + \text{const} \tag{4.64}$$

where:

$$\frac{\Xi_m(f,u)}{m!} = \sum_{i=0}^{m} (-1)^i \frac{u^{\mu_f i}}{(1+i)!(m-i)!} F(\alpha_i, \alpha_{i-m}; \alpha_i + 1; -u) \tag{4.65}$$

and $F$ is a hypergeometric function of $u = \frac{\lambda}{\Lambda}$, with $\alpha_k = (k+1)\mu_f$ ($k \in \mathrm{N}$). It generalizes $\mathcal{Z}_f$ to a pair of length scales ($\lambda$, $\Lambda$) and "modes" ($m$, $f$), extending the trivial lowest contribution ($m = 0$) to any higher order ($m > 0$). In fact, $\forall \lambda = \Lambda \in (l_\ell, \Lambda_F]$, one has $\Xi_0(f,u) = F(\mu_f, 0; \mu_f{+}1; -u) = 1$ and $\mathrm{S}_{0f} \sim \lambda^{\mu_f}$. Otherwise, for any integer $m > 0$, polymer statics will be "distorced" according to a new partition sum.

A relevant case arises when $m$ tends to large values (i.e., an infinite series). For $\alpha_{|i-m|} \gg 1$, $F$ can be approximated to a confluent hypergeometric function ($\Phi$) of $x = mu$:

$$F(\alpha_i, \alpha_{i-m} \sim \alpha_{-m}; \alpha_i + 1; -u) \sim \Phi(\alpha_i; \alpha_i + 1; \mu_f x) \tag{4.66}$$

and Stirling's approximation $k! \sim \sqrt{2\pi k}(\frac{k}{e})^k$ in each factorial of $m$ gives:

$$\Xi_{m\gg 1}(f,u) \to \widetilde{\Xi}(f,u) \sim \sum_{i=0}^{\infty} (-1)^i \frac{m^i u^{i\mu_f} \mathrm{e}^{-i}}{(i+1)!} \Phi(\alpha_i; \alpha_i + 1; m\mu_f u) \tag{4.67}$$

To get and handle a closed-form equation, we may expand $\Phi$ in Taylor's series centered at the origin. By doing so, the polymer structure function can be evaluated at various orders $\mathrm{O}(x^j)$:

$$\mathrm{S}_{mf} \sim \left(\Lambda^m \lambda\right)^{\mu_f} \widetilde{\Xi}_j(f,x) \tag{4.68}$$

with:

$$\widetilde{\Xi}_j(f,x) = \sum_{k=0}^{j} \frac{a_k}{k!} (\mu_f x)^k \to \widetilde{\Xi}(f, \mu_f x) \tag{4.69}$$

Coefficients converge to a "lower incomplete gamma function" ($\widehat{\boldsymbol{\gamma}}$) of $y = \frac{mu^{\mu_f}}{\mathrm{e}}$:

$$a_k = \sum_{i=0}^{\infty} (-1)^i \frac{y^i}{(i+1)!(1+\frac{k}{\alpha_i})} = y^{-\frac{k}{\mu_f}-1} \widehat{\boldsymbol{\gamma}}(1 + k/\mu_f, y) \tag{4.70}$$

so that the following representation holds:

$$\mathrm{S}_{mf} \sim \frac{\Lambda^{\mu_f m}}{m} \sum_{k=0}^{j-1} \frac{\chi^k}{k!} \widehat{\boldsymbol{\gamma}}(1 + k/\mu_f, y) + \mathrm{O}\left(\chi^j\right) \tag{4.71}$$

We will limit ourselves to $\mu_f < 1$, for which $\chi(m \gg 1) = m\mu_f(\frac{\mathrm{e}}{m})^{\frac{1}{\mu_f}} \to 0$ independently of $u$, and seek if the polymer exponent converges to an average value of the form:

$$\tau_f = \lim_{m\to\infty} \frac{1}{m}\left(\frac{\partial \ln \mathrm{S}_{mf}}{\partial \ln u}\right) \tag{4.72}$$

By starting from $\mathrm{S}_{mf}$ at first order in $\chi$, and expanding its logarithm:

$$\ln \mathrm{S}_{mf} = -\ln m + \mu_f m \ln \Lambda + \ln \widehat{\boldsymbol{\gamma}}(1,y) + \frac{\widehat{\boldsymbol{\gamma}}(1+\frac{1}{\mu_f},y)}{\widehat{\boldsymbol{\gamma}}(1,y)}\chi + \mathrm{O}\big(\chi^2\big) \tag{4.73}$$

some algebraic developments yield:

$$\frac{1}{m\mu_f}\left(\frac{\partial \ln \mathrm{S}_{mf}}{\partial \ln u}\right) = \left(\frac{\partial \ln \Lambda}{\partial \ln u}\right)_\lambda + \frac{u^{\mu_f}}{\mathrm{e}}\left[-\frac{1+\mu_f m u}{\widehat{\boldsymbol{\gamma}}(1,-y)} + \frac{\widehat{\boldsymbol{\gamma}}(1+\frac{1}{\mu_f},y)}{\widehat{\boldsymbol{\gamma}}(1,y)\widehat{\boldsymbol{\gamma}}(1,-y)}\chi\right] \tag{4.74}$$

which, as $\widehat{\boldsymbol{\gamma}}(1,y) = 1 - \mathrm{e}^{-y}$, returns:

$$\mathrm{e}u^{-\mu_f}\left(\frac{\tau_f}{\mu_f}+1\right) = \frac{1+\mu_f m u}{\mathrm{e}^y - 1} - \frac{\widehat{\boldsymbol{\gamma}}\big(1+\frac{1}{\mu_f},y\big)}{\cosh y - 1}\frac{\chi}{2} \tag{4.75}$$

Hence, approximating each sum by its leading term, with $y \simeq \frac{m\bar{u}^{\mu_f}}{\mathrm{e}}$:

$$\widehat{\boldsymbol{\gamma}}(1,-y) = \sum_{n=1}^{\infty}\frac{y^n}{n!} \tag{4.76}$$

$$\cosh y = \sum_{n=1}^{\infty}\frac{y^{2n}}{(2n)!} \tag{4.77}$$

$$\widehat{\boldsymbol{\gamma}}(1+1/\mu_f,y) = \sum_{n=0}^{\infty}\frac{(-1)^n y^{n+1+\frac{1}{\mu_f}}}{n!(n+1+\frac{1}{\mu_f})} \tag{4.78}$$

one arrives at generalizing $\mu_f$ to:

$$\tau_f = \mu_f\left(\bar{u}\frac{\mu_f}{1+\mu_f} - 1\right) \tag{4.79}$$

The parameter $\bar{u}$ denotes a (mean) coupling correction, due to changing scale along polymer branches. Do not forget the above calculations rely on $\chi \ll y$, which is equivalent to ask:

$$\bar{u} \gg m^{-\frac{1}{\mu_f^2}}, \qquad \mu_f \in [0,1) \tag{4.80}$$

To assign the formalism a physical significance, one may set $\Lambda$ to bound a local region characterized by isolated chain statistics. For instance, in swollen conditions, each branch may be described by a self-avoiding walk of statistically independent blobs. A second physical identification is between the polymer function order and the arm monomer number ($m = N$). We come in this way to the scheme of

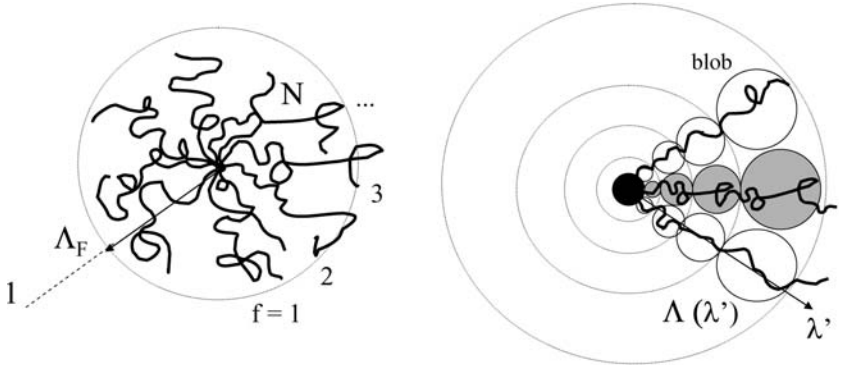

**Figure 4.4** Star polymer and blob model in the Daoud–Cotton picture ($f = 10$).

Fig. 4.4, to be regarded with $\mu_f < 1$ and provided the condition $\ln N \gg -\mu_f^2 \ln \bar{u}$ is sufficient to enter the scaling domain. From the renormalization group approach, $\mu_f \in [0, 1)$ both when $f \leqslant 3$ ($\eta_1 = 0$, $\eta_2 \simeq -0.28$, $\eta_3 = -0.75$) and the most accurate perturbative result ($\nu \simeq 0.588$) is used in place of $\nu_F$ ($= 0.6$).

The relation for $\tau_f$ can thus be exploited to describe intermittency in passive scalar advection. Accordingly, the transformed exponents of the flatness factor, $\sigma_{2f} = \tau_{2f} - f\tau_2$, read:

$$\sigma_{2f} = \left(1 - \bar{u}\frac{\mu_2}{1+\mu_2}\right)\mu_2 f - \left(1 - \bar{u}\frac{\mu_{2f}}{1+\mu_{2f}}\right)\mu_{2f} \tag{4.81}$$

where $\mu_f = \nu(\eta_f - f\eta_2)$ follows from Duplantier's results on self-contacting exponents, $\eta_f \simeq -Af(\sqrt{f}-1)$ and $A = 5/[36(\sqrt{2}-1)]$. In particular, $\eta_2 = (1-\gamma)/\nu$, a result first pioneered by des Cloizeaux (1974) for single linear chains. Exploiting these relations for a 3-dimensional network ($\nu_F = \frac{3}{5}$, $\gamma = \frac{7}{6}$) returns:

$$\mu_f \simeq \widetilde{\mu}(f) = -\frac{1}{3}\left(1 + \frac{1}{\sqrt{2}}\right)f^{\frac{3}{2}} + \frac{1}{2}\left(1 + \frac{\sqrt{2}}{3}\right)f \tag{4.82}$$

from which $\sigma_{2f} = \tau_{2f} - f\tau_2$ can be determined, i.e.:

$$\sigma_{2f} = \left(\frac{1}{6} - \frac{\bar{u}}{42}\right)f - \left[(1-\bar{u})\widetilde{\mu} + 1\right]\frac{\widetilde{\mu}}{\widetilde{\mu}+1} \tag{4.83}$$

and the linear coefficient expliciting:

$$\tau_2 = \left(1 - \gamma^{-1}\right)\left[\bar{u} + \gamma(1-\bar{u})\right] \tag{4.84}$$

To make interpolations more severe, all polymer features were set to their exact numerical values, and $\bar{u}$ interpreted by the blob model. Limiting ourselves to the scaling theory by Mohamed Daoud and Cotton (1982), at a given distance (λ) from the core there are $f$ blobs, one per each polymer chain and forming a succession of concentric shells. Because they cover a sphere of radius λ, distance and blob radius

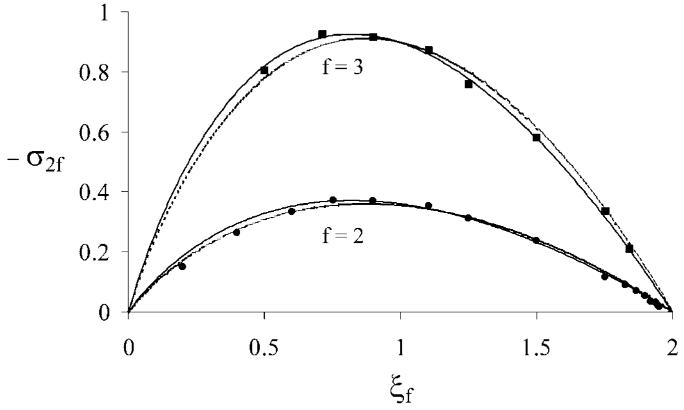

**Figure 4.5** Anomalous structure function exponents (Mazzino and Muratore-Ginanneschi, 2000) interpreted as anomalous star polymer exponents.

will stand in the ratio $\bar{u} = \frac{\lambda}{\Lambda(\lambda)} \simeq \sqrt{f}$. Otherwise, the coupling term can be set to a heuristic parameter, valid in all the experiment domain and independent of $f$.

