Scaling Laws for Ideal and Real Macromolecular Chains from Relativistic Theory of Self-Diffusion in a Liquid Medium

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Scaling laws concerning a solution of linear macromolecules have been investigated by means of a relativistic theory of self-diffusion in a simple liquid. A pure liquid medium has been modeled as a four-dimensional continuum characterized by a spacetime metric, where the equation for the Brownian movement, $\overline{r^2} \propto Dt$, is interpreted as a covariant law provided by an invariant self-diffusion coefficient. The local diffusivity change due to the presence of a chain molecule has then been associated with a geometrical coordinate transformation that can be studied by using classical relativistic formalisms. Special and general theories of relativity (SR and GR) have been used to study the behavior of ideal and real chains, i.e., single coils and concentrated polymer solutions, respectively. Application of SR gives scaling laws for the average end-to-end distance and global relaxation time of an ideal macromolecule (i.e., with no excluded volume effects). Einstein equations of GR for a curved and empty space return the Stokes law and the Flory formula for a real coil in a four-dimensional space. In a concentrated dispersion, they predict a new scaling behavior (involving mean size, time, viscosity, and diffusion coefficients) of which the current values of universal exponents represent a solution in both low and high molecular weight regimes and for ideal and real chains. In the end, it is suggested a correspondence between Brownian motion and field theory, and the interpretation of a polymer chain-in-a-tube as a geodesic path.

Introduction

Polymeric fluids represent a field of extraordinary interest for both theoretical and experimental workers, and have significance for many industrial applications.[1−5] As a consequence of the unique features, their behavior is quite different from that of simple liquids.[6] Transport properties of macromolecular solutions are essentially determined by topological characteristics of the chain molecules,[7] whose analysis has long been one of the key jobs of soft condensed matter and physical chemistry. Nowadays, the progress made has become remarkable, but properly describing dynamics of macromolecules in nondilute regimes remains a challenging task in polymer physics.[8−16] Although the reptation idea[1,17] gives a successful starting point for the mechanistic interpretation of the complex motion of an entangled macromolecular chain, there is still much debate about the validity of the tube model.[8,9,18−23] Several shortcomings of the reptation theory have been pointed out by experiments conducted on different systems[8,11,14,18] (see ring and star polymers, block copolymers with spherical morphology, model ionomers, etc.) and regimes (i.e., semidilute[19,20]), and other nonreptative models for macromolecular solutions (see, polymer-mode-coupling PMC, microscopic theories, topology, etc.) have already been advanced.[9,14,16,24,25] In any case, the current literature still reports some discrepancies and open questions.[8,15,22,23,26]

In this paper, a theoretical method is proposed to explain some scaling laws arising in a macromolecular solution (i.e., average size, relaxation time, diffusion, and viscosity coefficients of monodisperse linear polymeric fluids). A coil is basically considered as a perturbation to a liquid of simple molecules, which is interpreted as a four-dimensional continuum. For a

chain molecule, time and space respectively refer to a complete renewal of the chain conformation and to the associated end-to-end distance (see, global relaxation time and average chain size). It is worth noting that the concept of a relativistic space has been very helpful to enable more general formulations of dynamical problems in other contexts of physical significance.[27] The relativistic formalism, which returns local laws essentially depending upon metric ($g_{\mu\nu}$) and matter ($T_{\mu\nu}$) tensors, consists of a formal apparatus that is well-stated geometrically and can therefore be helpful to clarify the microscopic description of macromolecular dynamics. For instance, the main limit of the reptation paradigm is that the idea of the tube configuration was not determined from any molecular theory.[9] Moreover, the connections with differential geometry and topology can also be effective in investigating other systems, where the concept of "chain in a tube" is not valid anymore[7] (i.e., melts of ring and star polymers) or exhibiting complex geometrical behaviors (i.e., micellar systems[28]). Formal and conceptual developments are organized within two basic sections, while results following from usual tensor calculations are illustrated in three appendixes. In Appendixes I and III, some basic notions of special and general theories of relativity will be recalled.

