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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

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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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