Regarding the velocity scaling exponent ($\xi$), it is out of a direct counterpart in polymer statics. One can make again the simplest choice, and reparametrize $f$ into a continuous variable, $f \rightarrow c\xi_f$, still in $\xi_f \in (0, 2)$ (here we could equally work in $[0, 2]$) and for some scale factor ($c$). It fixes the (maximum) separation distance along a linear chain in the network, and can be set to $c = \frac{1}{2}$ (i.e., one polymer branch). Accordingly, the above semiheuristic equation takes the form:

$$\sigma_{2f} \propto \frac{1}{12}\left(1 - \frac{\bar{u}}{7}\right)\xi_f + \left[(\bar{u} - 1)\widetilde{\mu} - 1\right]\frac{\widetilde{\mu}}{\widetilde{\mu} + 1} \tag{4.85}$$

with:

$$\widetilde{\mu}(\xi_f) = -\frac{1}{6\sqrt{2}}\left(1 + \frac{1}{\sqrt{2}}\right)\xi_f^{\frac{3}{2}} + \frac{1}{4}\left(1 + \frac{\sqrt{2}}{3}\right)\xi_f \tag{4.86}$$

Though the approximation degree may be certainly improved, such relationships point out a universal law for turbulence statistics in a (star) polymer representation. Our aim, however, is mainly to reproduce the anomalous behavior of passive structure exponents at Flory's scale. Thus, with no lack of generality, a homogeneous proportionality forefactor has been introduced. Fig. 4.5 reports best fits and numerical coefficients extrapolated when the anomalies at $f = 2$ and $f = 3$ are described by earlier numerical data (Mazzino and Muratore-Ginanneschi, 2000) for $\sigma_{2n}$ vs $\xi$ at fourth ($n = 2$) and sixth ($n = 3$) orders. For comparison, curves using a result from Daoud–Cotton's theory, $\bar{u}^2 \sim \xi_f/2$, were superimposed to those at constant coupling term (dotted lines, $\bar{u} = 0.2$), adopting in either cases also the same forefactors (4.4, $f = 2$ and 8.5, $f = 3$). The formers are less precise in $\xi_f \in [0, 1)$, where $\bar{u}$ is taking the largest values, but the found universal function is satisfactory in both cases.

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CHAPTER FIVE

# FUNDAMENTAL IDEAS FOR A SHAPE MECHANICS

## Contents

The role played in science by geometry is generally superior to topology, and one reason is certainly due to the mathematical status of such disciplines. Topology is a modern but qualitative version of geometry, which only recognizes the continuity properties of figures. A topologist does not look into the extension of volumes and surfaces, but those features that remain unchanged under particular transformations, just called topological. Formally, they can be described as one-to-one mappings of a surface onto itself, in such a way that the image of any continuous curve on it is a continuous curve too. Conceptually, as figure deformations by arbitrary distortions of the plane, conceived as it were some elastic sheet. It is therefore no surprise that, while the extensions of bodies and spaces were thoroughly accounted for, shape has not been regarded so much in itself. The relative arrangement taken by any

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particle ensemble comes in addition from the involved interaction potentials and the mechanical theory in which they act. Thus, while the relevance of geometry in natural phenomena was carefully deepened, as already witnessed by classical field theory, the quest for a "physical" approach to forms or shapes has never been started.

It is a conviction of this author that topology and geometry of shapes may be a source instead of autonomous physical principles and an own phenomenology. The search for a more general statistical theory of forms and shapes lays partly in the roots of the former theory of Brownian relativity, which reformulates the basic laws of statistics into the same geometrical assessment of mechanics. To make an example, imagine that a shape in two or three dimensions (e.g., polyhedral) characterizes some distribution of matter, such as an electron (orbital), atom or molecule specify the geometrical arrangements taken on by their elementary constituents. Several questions could be asked about a mechanical theory of forms and shapes. Is there any law of nature ruling shapes in themselves? Is there any "physical" law, by which they can get and govern larger or smaller scales?

Aside from the former scaling pictures, in the monomer number and probability, another universal mechanism has already been introduced with the name of "geometrical scaling." Rather than counting over the monomer number only, polymer configurations can be conceived as shapes, carrying a statistical information that scales geometrically from the characteristic length of its monomeric unit. Similarly to Brownian relativity, what is geometrical at small (molecular) scales would get statistical at larger ($n$-molecular) scales. The length scale increase, to pass from monomer to polymer molecules, would "distorce" the repeat unit shape into some "average" macromolecular configuration, as some images that are optically out of focus reproduce only approximately an original picture or a real object.

In this chapter, we start to discuss and elaborate some ideas for a statistical theory of shapes, named hereinafter "shape mechanics" and aimed at describing how a "shape," defined for instance at some microscopic level, may "Brownianly diffuse" up to larger spacetime scales. To be very sketchy, it will consist of a mechanical formalism endowed with Brownian relativity concepts. We wish also to stress that the following analysis is in no way meant to contradict or be antagonistic to the current knowledge of statistical physics. Rather, it is hoped that a shape mechanical theory could contribute to widen its paradigms, and enhance the chances for a full statistical mechanics description of tougher molecular systems (as biochemical and biological).

## 1. BROWNIAN SIMULTANEITY AND UNCERTAINTY RELATION

The first point to note is that Brownian relativity encloses a local uncertainty relation for diffusion. It is a consequence of the severe critique to the simultaneity concept met in Einstein's relativity and taking an important role in Newtonian mechanics. In the special theory, all velocities are bounded from above ($v \leqslant c$) and any couple of clocks in relative motion can no longer be synchronized with arbitrary precision. In fact, from the Lorentz–Poincaré transformation for the temporal coordinate (in natural units):

$$\Delta t'' = \gamma_L \big( \Delta t' - \beta \Delta x' \big) \tag{5.1}$$

two events, for which $\Delta t' = 0$ in O′, will not necessarily be simultaneous in O″ ($\Delta t'' = 0$), unless they be "co-local" ($\Delta x' = 0$). Hence, two signals emitted simultaneously ($t'_2 = t'_1$) from distinct spatial positions ($x'_2 \neq x'_1$) in O′ will be detected by O″ with the following delay:

$$\Delta t'' = -\beta \gamma_L \Delta x' \tag{5.2}$$

In Brownian relativity, the lack of simultaneity (and of complete covariance) causes distinct delays and, in O″, it turns out:

$$\Delta t'' = \frac{(D'' - D')}{D' D''} \Delta \overline{\mathbf{r}'^2} \tag{5.3}$$

while, in O′:

$$\Delta t' = \frac{(D' - D'')}{D' D''} \Delta \overline{\mathbf{r}''^2} \tag{5.4}$$

We may also say that two events, simultaneous for a time-like observer, correspond to a shape-like frame obeying the first of the last two equations. Vice versa, a temporal trajectory is equivalent to a time-like observation of two events which take place simultaneously along a polymer molecule.

Consequently, the overall spatial uncertainty ($\delta r$) evaluated from O is:

$$(\delta r)^2 = \big| D' \Delta t' - D'' \Delta t'' \big| = \big| D' - D'' \big| \left( \frac{\Delta \overline{\mathbf{r}''^2}}{D''} + \frac{\Delta \overline{\mathbf{r}'^2}}{D'} \right) \tag{5.5}$$

that, using a common spatial unit, $\Delta \overline{\mathbf{r}'^2} = \Delta \overline{\mathbf{r}''^2} = l^2$, gives us:

$$\left( \frac{\delta r}{l} \right)^2 = \frac{|D''^2 - D''^2|}{D' D''} \tag{5.6}$$

We now avail of a relation of kinetic theory, $D' - D'' = l \delta v / 3$, achieving:

$$\frac{1}{3} |\delta r \delta v| = \sqrt{\frac{\big| D'^2 - D''^2 \big|}{D' D''}} \big| D' - D'' \big| \tag{5.7}$$

where the mean free path between collisions can equally mean a statistical segment ($l$), and $\delta v = \bar{v}' - \bar{v}''$ is the difference between the average velocities of the two subsystems. The right-handed side will tend to diverge with increasing $D' - D''$ ($''\Delta' \rightarrow \infty$) and, when the two diffusion coefficients approach each other (e.g., to a value $D$), the vanishing of the uncertainty may be compactly expressed as:

$$(\delta r \delta v)^2 \propto \big| \delta D \big|^{3/2} \tag{5.8}$$

still with $|''\Delta'| \rightarrow |\delta D|$. It may be interpreted as a Brownian-like uncertainty relation. Any observer at rest in the laboratory will not detect the discrepancy on the root mean squares, measured instead from the Brownian frames, thus will ascribe the origin of this disagreement to the relative movement. The observer will give the above equation the significance of an intrinsic relation for Brownian diffusion, $\delta D$ playing the role of an uncertainty source, and $\delta r \to 0$ of the limiting case of two chain shapes with very different "resolution" ($\delta v \to 0$).

Still under a macromolecular interpretation, an interesting example can be built upon considering a shape-like observer tending to universality. In this reference system, as soon as $N \to \infty$, any pair of time-like events will seem to be simultaneous. Think, for instance, of a couple of chain points crossed by a liquid molecule, or in general any portion of a Brownian trajectory. Insofar as $\frac{t'}{t''} = \frac{1}{N} \to 0$, such events will tend to be detected simultaneously. Universal shape-like frames are evidently "static," they cannot know if other systems in their neighborhood may evolve or not. As they annul the diffusive horizon of the host medium, a macromolecule can also be seen as a coordinate change that tends to "kill" any temporal evolution around, in a certain analogy to what is a locally inertial frame for the effect of gravity. What is more, from $\lim_{D'' \to 0} |\delta r \delta v| = \infty$, polymer events could never be contemporary with time-like observers but would rather belong to their statistics at past outlying times. We come back to the conclusion that universal polymer shapes immersed in a solution would "store" every statistical information on the motion of the liquid molecules. Again, statics of infinitely long macromolecules and dynamics of single molecules are counterparts of a unique phenomenology. Because of this, making contemporary events which are not, macromolecules in Brownian relativity almost behave as "fossils" in the host liquid medium. To get rid of the problem of covariance and "remove time," the search for a quantum-like formalism, coming from an indetermination principle out of time, is henceforth embraced and pursued in terms of geometry alone. The focus is on seeking the laws by which this geometrical uncertainty may propagate at different observational (length) scales.

## 2. LORENTZ–POINCARÉ TRANSFORMATION: A TOY MODEL FOR GEOMETRY

To attempt a first reduction of Brownian relativity into (mere) geometrical quantities, and fixing some ideas, consider the simplest case possible. Compared to a liquid molecule, a polymer in solution diffuses more slowly, depicting at any time a smaller root mean square displacement. We can therefore look at lowering a diffusion coefficient as the analogous spatial operation of localizing a volume, an area, a length, in some extended space. Imagine so to measure a "length" ($\textsc{l}$) by drawing a "shape" ($\phi$) within some underlying "extension" ($\mathrm{L}$), and suppose these three quantities be given a geometrical Lorentz–Poincaré symmetry. The most elementary way to mean it is, for instance, considering the 1-dimensional formula:

$$\mathrm{L}\phi = \textsc{l} \tag{5.9}$$

as it were a kinematic law, with length → $\mathrm{L}$, velocity → $\textsc{l}$, time → $1/\phi$. Any dimensional or physical extension, to volumes and surface areas, or to diffusive kinematics, would be immediate and require no important amendment. We endow this picture with positing some observational horizon, a limiting and invariant length scale $\ell \geqslant \mathrm{L}$, and define two reference frames $G = (\mathrm{L}, \phi)$ and $G' = (\mathrm{L}', \phi')$, comprising each a given extension and a scalar shape factor such that, $\phi, \phi' \in [0, 1]$. What matters here is rewriting the laws of time dilation and Lorentz–FitzGerald's, and it follows that drawing a shape in an empty space ($\mathrm{L} = 0$) produces a joint extension and shape contraction rule:

$$\frac{\Delta \mathrm{L}_{\mathrm{L}}}{\Delta \mathrm{L}_0} = \frac{\Delta \phi_{\mathrm{L}}}{\Delta \phi_0} = \gamma_\ell^{-1} \tag{5.10}$$

where indices refer to the measurements (the length scale) and $\gamma_\ell = (1 - \mathrm{L}^2/\ell^2)^{-\frac{1}{2}}$ is Lorentz's factor for geometry. An interesting feature is that, when a shape increment may be a function of the extension, their derivatives would be preserved at any scale:

$$\left(\frac{d\phi}{d\mathrm{L}}\right)_{\mathrm{L}} = \mathrm{invar} \tag{5.11}$$

The calculations heretofore developed might only look like a mathematical game, a toy model of no interest in itself and unlikely to be applicable. Yet in the framework of Brownian relativity, it becomes more meaningful however when $\phi$ is given the natural interpretation of a spatial probability. By doing so, the former constraint would state that there is some probability density which is form-invariant upon changing scale.

To give an example, consider two events located far apart, for instance, the localization of an electron ($G$) in a given atom and that of the same atom in a simple liquid ($G'$) of equal chemical nature. That also the former phenomenon involves a Bachelier–Wiener process is known from some of Feynman's work. Thus, our invariance would assign $G$ and $G'$ a conserved distribution function. One does not know yet which probability or statistical laws can be preserved, but Brownian relativity and its geometrical reduction would suggest it is there.

We have actually already met a situation like this, when van Hove's distribution function was written in invariant form at any molecular scale (of a dilute solution). There, the measurement associated with a $M$-mer molecule was the displacement from the diffusive coefficient of the liquid ($\ell$), whence the condition $''\Delta' \rightarrow 0$ ($\mathrm{L} \rightarrow 0$) corresponded to (polymer) universality. In Brownian relativity, molecular dynamics and macromolecular statics are notwithstanding equivalent and in fact, similarly to the previous equation, it turned out $G_M(t, \mathbf{r}) = \mathrm{invar}$. Recall that the Lorentz–Poincaré symmetry was related a long time ago to the Bolyai–Lobačevskij geometry by Vladimir Varičak (1910), in the context of Doppler's effect, the light aberration and reflection by a moving mirror, pointing out an analogy between the sum of segments in a hyperbolic space and the velocity composition in special relativity. In case of further developments, that would be an interesting framework to take back and work with.

# 3. THE STATIC UNCERTAINTY RELATION

## 3.1 For geometry

When an extension is calculated in a space of arbitrary dimensionality, the shape of the figure involved is, mathematically, never implied directly. Elementary formula for volumes and areas are clearly available for well defined geometrical figures, but they simply result from definite integrations. Shape is certainly a fundamental property but does not enter any calculation explicitly, as an independent variable. Despite determining the extension of an object does not fall under the domain of topology, shape always attends geometrical calculations indirectly, as it were staying behind and hidden by geometry itself. The most representative example comes likely from the metric tensor, whose fields ($g_{\alpha\mu}$) contain all the available information about the change of form caused by a deformation. Wishing instead to incorporate it as a "physical" observable, with own fundamentals, an uncertainty relation for geometry was formerly introduced. It relies on the evidence that any information about the shape of a body always carries (or requires) the knowledge of its geometrical properties. On the contrary, calculating the extension of an object needs in practice knowing which shape it takes. We summarized these considerations by stating that "measuring a geometrical quantity undetermines (the underlying) extension and shape."

To visualize this statement, imagine being in front of some "empty" extension, formed by spatially indistinguishable points. Measuring a geometrical object needs first to specify its shape and then comparing its extension to that of the background space. In an analogous circumstance, consider the identical molecules that diffuse indistinguishably in a homogeneous and isotropic (relativistic) Brownian medium. Every time that one of them displays the value of its diffusion coefficient from that taken by every other ($D'' \neq D'$), it will get distinguishable, and "localized" in the medium (Fig. 5.1). In other words, any local diffusion coefficient variation inside a homogeneous and isotropic medium is conceptually close to tracing a shape in a spatially indistinguishable space. In both cases, some structure (or order) is partially assigned to a fully unstructured (or disordered) environment, just "shaped" by a measurement performed therein. The way it is affected in a Brownian–relativistic theory was derived at the beginning of this chapter. Here, instead, the nature of the measurement will have to be static, and undetermined by an analogous uncertainty relation out of time. In formula, it suffices to express and discuss the former statement in the simplest fashion possible, i.e.:

$$\delta X \delta \phi \geqslant x \tag{5.12}$$

where, again, $X$ is a starting linear extension, $\phi$ takes shape into account, and $x$ denotes the measurement (i.e., a length). Using both a capital and a lower case letter "ecs" means they denote similar quantities, but provided with different roles. The former ($X$) is undetermined, while the latter ($x$) is undetermining or, in other terms, the indetermination source. In comparison with Heisemberg's formulation, where uncertainties are due to an intrinsic constant quantity (Planck's constant, $\hbar$), here the source may be arbitrarily small ($x \to 0$).

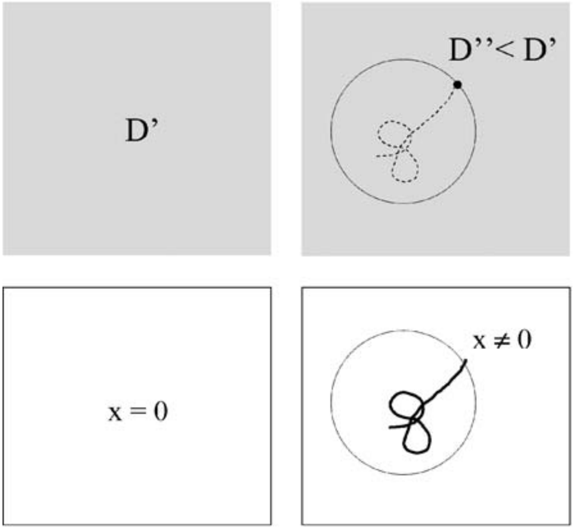

**Figure 5.1** Localizing a Brownian molecule and drawing a figure.

Of course, depending on how $\delta\phi$ is dealt with, there is a multiplicity of ways of carrying the above relationship out. In previous work for example, $\phi$ was interpreted as in the last section, that is, an "extension fraction," denoting the relative portion of the starting space enclosed by a figure drawn therein. Such a definition, quite natural on the one hand, has nevertheless the disadvantage of rendering extension and its measurement not conceptually equivalent, and the introduction of topology quite difficult. So, in this analysis, the shape uncertainty will be simply identified with the relative uncertainty on the measurement, $\delta\phi = \delta x/x$, giving:

$$\delta X \delta x \geqslant x^2 \tag{5.13}$$

Notice the symmetries of this formula upon exchanging the two spatial quantities ($x \leftrightarrow X$) and reverting their signs together ($x \rightarrow -x$, $X \rightarrow -X$).

## 3.2 For topology

To deal with topology, the Gauss–Bonnet theorem should now be recalled. It consists of a global result, valid for compact and smooth Riemannian manifolds in two dimensions (M), and expresses the total curvature from a surface integration of the Gaussian curvature ($k_G$):

$$2\pi\chi = \int_{\mathrm{M}} k_G \, dA \tag{5.14}$$

where $\chi$ is said the Euler–Poincaré characteristic. This theorem is independent of the metric, and assigns to $\chi$ a fundamental topological invariance. Thus, if one multiplies by $k_G$ the former inequality and sets $\delta A = \delta X \delta x$, then obtains:

$$2\pi\delta\chi \geqslant k_G x^2 \tag{5.15}$$

the differential on the left being evidently of second order. Now, introducing time by a (uniform) measuring process, as $x = v\delta t$, and dividing twice by $\delta t$, the uncertainty relation for geometry is redefined in the temporal domain:

$$k_G v^2 \leqslant 2\pi \left( \frac{\delta^2 \chi}{\delta t^2} \right) \tag{5.16}$$

Provided the "static acceleration" on the right be limited from above, this inequality would infer the velocity bound stated by the second postulate of special relativity ($v \leqslant c$). When velocity equals the light speed in vacuum, a differential relation should follow as:

$$k_G = 2\pi \left( \frac{d^2 \chi}{ds^2} \right) \tag{5.17}$$

with line element fixed (or "staticized," see the next section) to $ds \equiv c\,dt$. One could revert it and say that, every time the Euler–Poincaré characteristic is varying, space "bends" with a Gaussian curvature equal to this "acceleration."

One of the first evidences of nature is that extension and shape are never separated, but join together into physical objects. According to the previous relation, light would provide thus a velocity bound to the propagation of any information about extension and shape of a body. We mean that, without geometrical uncertainty, material things may look rather different. Shape and extension could "escape" from the objects they join in, separating from each other into independent observables. Thus, the second postulate of special relativity becomes representative of a best reconciliation of extension and shape into physical bodies, as they are daily experienced. By allowing this common evidence to be invalidated, shape mechanics will try to set a phenomenology in which extension and shape, to use a (quantum) mechanical notion, may "commute" together.

## 3.3 For matter and position

The role played by mass can be accounted for by a second type of measurement, the variance of a Brownian particle, $x^2 = D\delta t$. Since diffusion coefficients are dimensioned to an action divided by a mass, the condition $D = \frac{\hbar}{2m}$ gives evidently Heisemberg's (one-dimensional) uncertainty relation:

$$\delta x \delta p_x \geqslant \frac{\hbar}{2} \tag{5.18}$$

$\hbar$ being Planck's constant and $p_x = m\delta x/\delta t$ denoting the linear momentum of a particle of mass $m$. Momentum and position become thus "complementary," they cease to be particle properties, and every observable is no longer required to take a sharp value in each state.

The expression for $D$ is the same assigned to all physical bodies by Edward Nelson (1966) in a stochastic derivation of Schrödinger's equation somewhat in line with the work of Imre Féynes (1952). Note that the arise of an intrinsically constant uncertainty term depends here on the type of measurement. While it

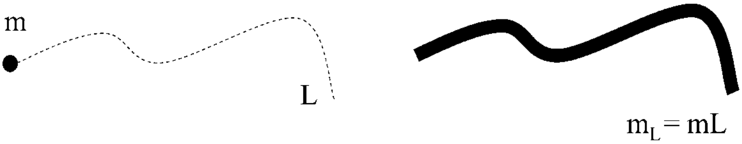

**Figure 5.2** The (static) quantity of extension of an evolving body.

would never take place for a process which is linear in time ($x \propto \delta t$), in a Brownian-like measurement ($x^2 \propto \delta t$) the uncertainty source is driven by an intrinsic diffusion coefficient, as in Nelson's view.

When only mass is concerned with geometry, an intermediate level between Heisemberg's and ours appears. From simple dimensional arguments, getting rid of time in the particle momentum ascribes the uncertainty source to the moment of inertia (I) of the implied material shape. This transforms the former relation into:

$$\delta x \delta m_x \geqslant \mathrm{I}_x \tag{5.19}$$

where, in analogy to $p_x$, the variable $m_x = mx$ can be named as "quantity of extension." By a useful image, when a particle of mass $m$ is traveling in time a path of length $x$, its quantity of extension will equal a static body which is built by "prolonging" the mass along the traveled path. In this case too, a macromolecular analogy can help (Fig. 5.2).

## 4. MATERIALITY AND GEOMETRY OF ENERGY

### 4.1 Energy surface as a "material shell"

To interpret the former relations in concrete terms, concepts like "shape," "Euler–Poincaré characteristic," "uncertainty," and even "curvature," which does not have the same significance of Einstein's view, are to be spelled out in natural phenomena. We are not certainly in a position to formulate axiomatically a theory, but will attempt to arrive at some considerations and to state some of the necessary mathematics. The first question to pose ourselves is: Which physical observable is prior involved when a "shape is traced," or some object localized? Answering this question passes certainly through the concept of energy, and it will be seen that our approach may shed new light on it. The simplest case to think of is to regard an energy function, $E = E(\mathbf{r})$, showing as usual a repulsive and an attractive region near a stable minimum. We can say that $E_k$ is the energy value necessary to localize a particle in a neighborhood $D_k$ of the equilibrium point, such that $E(\mathbf{r} \in D_k) \leqslant E_k$. A general insight, employed in this chapter, is to regard $E = E(\mathbf{r})$ more than a discrete or continuous population of energy levels. What matters to us is also its "shape," and we will start thinking of it as the "shell" of a material "object," the geometry and topology of which being related by another, alternative description.

In the framework of the joint contraction rule, met in the previous toy model, these comments catch our attention on the meaning of changing energy state. "Distances" between pairs of levels are normally regarded as energy differences, for

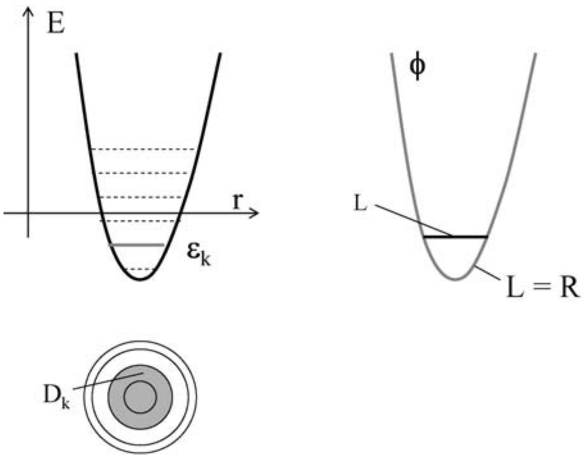

**Figure 5.3** Energy surface and drawing a material shell.

geometrical effects are not taken into account directly. This, for instance, would suggest comparing the Lorentz–FitzGerald contraction for the extension with the well-known relationship (Fig. 5.3):

$$dR = \sqrt{1+\varepsilon'^2}\,dr \tag{5.20}$$

where all quantities are dimensionless, set in characteristic energy and length units $(\ldots' \equiv \frac{d}{dr})$. It links the (straight) radial element $(dr)$, connecting two points of an energy level, to that $(dR)$ following the (curved) path on the energy shell, of equation $\varepsilon = \varepsilon(r)$. In other words, the spatial excursion that contracts when a particle confines to some energy level would just be in this example the extension of its shell. We should now take a further step, and ask ourselves which (statistical) description may correspond to this reinterpretation of distances and levels on an energy surface. The Maxwell–Boltzmann statistics relies on differences of energy levels, $p(k \to s) = \mathrm{e}^{\varepsilon_k - \varepsilon_s}$ but, according to Brownian relativity and its implications, it would not be the only approach to thermal physics. We expect a viewpoint in which statistics could be reformulated geometrically or, equivalently, brought back to a (more) deterministic problem. This will require state transitions $(k \to s)$ to be described differently from energy jumps alone.

## 4.2 Horocyclic energy projection

Our belief, that energy profiles stand somehow for material objects, whose own shapes matter in themselves, meets immediately a point which has not received a great deal of attention in the analysis of natural phenomena. The visual world is foremost projective, rather than non-Euclidean or Euclidean, and the shape of an object constantly changes with the adopted geometrical viewpoint. Experience itself suggests that any geometrical description holds within a projective interpretation of distances and angles. We cannot help remembering here the seminal papers on this subject, specially by Arthur Cayley (1859) and Felix C. Klein (1871–1872). Projective geometry generalizes the Euclidean geometry, and is not meant to replace it, as the Bolyai–Lobačevskij's. Thus, when an experimentalist derives the potential function that a particle undergoes along the radial direction (or projection), $E = E(r)$, one can be interested to see if some viewpoint is implicitly set for this operation, bringing the particle from $\infty$ to $r = 0$. In our context, this functional dependence will be in effect an "energy projection," as it were drawn from a point (or reference frame) at infinity.

We saw that, in Brownian relativity, the hydrodynamic limit could be idealized to a horocycle, carrying the strength of molecular correlations into the value of some (average) Gaussian curvature. A horocycle behaves at the same time as a straight line and a circle with center at infinity, and has the special feature to give rise to simultaneous translations and rotations. Thus, when a geometrical figure translates along it, the resulting move will be also equivalent to a rotation. Consider thus the coordinate change:

$$\begin{aligned} -\varepsilon &= \ln \tan \frac{\theta}{2} \\ \rho &= \varphi \end{aligned} \tag{5.21}$$

carrying the plane $(r, E)$ into a latitude and a longitude angle, $(\theta, \varphi)$, still with given characteristic energy ($k_B T = E/\varepsilon$) and length ($\ell_r = \rho/\varphi$) units. It interprets the energy function as a modified Bolyai–Lobačevskij formula, where $\mathrm{e}^{-\varepsilon(\ell_r)}$ is the arclength ratio between horocycles displaced by the unit distance, and the parallelism angle $\alpha_L \equiv \theta$. Clearly, if $\varepsilon \to \infty$ then $\alpha_L = 0$, while geometries at zero energy will be locally Euclidean ($\alpha_E = \frac{\pi}{2}$).

This is not the sole transformation fulfilling our initial requirement, namely, setting the problem in a horocyclic frame, and might suffer from a high idealization. However, it takes part conveniently in another famous issue, known as Mercator's conformal projection. Accordingly, on a spherical domain of radius assigned, the energy function becomes a "loxodrome," or "rhumb-line" (from the Greek "loxos" = oblique). It is a curve evolving at constant bearing, meaning that it is equally oriented with respect to all lines of constant longitude ("meridians"). Its stereographic projection, when the spherical poles are mapped onto the equatorial plane, is a logarithmic spiral, wounding each pole infinitely many times. Mercator's map is mostly employed for navigational purposes, to get straight lines from (globe) loxodromes, but the concept of loxodromy should not be confused with the dual "orthodromy," and the geodesics thereof.

## 4.3 A geometrical system of units

The previous energy transformation would be fully aseptic, of no avail, if no further physical principles could come to our rescue. Nonetheless, the analysis of our uncertainty relation has not gone through yet and, to go ahead, we compare the (1-dimensional) equation:

$$a_\chi = k_G \tag{5.22}$$

with Newton's and Einstein's:

$$f = a, \qquad E_0 = m \tag{5.23}$$

defining for convenience $a_\chi \equiv 2\pi(d^2\chi/ds^2)$. We remind that the force per unit mass in Newton's law, $f = F/m$, resembles a curvature definition. If it could be rewritten under $t \to s$ (a length), the acceleration would turn evidently into a term like $\kappa \equiv (d^2x/ds^2)$. With this in mind, replace the mass–energy equivalence in Newton's second law (still with $s \equiv ct$):

$$F = E_0\kappa \tag{5.24}$$

i.e., $a \to \kappa$ and $m \to E_0$, and note that our geometrical equation is intermediate between these two. Looked at from the side of Einstein's equivalence, then $E_0 \to a_\chi$ and $m \to k_G$. Otherwise, it represents Newton's law upon $a \to a_\chi$ and $f \to k_G$. The hint is that this (geometrical) framework may lead to a treatation in which energy and force get (dimensionally) indistinguishable.

To enter this interpretation, imagine following the particle evolution along a path long $x$ by the evolution of a dimensionless ("shape") quantity, times $x$ itself. In other words, let us "staticize" the equations by taking lengths out, e.g.

$$a = x\left(\frac{d^2\chi}{dt^2}\right) \tag{5.25}$$

The scope of this, apparently inconvenient, operation may be guessed again from Brownian relativity, by the equivalence of static (chain) shapes and dynamic (molecular) paths. There, a random path in time of a single molecule was staticized into an identical linelike configuration. Here, a particle trajectory is taken again as a static "material object," which no longer evolves. In this way, the dimensions of a velocity square and an acceleration reduce to be equal (to a time$^{-2}$).

Our aim will be to employ the horocyclic energy projection, and exchanging translations with rotations by some shape-mechanical rules. This discussion can thus be concluded by a dimensional comparison of translational and rotational quantities, observing that:

$$\begin{gathered}
[F] = [m][x][a_\alpha] \\
[\tau] = [\mathrm{I}][a_\alpha] \\
[K_T] = [m]\left[x^2\right]\left[\omega^2\right] \\
[K_R] = [\mathrm{I}]\left[\omega^2\right]
\end{gathered} \tag{5.26}$$

The second and fourth equations rely respectively on the rotational motion equation (for a torque, $\tau$) and the kinetic energy, of a body with given moment of inertia, where the "staticized" $\omega \equiv (d\chi/dt)$ and $a_\alpha = (d^2\chi/dt^2)$ play either the roles of angular or translational velocities and accelerations. Note that Newton's is the only law not to be concerned with a moment of inertia, but a quantity of extension ($m_x$), as defined in the uncertainty relation for matter and position.

Therefore, our approach will take a couple of directions. Choosing to observe the position, the quantity of extension will be indetermined, and a quantum-like operatorial formalism will be needed to deal with the potential energy (or force). This will be started in two sections. Otherwise, the statistics of (Brownian) particles can be investigated by the geometry of their "material energy shells," as we have already outlined and are going to continue.

# 5. $n$-Molecular Systems and Pairwise Potential

## 5.1 Total curvature equation

Let us recapitulate. We have seen that, when an experimentalist detects a potential energy as a function, for instance, of the radial distance between two atoms or molecules, the outcome is like a phantom material object, seen (or "shadowed") from the viewpoint of a horocyclic frame, where translations and rotations are equivalent operations. For any energy level, the uncertainty relation for geometry would assign its shell a "quantity of extension," indetermined by the localization process corresponding to that energy content. It would "quantify the extension" of a large amount of molecules, as they would be disposed onto (or be the concrete material that is forming) the energy shell. Thus, in dealing for example with a liquid, one may think of a crowded molecular shell, having the geometry and topology of the same energy profile by which the molecules interact. The horocyclic transformation, on the other hand, has been seen to map energy lines into loxodromes. Any energy change corresponds here to a spiral-like trajectory on a spherical co-domain, and we argue this is the (deterministic) move that each atom or molecule makes in transiting between two different (energy) states of a $n$-molecular Brownian system.

One could say that, while the energy representation is "shape-like," the other describes a "material space" occupied by the molecular ensemble. We should now comprehend how to move on it, and whether other geometrical equations may join that for the total and Gaussian curvatures. In (classical) thermal physics, the basic tool is the Boltzmann's partition function, the probability sum over energy states. What we need here is a function of coordinates, joining different positions in a similar fashion to a space roto-translation. The first demand is to involve all energy states of the starting surface, as one were circumnavigating, or "circling" the entire ensemble of atoms and molecules (Fig. 5.4).

To this end, recall a useful result of Hamiltonian dynamics, the perturbation of a "twist map" for a near integrable conservative system in the canonical action-angle representation, $(S_s, \beta_s)$ $(s = 1, 2, \ldots, m)$. When $m = 2$, the dynamics of a conservative system, $H(S_1, S_2) = E$, can be represented on a torus by the equations, $\beta_s = \omega_s t + \text{const}$ $(s = 1, 2)$, with $\omega_s = E/S_s$. Think, for simplicity, of following the angles on two separate circles. Twist maps belong to the family of "Poincaré sections" of motion. By plotting the orbit intersections with the plane transverse to the torus, every time that one of the angles (e.g., $\beta_1$) advances through $2\pi$, one would obtain $(\ldots_n \equiv \ldots_{2,n})$:

$$\begin{aligned} S_n &= S_{n-1} \\ \beta_n &= \beta_{n-1} + 2\pi \mathsf{W} \end{aligned} \tag{5.27}$$

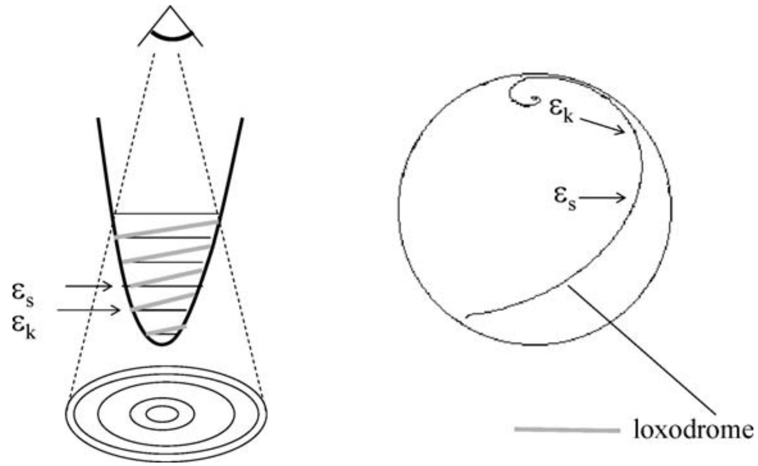

**Figure 5.4** Energy surface as the loxodromic projection of a horocycle.

with "winding (or rotation) number" $\mathsf{W} = \omega_1/\omega_2$, the mean number of rotations (through $2\pi$) per each iteration $n \to n+1$. It is in other words the average frequency of the motion around the circle and provides a measure of periodicity.

This result is rather intuitive and, if $\mathsf{W} \in Q$, twist maps are formed by a finite set of points. Otherwise, if $\mathsf{W} \in \Re \setminus Q$ (irrational), the motion becomes "quasi-periodic," covering densely the circle upon $n \to \infty$. Such transformations preserve the area of the action-angle plane, that is, comply with the Liouville's theorem:

$$\left\| \frac{\partial(S_n, \beta_n)}{\partial(S_{n-1}, \beta_{n-1})} \right\| = 1 \tag{5.28}$$

and can be allowed to vary, by small perturbations in a common parameter ($\lambda$):

$$\begin{aligned} \delta S_n &= \lambda f_S \\ \delta\beta_n &= \lambda f_\beta \end{aligned} \tag{5.29}$$

meaning $\mathsf{W} \equiv \mathsf{W}(S_n)$ and each $f_i \equiv f_i(S_n, \beta_{n-1})$. Imposing the validity of Liouville's theorem yields in the end a condition expressible as:

$$\left(\frac{\partial f_S}{\partial S_n}\right) = -\left(\frac{\partial f_\beta}{\partial \beta_{n-1}}\right) \tag{5.30}$$

In summary, rotating $\delta\beta_1 = 2\pi n$ in a conservative (integrable) system generally advances the other angle by $\delta\beta_2 = 2\pi n\mathsf{W}$. In order to vary the twist map by small action and angle perturbations needs to fulfill a continuity-like condition. This scheme, endowed with the necessary amendments, is going to be embodied in our problem, where any energy change should be equivalent to some angular displacement ($\delta\beta$) performed inside what we have called as "material space." In other words, for any $E_s \to \beta_s$, a (continuous) roto-translation of the former type will be adopted to advance through (all) the angular excursions made available through (all) the levels of the energy shell. This "angular revolution" will be finally interpreted as a variation of the Euler–Poincaré characteristic along the surface ($\delta\chi$).

For a continuous function, the rate at which this movement proceeds will locally depend on the surface orientation and shape. We should distinguish between full ($\delta\varepsilon$) and normal ($\delta\varepsilon_\perp$) energy displacements, and realize that the latter assumes the meaning of $\lambda$. The previous constraint will thus be developed with $\varepsilon \equiv \varepsilon_n \rightarrow \varepsilon_n + f_\varepsilon \delta\varepsilon_\perp$, for an action "staticized" into our dimensionless energy, i.e.:

$$\delta\varepsilon = f_\varepsilon \delta\varepsilon_\perp \tag{5.31}$$

If $\delta\varepsilon \equiv \delta\boldsymbol{\rho} \cdot \vec{\nabla}\varepsilon$ and $\delta\varepsilon_\perp \equiv |\vec{\nabla}\varepsilon|\delta\rho$, then:

$$f_\varepsilon = \mathbf{u} \cdot \mathbf{n}_\varepsilon \tag{5.32}$$

where $\mathbf{n}_\varepsilon = \vec{\nabla}\varepsilon/|\vec{\nabla}\varepsilon|$ is the unit vector normal to the surface and $\mathbf{u} = \delta\boldsymbol{\rho}/\delta\rho$ is a virtual displacement unit vector, along which the energy surface is differentiated. We so assign the term $-\vec{\nabla}\mathbf{n}_\varepsilon$ the meaning of a "shape operator" (or Weingarten's map), which is diagonal in any orthogonal basis, with eigenvalues equal to the principal curvatures. In this way, one is left with:

$$\frac{\partial f_\varepsilon}{\partial(\mathbf{u} \cdot \mathbf{r})} = \vec{\nabla} \cdot \mathbf{n}_\varepsilon \tag{5.33}$$

that is proportional to the mean curvature of the energy surface, and the final condition, for $\chi \equiv f_\varphi$, can be written as:

$$\left(\frac{\partial\chi}{\partial\varphi}\right) = 2\pi k_{H\varepsilon} \tag{5.34}$$

where $2\pi$ makes the notation homogeneous with the Gaussian curvature equation. It says that $\chi$ advances with rate equal to twice the (dimensionless) mean curvature ($k_{H\varepsilon}$) derived from the shell. The latter means for a surface what $\kappa$ stands for the length of a curve, that is, it expresses the rate of change of the area of an "evolving" surface.

In conclusion, while the equation for $k_G$ can be regarded as the "intrinsic" geometrical counterpart to Newton's law, that involving $k_H$ is an "extrinsic" equation, more analogous to a kinematic law and arising from conceiving the energy surface similarly to a material object. Ordinary mechanics separates kinematics from dynamics, energies from forces, lengths from angles, and so on. Shape mechanics aims instead at uniting these descriptions and, in light of the previous developments, a simple "curvature equation" meeting these purposes would be:

$$\left(\frac{d^2\chi}{d\varphi^2}\right) = \chi_G + \left(\frac{d\chi_H}{d\varphi}\right) \tag{5.35}$$

to be carried out in the Mercator-like projection, with $\chi_G = k_{G\varepsilon}/k_{G\ell}$, $\chi_H = k_{H\varepsilon}/k_{H\ell}$, in "units" of $k_{G\ell} = \frac{2\pi}{\ell^2}$ and $k_{H\ell} = \ell^{-1}$.

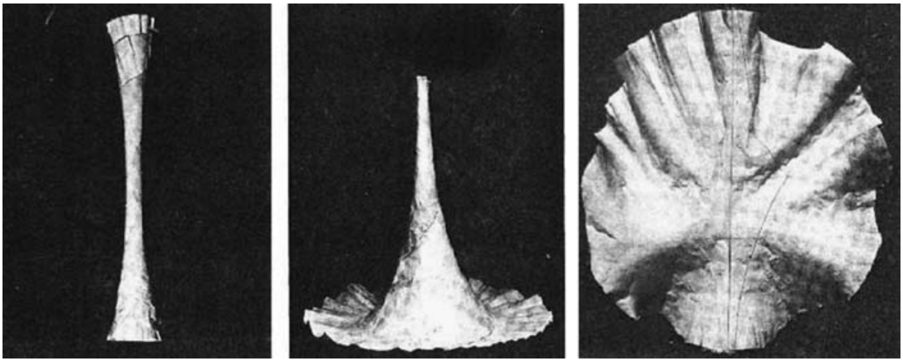

**Figure 5.5** Beltrami's "cuffia" (cap), Euclidean model of the hyperbolic plane. From the Archive of the Mathematics Department at the University of Pavia, http://www-dimat.unipv.it/biblio/modelli/cat-XIV/fXIV-1.html.

## 5.2 Liquid density correlation functions

To exemplify how the Maxwell–Boltzmann statistics transforms in our description of a liquid, imagine "laying out" an energy surface onto a flat (Euclidean) one. Naturally, due to the impossibility of covering it uniformely, a number of "bends" and "corrugations" will appear, and the energy shell will have to be pressed down to the plane. If the surface were spherical (positively curved), it would burst into a foliation with "open" interstitial spaces, otherwise a pseudosphere will produce "wriggles" or "wrinkles." Beltrami's surface in Fig. 5.5 is a good example for the hyperbolic case. We envisage that similar geometrical patterns should reproduce the fluctuation profiles met in density correlation functions of a liquid, and we will support this argument by a simple shape-mechanical model.

Consider thus two molecules of a (simple) liquid, with positions $\mathbf{r}_{1,2}$, and interacting through a pairwise potential $E = E(r = |\mathbf{r}_1 - \mathbf{r}_2|)$. According to our view, it will stand for a "rhumb line" ($\varepsilon$) projected onto a horocyclic frame, to be brought back into a material space with coordinates $\varphi_s = r_s/\ell_r$ ($s = 1, 2$). At constant temperature and (average) molecular size ($r_a$), the dimensional units to work with will be obviously $k_B T$ and $\ell_r \equiv r_a$. Remember that, contrarily to the usual (independent) position variables appearing in the energy surface, the angles $\varphi_{1,2}$ specify the "concrete" molecular locations, which are those "linked" materially to the molecules. We can imagine to "transport" the first through an angle $\varphi_1 \rightarrow \varphi_1 + 2\pi w$ and follow the advancement of the second, $\varphi_2 \rightarrow \varphi_2 + 2\pi w \mathsf{W}$. In this case, one is left with a map like:

$$\varphi \rightarrow \varphi + 2\pi w \chi \tag{5.36}$$

intending $\varphi \equiv \varphi_2 - \varphi_1$ and $\chi \equiv \mathsf{W} - 1$. More generally, the Euler–Poincaré characteristic will denote a difference of "rotation numbers."

In a first description, we can ignore any perturbation coming from the surrounding (i.e., a dilute system), and limit ourselves to $n$ iterations about a constant angle, $\varphi_n = 2\pi n \chi$. Note that the ratio $g_n = r_n/(2\pi \ell_r n)$ spells out the definition of pair correlation function in our coordinate setting, from which $g(\varphi) = \chi(\varphi)$. This

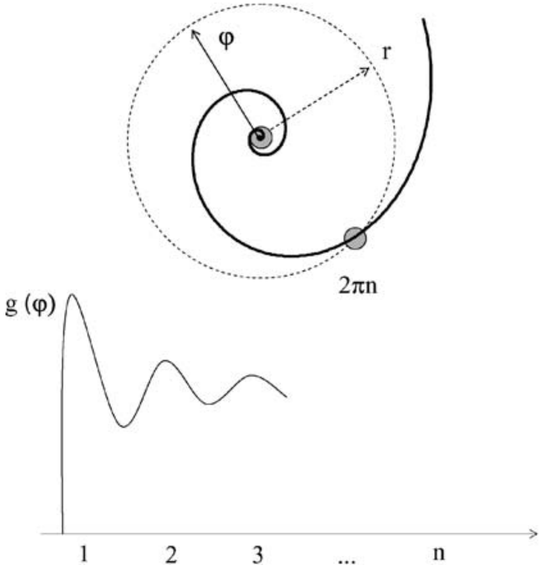

**Figure 5.6** Sketch of pair correlation function as a winding number.

assigns $g = g(r)$ the meaning of a "winding number" for the relative advancement of the two molecular maps. It detects in other words the change of the Euler–Poincaré characteristic when the pair of molecules is displaced across the material space of the liquid Fig. 5.6.

To continue, any energy level should be recalculated by Mercator's conformal map, and the result comes immediately from the transformed line element:

$$\left(\frac{ds}{\ell_R}\right)^2 = \operatorname{sech}^2 \varepsilon \big(d\rho^2 + d\varepsilon^2\big) \tag{5.37}$$

where the radius $\ell_R$ fixes an (arbitrary) outer length scale, over which representing the liquid. It plays a similar role of $\ell_r$, and will not be very important here. Note that the (first-order) differential is defined up to its sign and, at $\rho = \text{const}$, is an even energy function, $-ds(\varepsilon) = ds(-\varepsilon)$. Moreover, it is $-\varepsilon$ (the horocyclic surface) to be conformally projected onto the $\theta$-axis. We can map thus any energy level through the angle described along the (dimensionless) curvilinear coordinate ($\alpha_R = s/\ell_R$):

$$\alpha_R(\varepsilon) = \int_{-\infty}^{-\varepsilon} \operatorname{sech} \varepsilon \, d\varepsilon = 2 \arctan \mathrm{e}^{-\varepsilon} \tag{5.38}$$

and set $\chi = \alpha_R/\alpha_E$. In words, increasing the energy level raises the Euler–Poincaré characteristic, and the "ground" shape contribution to the pair correlation function is:

$$g_0(\varepsilon) = \frac{4}{\pi} \arctan \mathrm{e}^{-\varepsilon} \tag{5.39}$$

Observe that, for a typical molecular potential, $\varepsilon \to \infty \Rightarrow g_0\ (r \to 0^+) \simeq 0$ and $\varepsilon \to 0 \Rightarrow g_0\ (r \to \infty) \simeq 1$, giving two expected properties. This result can be commented in light of the total curvature equation. When $k_{H\varepsilon} = 0$, one is left with the intrinsic term, generally expressible as a Laplacian, $k_{G\varepsilon} \sim \vec{\nabla}^2\varepsilon$. Now, if $s \to r$, then $\chi = \varepsilon$. Redefining any length (or angle) as above "focuses" instead the Euler–Poincaré characteristic on the projected energy value.

The function $\chi$ is therefore a building block for density correlations, but is not of true statistical nature. It stands for an "energy projection," which is always of course a partial projection, and is to be rebuilt from the surface of the shell. In the present interpretation, statistics and statistical fluctuations follow from the impossibility of handling, in any circumstance, the absolute shape of an object. Any information we can get from it will be ever incomplete, depending on the adopted "projective" viewpoint.

To account further steps for $(g_{>0})$, it is necessary to develop the extrinsic term in the total curvature equation. For a loxodrome in the limit of infinitesimal bearing angles, the actual curvature radius can be set to $R_c/\ell_R = \cos\varphi$, thus the extrinsic contribution to be added to the former is:

$$\frac{1}{\ell_R}\int_0^{2\pi w\chi} R_c\, d\varphi = \sin(2\pi w\chi) \tag{5.40}$$

By iterating $n-1$ times, the pair correlation function will follow at any step a (sine) "circle-map" scheme ($n \geqslant 0$) of the form:

$$w^* g_{n-1}(\varepsilon) = \chi_w + k_1 \sin\chi_w + k_2 \sin(\chi_w + k_1 \sin\chi_w) + \cdots \tag{5.41}$$

where $\chi_w = w^*\chi$, $w^* = 2\pi w$, and $k_s$ form a set of $n$ coupling coefficients, one per each sine function composed $s$ times ($k_0 \equiv 1$). It should be observed that every single term on the right does not correspond to (fixed) molecular shells in the liquid. However, the non-linear contribution (sum over $n \geqslant 1$) replaces in practice the tough functions that, in liquid and soft states of matter, describe $n$-body correlations. There is no room here to examine such connections to the existing statistical–mechanical theories. We illustrate nonetheless an application to liquid argon, making use of a Lennard–Jones potential, $v_{LJ} = 4\epsilon^*(\rho^{-12} - \rho^{-6})$, in the projective function, $\chi = \chi(\varepsilon = v_{LJ})$ (Fig. 5.7).

Remember that a circle map (or "diffeomorphism of the circle") is a regular and increasing function, $\varphi : \Re \to \Re$, fulfilling the "circle map identity," $\varphi(x+1) = 1 + \varphi(x)$. Again, the idea is that the real line and its co-domain can be rolled up on two circles (of unit circumference), so that the image of two points, $x$ and $x+z$ ($z \in Z$), superimposed on the first circle, will also get superimposed on the second circle, still separated by a number of $z$ turns.

## 6. THE SHAPE-MECHANICAL ISSUE

In classical mechanics, the laws of motion follow from the (variational) principle of least action recalled in the first chapter. The action functional is set to the

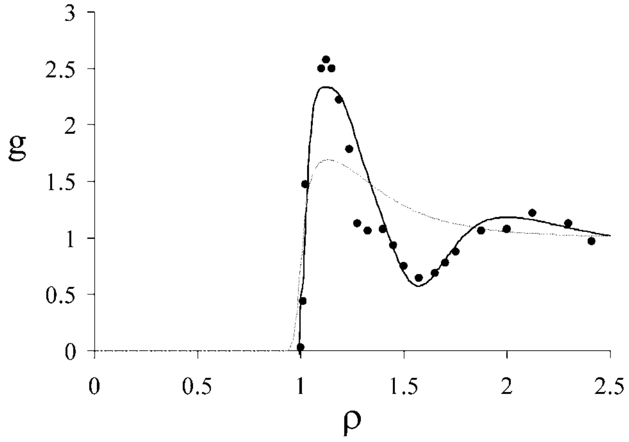

**Figure 5.7** Pair correlation function of Ar (l) (Henderson, 1971) with $n = 1$ and $n = 6$ [$T = 91.8$ K, $\varepsilon^* = \varepsilon_{LJ}/(k_B T) = 1.39$ (Tóth and Baranyai, 2000)]. Coefficients were extrapolated to $w^* = 2.16$, $k_1 = 0.92$, $k_2 = -5.92$, $k_3 = 2.30$, $k_4 = -1.49$, $k_5 = 3.32$.

time integral of the Lagrangian, which depends on all degrees of freedom of the system, generalized positions and velocities. Imposing stationarity with respect to small coordinate variations gives the Euler–Lagrange equations, and so the trajectory of motion. In the mechanics we set out to state, all trajectories will generally consist of two parts, one time-like and the other shape-like, bringing about temporal and configurational random paths. In analogy with copolymers, i.e., polymers formed by two or more different kinds of repeat units, they could take the name of "co-trajectories." We can think of them as extended paths in a polymer solution, where the random path of a liquid molecule is "linked" to the shape of a chain molecule dissolved in it. This is just the connection set in Brownian relativity, which taught us to intend the plenty of stochastic paths in a polymer solution as forming equivalent classes of reference frames for the law of statistics, regardless of their static ($N$) or dynamic ($t$) realizations. In a few words, the "evolution in time," undergoing any moving or evolving object, will leave the place to an "evolution in shape," of a (statistical) sequence of forms, or to a mixed "co-evolution" in time and shape.

This section is devoted the begin the pure static analysis, when only shape-like frames are concerned. There is a lot of work to do, when both representations interplay together, to be started in a near future. Here we will see that, on continuing the bridge between geometry and statistics set by Brownian relativity, a wave equation is achieved.

## 6.1 Figures as slits in Young's experiment

Young's two-slit thought experiment illustrates the dual nature of matter. Along with discrete spectra of atoms and molecules, it was one of the two puzzles suggesting the quantum-mechanical interpretation of atomic physics. In brief, a photon issuing from a given source passes through a doubly-slitted screen, hitting another one that detects its final position. Despite particle arrivals being sharply localized indivisible events, their probability exhibit a diffraction pattern which is typical instead of a wave motion. If one of the slits is closed, the interference pattern disappears. Attempting to experimentally "observe" the hole through which particles go (i.e., with light of short wavelength), patterns disappear again. Young's interferometer was a key tool for suggesting the wave nature of matter and radiation, from which the founders of quantum and wave mechanics could formulate a radically new physical picture.

In the present case, there is seemingly no Young's experiment to work with. Intending a geometrical figure to be light-diffracted would set a plain link to Heisemberg's principle, but we wish to go a little beyond and discuss this experiment by our geometrical means. It is useful, to this end, to step back to the Brownian–relativistic interpretation of a polymer solution, and consider an ideal "phantom chain" in a liquid. The chain vector probability density is described by Fick's heat-diffusion equation in the monomer number, admitting the Gaussian distribution as a fundamental solution, the variance of which providing the statistical dispersion of the monomer random walk on the polymer configuration around its mean baricenter. Identical arguments would hold for a liquid molecule diffusing in time ($N \rightarrow t$), whose statistics comes again from a heat-diffusion equation with given self-diffusion coefficient. We have seen that Brownian relativity conceives the (statistical) perturbation provided by (single) polymers in solution close to the outcome from a scattering experiment, where the liquid suggests itself to be the "radiation" source in terms of "correlation waves," diffusing anywhere around.

Thus, switching from one to two slits in Young's experiment corresponds here to a framework change, Einstein's Brownian motion to Brownian relativity. The extended heat-diffusion equation derived in the third chapter, for instance, suggests itself a phenomenology for both wave and diffusive motions whereas, in the quantum theory, Schrödinger's is just an elliptic differential equation for a wavefunction. In our picture, drawing a (or changing the) shape in an extended space is thus the analogue of opening a second slit. Since a change of units can connect the uncertainty relation for geometry to Heisemberg's, we will remain anchored to wave mechanics as much as possible, and describe probability by a wavefunction. This time, nevertheless, it will be of geometrical and topological nature, and denoted by $|\mathrm{o}\rangle$.

## 6.2 The wavefunction $|\mathrm{o}\rangle$

Such a geometrical concept brings the information enclosed by the metric tensor (determinant) into a statistical significance. The idea is simple. The shape factor, discriminating among the volumes of a multiplicity of forms, drawn in some extended space, will identify the metric tensor determinant. Alongside, to measure a (unitary) volume, will be thought of as a condition of probability conservation:

$$\int \sqrt{-\mathrm{g}}\, d\mathbf{r} \rightarrow \langle \mathrm{o}|\mathrm{o}\rangle = 1 \tag{5.42}$$

In other words, every time that a form specifies a measure of some extension, the probability density joint with it will behave as its metric tensor (determinant):

$$\sqrt{-\mathrm{g}} \rightarrow \mathrm{o}^{*}(\mathbf{r}, \tau)\mathrm{o}(\mathbf{r}, \tau) \tag{5.43}$$

for some evolutionary parameter ($\tau$). Again, this (symbolic) operation needs to be "tuned" on the base Minkowskian metric:

$$\sqrt{-\eta} \rightarrow \delta(\mathbf{r})\delta(\tau) \tag{5.44}$$

and, in this way, the Jacobian of an arbitrary coordinate transformation, i.e.:

$$\left\| \frac{\partial x'}{\partial x} \right\| \sqrt{-\mathrm{g}} = \sqrt{-\eta} \tag{5.45}$$

becomes corresponding to the heat-diffusion operator, applied to Green's function of a free Brownian particle:

$$\left\| \frac{\partial x'}{\partial x} \right\| \rightarrow \Box_D \tag{5.46}$$

We put for now this aspect aside, but are brought back to the interpretation, given in the second chapter, of the Fickian diffusion equation as a (statistical) gauge transformation, near a coordinate change in Einstein's relativity.

Seeing the metric tensor (determinant) as a probability function can already be found in a work by Carlton Frederick (1976), devoted to reconciliate quantum and relativistic mechanics. He imposed an uncertainty on the metric tensor, and exploited it to show that a quantum-mechanical description can follow accordingly. His analysis reverted another argument, on the basis of which quantum energy fluctuations would couple metric fluctuations via Einstein's field equations. To suggest that the deep roots of quantum mechanics lie in a stochastic spacetime, five postulates were stated, including Mach's principle. Frederick ascribed the statistical states of the system to the metric tensor, assuming nearly the role of a wavefunction. His third postulate of "metric probability" resembles ours, up to a proportionality constant, for $\sqrt{-\mathrm{g}}$ and $|\mathrm{o}\rangle$.

## 6.3 Geometrical wave equation (in harmonic form)

The starting point is the general form of the Einstein–Hilbert action:

$$\chi = k \int \sqrt{-\mathrm{g}} R \, d^{d}x \tag{5.47}$$

up to some constant coefficient ($k$). We will continue to see it as a generalization of the Gauss–Bonnet theorem, rewritten in terms of $|\mathrm{o}\rangle$ as a statistical relation for a mean Euler–Poincaré characteristic:

$$\chi = \langle \mathrm{o} | R | \mathrm{o} \rangle \tag{5.48}$$

This suggests a wave equation like:

$$\mathrm{R}|\mathrm{o}\rangle = \chi|\mathrm{o}\rangle \tag{5.49}$$

where the curvature scalar operator (R) is dimensionless and, from Einstein's field equations, still taken as proportional to the trace of the energy–momentum tensor (as $R \propto \mathrm{T}^{\mu}{}_{\mu}$). In seeking the operator it stands for, consider (for now) the only Hamiltonian term (the time–time component $\mathrm{T}^{00}$). In close analogy to Schrödinger's stationary equation, the above relation becomes:

$$\mathrm{K}|\mathrm{o}\rangle + \mathrm{U}|\mathrm{o}\rangle = \chi|\mathrm{o}\rangle \tag{5.50}$$

where K and U are the new operators for kinetic and potential energies. Because of the uncertainty relation for geometry, however, the way we have to deal with them is rather different. Hamilton's function ($H$) of the simplest stationary quantum problems writes as a sum of kinetic and potential energy operators. When the wavefunction is set in the position representation ($\psi(\mathbf{r})$), the kinetic energy gives rise to a Laplacian operator ($\vec{\nabla}^2$), while interactions ($U(\mathbf{r})$) act as a multiplicative term. Expressing the energy conservation produces in this case Schrödinger's (stationary) equation ($H\psi(\mathbf{r}) = E\psi(\mathbf{r})$), giving an eigenvalue problem for the total energy ($E = T + U$).

In the present case our "potential shell," function of coordinates, will have to be represented by a differential operator. It will formally take the role of that kinetic, which becomes here multiplicative. The reason is to be found in the changed meaning of physical coordinates, transforming themselves into operators, and in the static framework which we work in. Consider so the uncertainty which originates from observing a (characteristic) length ($\ell$) from a contravariant and a covariant frame:

$$\delta x^s \delta X_{s'} \geqslant \ell^2 \tag{5.51}$$

The two coordinate representations will serve to introduce (and distinguish) a couple of different scales, sharing the observation. In shape mechanics, changing scale is not an "aseptic" operation, but a part of the operator problem to work with. Dealing with coordinates as their contravariant values means that, whenever a measurement can be reduced to a displacement in a given frame, it will be set in a contravariant form. An example of a close circumstance is given by measuring the (radial) distance to Schwarzschild's singularity. While the covariant value will tend to diverge, that contravariant remains finite and is thus the only observable.

Compared to Heisemberg's, the previous relation exchanges particle momenta with contravariant coordinates, $x^s \leftrightarrow X_s$ and $p_s \leftrightarrow x^s$, bringing each square length ($s^2$) to be dimensionally representative of a geometrical action. Adopting similar commutation rules as those implied by the "correspondence principle" between Poisson's brackets ({ }) and quantum commutators ([ ]), one may write:

$$\left[x^s, x^{s'}\right] = [X_s, X_{s'}] = 0, \qquad \mathrm{i}\left[x^s, X_{s'}\right] = \ell^2 \delta^s{}_{s'} \tag{5.52}$$

In general, $X_s$ should collect any operation contributing to changing frame but, for simplicity, will be limited here to embodying translations and rotations, physically generated from linear and angular momenta, respectively. Their mathematical representations can be taken from the quantum formalism, keeping in mind they will have to be static, occurring independently, and be purely geometrical. We therefore write a translation by the gradient operator of Schrödinger's equation:

$$\mathrm{i}\vec{\mathbf{X}} = \ell^2 \vec{\nabla} \tag{5.53}$$

and a rotation by the curl operator:

$$\mathrm{i}\vec{\mathbf{R}} = \vec{\mathbf{X}} \wedge \mathbf{u} \tag{5.54}$$

To introduce the operatorial nature associated with $U = U(x^s, X_{s'})$, consider a potential energy function, expanded at second order around a (stable) equilibrium point. This will simplify the final differential equation, and get it closer to Schrödinger's. We can always rescale every coefficient (force constant, position and energy minimum), so to isolate for now its harmonic form, $U(|\mathbf{r}| = r) \sim \frac{1}{2}r^2$. As the Laplacian in spherical coordinates decomposes into $\vec{\nabla}^2 = \vec{\nabla}_r^2 - r^{-2}\vec{\mathbf{\Lambda}}$, the position $r \to \vec{\mathbf{X}} + \vec{\mathbf{R}}$ brings similarly to:

$$\mathrm{U}\big(|\vec{\mathbf{X}}| = r\big) = \frac{1}{2}\vec{\mathbf{X}}_r^2 + \mathrm{const} \tag{5.55}$$

where, in analogy to a full translation, the radial contribution:

$$\mathrm{i}\vec{\mathbf{X}}_r = \ell^2 \vec{\nabla}_r \tag{5.56}$$

is separated by the angular part, called the "Legendre's operator" ($\vec{\mathbf{\Lambda}}$), and writes $\vec{\nabla}_r \ldots = r^{-1}\frac{\partial r \ldots}{\partial r}$. We are working so with the (only) term from which Laplace's and rotational operators differ, preserving the (quadratic) dependence of the potential function. In other words, this is the contribution making the energy horocycle a (suitable and) non-trivial frame to describe a mechanics of shapes. These arguments do not change upon any radial transformation ($r \to s(r)$) and any energy shift (i.e., the minimum $\varepsilon_0$), so we take:

$$\mathrm{U} = -\ell^{-2}\vec{\mathbf{X}}_s^2 + \varepsilon_0 \tag{5.57}$$

Consider now the kinetic operator, $\mathrm{K} = \ell^{-2}\delta^{kk'}\frac{\partial}{\partial x^k}\frac{\partial}{\partial x^{k'}}$, and convert it into contravariant coordinates. This is promptly done by recalling the meaning of those covariant, acting as first derivatives, and our correspondence principle:

$$\mathrm{K} = \ell^{-2}\delta_{kk'}x^k x^{k'} = \ell^{-2}s^2 \tag{5.58}$$

so that, in the variable $\alpha = s/\ell$, our wave equation writes:

$$-\vec{\mathbf{X}}_\alpha^2|\mathrm{o}\rangle + \alpha^2|\mathrm{o}\rangle = (\chi - \varepsilon_0)|\mathrm{o}\rangle \tag{5.59}$$

namely, of that governing a quantum (isotropic) harmonic oscillator.

The differences between Schrödinger's and geometrical equations are mainly conceptual. In this harmonic approximation, the quantum kinetic energy is replaced by a "shape" operator, pointing out the intrinsic interaction form. By including higher-order (anharmonic) terms, the last equation could certainly become more complete, without adding anything to its physical significance. The potential energy yields instead the extrinsic contribution, defined in the material space of the

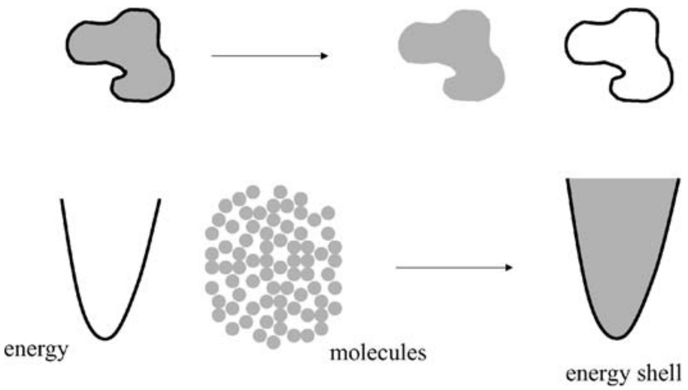

**Figure 5.8** Separating extension from shape and rebuilding a material energy shell.

molecules, and its physical meaning is a moment of inertia ($\sim s^2$). This identification, of course, is suggested by the conceptual route covered so far. We saw, in the presence of mass (or quantity of extension), that the moment of inertia is a carrier of geometrical uncertainty.

To sum up, the former equation describes the behavior of $\chi$ that comes from "shaping" a space, with given mass distribution, by a quadratic interaction form. Recall our point of departure, a Lorentz–Poincaré invariant relation:

$$\text{shape extension} = \text{measurement} \tag{5.60}$$

and compare it with the quantum-like equation, symbolically re-expressible as:

$$\text{shape} + \text{extension} = \text{measurement} \tag{5.61}$$

"Detaching" extension from shape was one of the central aims, and this is going to be illustrated by a macromolecular example. Note that, such as geometry joins extension and shape, nature separates energy and matter. These two situations are specular in shape mechanics, where energy shells are "rebuilt" and geometrical figures "destroyed" (Fig. 5.8).

## 6.4 *n*-Mer conformations versus *n*-mer configurations in polysaccharide molecules

Look at the chain conformations presented in Fig. 5.9. The main difference between "snapshots" in Figs. 5.9a and 5.9b is that the latters report some of the molecular details at the monomeric level. We know that scaling theories are (mostly) indifferent to them, and concentrates on polymer "skeletons" (Fig. 5.9a). However, from our viewpoint, we cannot help to think of the sequences of molecular shapes in Fig. 5.9b as examples of (static) co-trajectories, ruled by shape mechanics. As in the pair correlation function of liquids, the average length of a macromolecule should be described by a rotational mechanism defined at the scale of its repeat unit.

To predict non-universal properties from specific molecular configurations, the most popular approach is surely that by Flory (1969), well exposed in an important

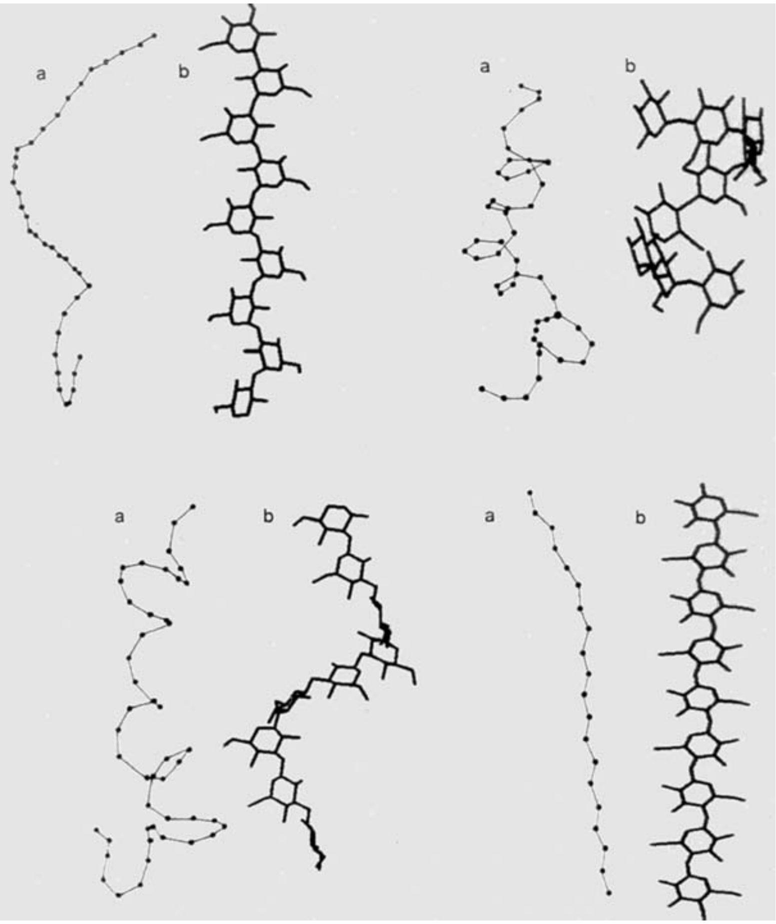

**Figure 5.9** Macromolecular snapshots (a) as co-trajectories of molecular shapes (b).

book thoroughly combining the principles of statistical mechanics with polymer chemistry. His "rotational isomeric state" approximation takes advantage of the fact that, as any conformation reflects the dihedral angle distribution along the chain skeleton, each repeating unit can be regarded as it were only existing in discrete torsional states around the energy minima (e.g., trans and gauche configurations). Limiting ourselves to the torsional mechanics of a few number of adjacent bonds has proved to suffice in order to achieve agreement between measured and calculated polymer properties. Flory's analytical method has been joined over the years to its numerical applications (i.e., Monte Carlo methods), extensively used nowadays to improve accounting for molecular details and generate useful instantaneous "snapshots" of chain shapes. The starting point is computing the repeat unit energy as a function of all relevant dihedral angles, and visualizing the energy levels in the whole configurational domain (e.g., $(-\pi, \pi]^2$) by a "Ramachandran's plot" (Fig. 5.10). It depends, in brief, on the employed molecular geometry and some

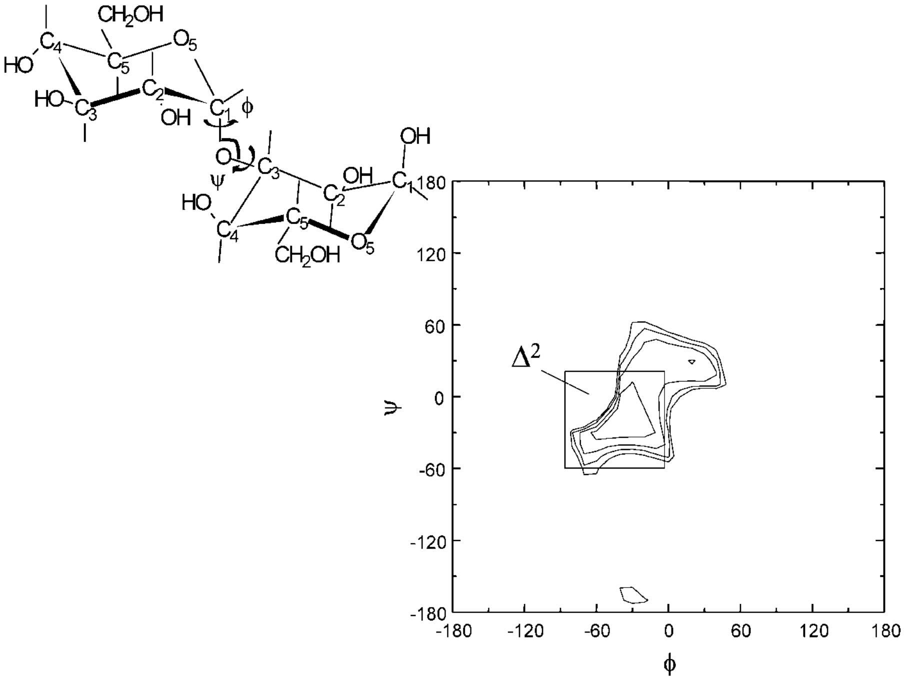

**Figure 5.10** Example (Mezzasalma et al., 2004) of Ramachandran's plot for nigerose with (average) allowed conformational area $\sim\Delta^2$.

(conventional) semiheuristic force fields, contemplating a number of adjustable parameters to model interactions and environment (e.g., solvent) effects. At this point, from the known distribution of energy levels, an ensemble of representative snapshots can be created in accordance with the Maxwell–Boltzmann statistics. When a large enough sample of (long enough) polymer molecules is finally available, one may proceed to average over it and get the mean quantities of interest.

In a previous work, however, chain conformations were interpreted as a geometrical shape "indetermined" by its end-to-end distance (or "extension"), the uncertainty of which scales with the observational (length) scale. If so, the characteristic ratio of nearly Gaussian macromolecules ($c_\infty \geqslant 1$) should be regained in terms of the (rotational) degrees of freedom, internal to the single molecules. This argument in fact, though semiheuristic and in a way unexpected, turned out to agree with numerical simulations of carbohydrate chains (Fig. 5.11). For our purposes, polysaccharides are specially suitable macromolecular systems. They exhibit Ramachandran's maps with one dominant energy minimum, two relevant dihedral angles, and rather simple molecular geometries. Furthermore, the presence of five asymmetric carbon atoms at the level of their structural units allows for a variety of isomeric states.

The geometrical scaling was described (again) by the sine-circle mechanism, applied to dihedral rotations in dimeric units. To investigate on the polymer extension as a function of the number of accessible states, all repeat units were constrained to

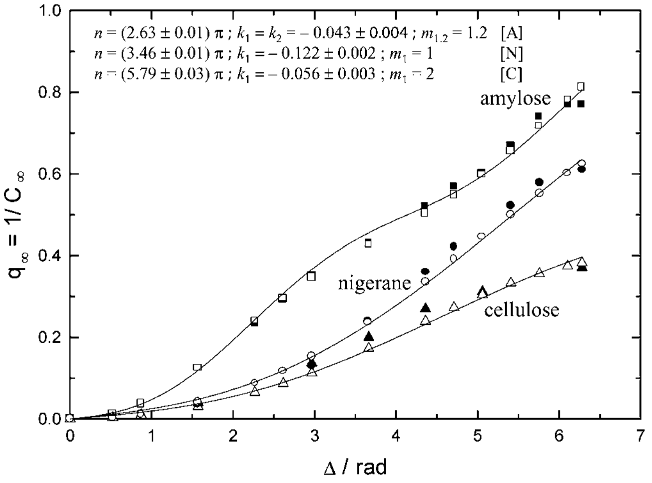

**Figure 5.11** Polymer characteristic ratio as a monomer sine-circle map (Mezzasalma et al., 2004) ($A$ = amylose, $C$ = cellulose, $N$ = nigeran).

"square–well" Ramachandran's maps, of allowed conformational area $\Delta^2$:

$$q_\infty(z) = z + \sum_i k_i \sin(2m_i \pi z) \tag{5.62}$$

where $q_\infty \equiv 1/c_\infty$, $z = \frac{\Delta}{n\pi}$ and $n, k_i \in \mathrm{R}$, $m_i \in \mathrm{Z}$, were microstructure-dependent coefficients. The only independent variable, $\Delta$, quantifies the angular range (freely) accessible to molecular torsions (i.e., the configurational entropy). We realized, pushing further the rotational analogy, that an "intrinsic" characteristic ratio could be introduced consistently as:

$$c_\emptyset \sim \frac{\mathrm{I}}{ml_b^2} \tag{5.63}$$

where $m$ $(= \sum_k m_k)$ is the total molecular mass, $l_b$ the virtual bond length and, for simplicity, the moments of inertia being referred to the (two) dihedral axes. Such as $c_\infty$ is an extrinsic statistical parameter, reflecting the polymer extension, $c_\emptyset$ is a deterministic quantity, intrinsically related to the single molecular shape.

Polysaccharides, of course, are still suitable to check our harmonic approximation, which should be regarded as a refinement of the previous work. The harmonic wave equation is known to be solved by the (radial-like) eigenfunctions:

$$|\mathrm{o}\rangle_n = C_n L_{\frac{n}{2}}^{(\frac{1}{2})}(\alpha^2) \mathrm{e}^{-\frac{\alpha^2}{2}} \tag{5.64}$$

with generalized Laguerre's polynomials $(L_k^{(m)})$ of order $k = n/2$ $(n = 0, 1, 2, \ldots)$ and normalization factor $C_n^2 = 2\pi^{-\frac{1}{2}} n!!/(n+1)!!$. We will work in the "ground state" $(n = 0)$, where the wavefunction is Gaussian $(L_0^{(m)} = 1)$, leaving the discussion of higher eigenstates for future work. What is relevant here is reminding the eigenvalues:

$$\chi_n - \varepsilon_0 = 2n + d \tag{5.65}$$

corresponding to (twice) the dimensionless energy $\bar{\varepsilon}_n = E_n/(\hbar\omega)$ of the quantum case. The contribution of I is enclosed thus into the dimensionality of the oscillator. This can be seen from the meaning of our wave equation, where the Euler–Poincaré characteristic embodies two contributions, an energy and a moment of inertia. In one dimension, $d = 1$ would stand simply for a scalar I. For any higher-dimensional particle distribution, of point masses $\{m_i\}$, I is easily generalized into the trace of $\mathrm{I}_{kk'}$, the tensor of inertia. To attain a meaningful comparison, all tensors will be calculated about the principal axes of rotation of each molecule, and set thus in diagonal form. Hence, the ground Euler–Poincaré characteristic reads:

$$\chi_0 = \mathrm{i}_0 + \varepsilon_0 \tag{5.66}$$

now with:

$$\mathrm{i}_0 \sim \frac{\mathrm{Tr}\,\mathrm{I}_{kk'}}{ml_b^2} \tag{5.67}$$

Since $\mathrm{I}_x + \mathrm{I}_y + \mathrm{I}_z = 2mr^2$, for a given configuration with radius $r$ and principal axes $(x,\ y,\ z)$, a factor 2 could be inserted in the denominator. In the harmonic approximation, odd statistical moments vanish, $\overline{(\Delta\alpha)^{2n+1}} = 0$, and:

$$\overline{(\Delta\alpha)^2} = \chi_{2n} \tag{5.68}$$

represents the family of second central moments at different $n$. The ground term can be easily approximated when the energy minimum denotes a dominant torsional state, with given mean number $(\Omega)$ of allowed configurations in its neighborhood. From the expression of the conformal line element, $|\frac{\Delta\alpha}{\Delta\varphi}| \sim \mathrm{sech}\,\varepsilon_0$, it turns out:

$$\chi_0 - \varepsilon_0 \sim \Omega\,\overline{(\Delta\varphi)^2}\,\mathrm{sech}^2\,\varepsilon_0 \tag{5.69}$$

In the Maxwell–Boltzmann statistics, the result is independent of the energy shift $(\varepsilon_0 = 0)$, thus we are left with a variance which just means an intrinsic characteristic ratio per allowed state $(\mathrm{c}_\emptyset = \mathrm{i}_0/\Omega)$:

$$\overline{(\Delta\varphi)^2} \sim \mathrm{c}_\emptyset \tag{5.70}$$

It is not difficult to recognize in the meaning of the standard deviation $(\sim\sqrt{\mathrm{c}_\emptyset})$, the reciprocal of the angular width of the square-well maps $(\Delta^{-1})$. In such terms, the uncertainty relation for geometry can be re-expressed as:

$$\sqrt{\mathrm{c}_\emptyset}\,\Delta \sim 1 \tag{5.71}$$

Ideally, for a helix molecule $(\Delta^2 \to 0)$, one has $\mathrm{c}_\emptyset \to \infty$, as expected because the molecular shape is determined. When the configurational space is fully allowed, the chain shape is a random coil, and (maximally) indetermined, thus $\sqrt{\mathrm{c}_\emptyset} \sim 1/(2\pi)$ (per turn).

**Table 5.1** Molecular details of eight saccharide molecules

| Repeat unit | $l_b$[a] | $\Omega$ | $c_\infty$[f] | $I_1$[g] | $I_2$[g] | $I_3$[g] | $c_\emptyset$ | $q_\infty$[h] |
|---|---|---|---|---|---|---|---|---|
| (1,3)-α-D-Glucose | 4.28 | 16[c] | 32÷37 | 674.00 | 941.59 | 374.46 | 5.31 | 0.87 |
| (1,4)-α-D-Galactose | 4.46 | 20.5[d] | 193÷235 | 676.00 | 392.69 | 965.37 | 6.08 | 0.14 |
| (1,4)-β-D-Galactose | 4.18 | 25[c] | 27÷42 | 676.00 | 392.69 | 965.37 | 6.22 | 0.87 |
| (1,4)-α-D-Glucose | 4.39 | 23[b] | 4.7÷10 | 674.00 | 941.59 | 374.46 | 6.33 | 4.08 |
| (1,3)-β-D-Glucose | 4.69 | 27[c] | 3.1÷6.1 | 656.30 | 425.33 | 1039.71 | 7.10 | 9.68 |
| (1,6)-β-D-Glucose | 4.16 | 36[e] | ~1.66 | 656.30 | 425.33 | 1039.71 | 7.27 | 18.07 |
| (1,6)-α-D-Glucose | 4.19 | 42[e] | ~1.48 | 674.00 | 941.59 | 374.46 | 8.17 | 20.27 |
| (1,4)-β-D-Glucose | 5.39 | 46[b] | 35÷154 | 656.30 | 425.33 | 1039.71 | 10.66 | 0.31 |

Virtual bond lengths ($l_b$) are expressed in [Å]. Moments of inertia ($I_k$) are in [amu Å$^2$].

[a] Courtesy of Urbani, R., Department of Biophysics, Biochemistry and Macromolecular Chemistry, University of Trieste.

[b] Rees, D.A., Scott, W.E., J. Chem. Soc. B (1971) 469.

[c] Whittington, S.G., Glover, R.M., Macromolecules 5 (1972) 55.

[d] Taken as the average value from references: Rees, D.A., Scott, W.E., J. Chem. Soc. B (1971) 469; Whittington, S.G., Glover, R.M., Macromolecules 5 (1972) 55.

[e] Extrapolated from the configurational entropy per residue in Burton, B.A., Brant, D.A., Biopolymers 22 (1983) 1769.

[f] Mattice, W.L., Suter, U.W., *Conformational Theory of Large Molecules*, Wiley, New York, 1994 [Table IX-4], and references therein.

[g] Estimated from the PDB files of the "Hetero-Compound Information Center" (Uppsala University), by the software referenced as Schuettelkopf, A.W., van Aalten, D.M.F., Acta Crystallogr. D60 (2004) 1355, http://xray.bmc.uu.se/hicup/, for brevity, principal axes of inertia are not reported.

[h] Taken as the average values coming from the column for $c_\infty$.

Resorting now to the same circle-map scheme employed for Δ, the intrinsic relation for $q_\infty$ refines into:

$$q_\infty = c_\emptyset^{-\frac{1}{2}} + k^* \sin\left(c_\emptyset^{-\frac{1}{2}}\right) \tag{5.72}$$

$k^*$ being the only heuristic coefficient. This equation reports probably the most "rudimental" example of a polymer shape-mechanical model. It is in essence a closed-form deterministic relation, affording a description of the "polymer extension" from geometry and energy details of the innermost "monomeric shape." We have used it here to interpret further numerical data, summarized and referenced in Table 5.1, of eight saccharide molecules of the families of (D-) galactoses and glucoses. Considering the simplicity of the approach, the few numbers of variables to work with, and the irregular behavior of $c_\infty$, the result is rather encouraging (Fig. 5.12).

## 7. OUTLOOK AND NOTES

Apart from liquids and polymer chains, the previous description is equally expected to apply to other systems. Since a general interpretation of the Euler–Poincaré characteristic has not yet given, the main problem remains to set case-by-case the shape (function) involved. In some circumstances, this identification is

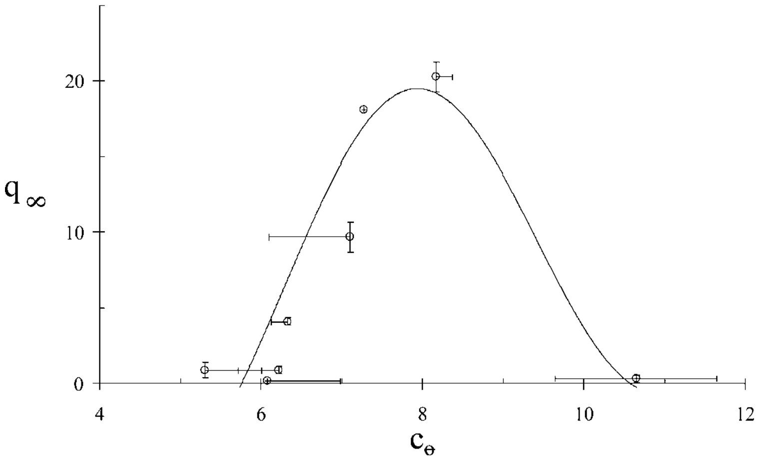

**Figure 5.12** Shape-mechanical model for the intrinsic versus extrinsic characteristic ratios (see Table 5.1). Values are rescaled by $c_{\emptyset} \to 30c_{\emptyset}$ and described with $k^* = -100$.

rather natural. Think, for instance, of a chemical reaction, where not only new forms of matter are created, but the energy dependence on the reaction path resembles (qualitatively) a sine-circle map (i.e., for the activation energy in Arrhenius's kinetics). Another analogy could be drawn, for instance, for the sequence of bases in proteins or other biopolymer molecules. Here, nothing is more natural than studying the repetitions of each unit as "rotations" on a circle, to be combined by a shape-mechanical model.

There is a further phenomenology which can be recalled, that pointed out by the shape of electron orbitals and the shape variations of electron transitions. Again, we may ask ourselves if the form of their probability functions is (shape-mechanically) related to the properties of matter at larger molecular scales. On the other hand, a former calculation already put forward that Boltzmann's constant may be expressible by other fundamental (electron) constants (Mezzasalma, 2000):

$$8\pi\varepsilon_B = 3\mathrm{R_y}\alpha_f^2 \tag{5.73}$$

i.e., Rydberg's ($\mathrm{R_y}$) and fine structure's ($\alpha_f$). The energy unit on the left stands for a thermal energy change per temperature degree, approximating well the absolute value of Boltzmann's constant, $\varepsilon_B = k_B \cdot 1 = 1.38(562) \times 10^{-23}$ J. This relation may be rewritten as an energy ratio, which depends on Bohr's radius ($a_0$), electron diameter ($d_e$) and a given measurement of length ($x$):

$$\frac{\varepsilon_B}{\varepsilon_Q} \sim \frac{d_e x^2}{a_0^3} \tag{5.74}$$

According to the uncertainty relation for geometry, it translates in energy terms the measurement of a distance ($x$) covered by an object of finite size (the electron) in an extension $\sim a_0^3$, relating the statistics of two (only apparently) separated domains.

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# SUBJECT INDEX