In the first section (i), the determination of the average size and relaxation time of an ideal macromolecular chain (i.e., with no excluded volume effects) has been addressed by means of a theory based on special relativity[29] (hereinafter SR). We start from a Euclidean flat space occupied by a homogeneous liquid, where each point is characterized by the self-diffusion coefficient (D) and provided with no mass. By regarding the equation for the Brownian movement[30] as a covariant law and the diffusion coefficient as an invariant property of each liquid molecule,

spacetime has been conceived like a continuum that is structured by diffusion. Conceptually speaking, this description is not completely new, since polymers share many features with random walks and diffusive mechanisms.[31,32] On the other hand, it makes possible relating the effects produced by a variation of D (i.e., replacing molecules with a macromolecule) to spatial and temporal chain characteristics. Obviously, the constraint between diffusion coefficients of chain and liquid molecules must not be intended as that between source (v) and light (c) velocities in SR. While the latter expresses a limit property of any physical phenomenon,[33] the former is weaker, only referring to the liquid system involved. This also means the covariant law introduced here (a) is solely governed by the system itself and (b) changes with the diffusional features of the liquid medium. Let D_N be the chain diffusivity, section (i) will show the following correspondences hold:

$$D_N \rightarrow D \leftrightarrow v \rightarrow 0$$

$$D_N \rightarrow 0 \leftrightarrow v \rightarrow c \qquad (1)$$

Section (ii-a) extends the previous concepts, by adopting the general theory of relativity[34] (GR) to investigate the behavior of a real coil (i.e., with excluded volume effects). The equations for a curve and empty space have been applied to a single chain in an indefinitely extended liquid medium. In the last section (ii-b), a concentrated polymer solution has been studied by employing the general Einstein equations provided with non-null matter tensor. While in (i) spacetime is described by the Minkowskian metric for the flat geometry[35] (infinite curvature), in (ii) the metric is regarded as a function of the space curvature and of some physical properties (here, diffusion and viscosity coefficients etc.). In order to follow basic assumptions of SR and GR, we will adopt a system of units where the diffusion coefficient is set to a nondimensional quantity (i.e., $6D = 1$). Last, complex mechanisms like simultaneous adsorption and aggregation processes,[36] molecular interactions (see Van der Waals and hydration forces,[37−39] etc.), solvent, hydrodynamic and dissolution effects,[40−42] percolation phenomena,[43] etc. will not be dealt with in this paper.

(i) Special Relativity and Ideal Chain. Consider a homogeneous liquid medium, where the motion of each molecule obeys the Brownian law for the mean square displacement:[44]

$$\overline{(r(t) - r_0)^2} = 6Dt \qquad (2)$$

$r = r(t)$ denoting the radial coordinate as a function of time t, $r_0 = r(0)$ the initial position, and D the diffusion coefficient. In order to measure the value assumed by D, one can imagine to follow the Brownian trajectory in a frame $O \equiv (r,t)$, located at the mass center of the motion $r = r_0$. In a reference system O' $\equiv (R, \tau)$, linked to another Brownian movement, the diffusion coefficient of the molecule which eq 2 is referring to must not change,[45] say:

$$\overline{(R(\tau) - R_0)^2} = 6D'\tau \qquad (3)$$

with $D = D'$. In this framework, we can formally summarize eqs 2 and 3 (i) by dealing with eq 2, i.e., the relation among mean square displacement, time, and diffusion coefficient, as a covariant law and (ii) by considering D as an invariant quantity for the system under investigation. These physical assumptions can be mathematically developed by making use of the same concepts and formalism employed in the special relativity[29,46] (SR, see Appendix I). Following some of the notations and
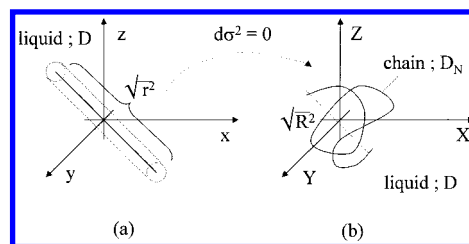

Figure 1. Scheme of the macromolecular chain as a geometrical spacetime transformation. In (a) N liquid molecules are collected in a tube and in (b) they are replaced by a chain (here ideal). Spatiotemporal features of the new conformation are constrained by the local diffusivity change, i.e., $d\sigma^2 = 0$, and can be expressed by the related Lorentz transformations (see eqs 4−10).

conventions adopted therein, we will work in $6D$ unit (in the SR language, this corresponds to setting the light velocity to c = 1) and with $r_0 = R_0 \equiv 0$. On this basis, the interval $d\sigma$ between two events in O that are infinitely close to each other can be introduced as[47]

$$d\sigma^2 = dt - d\overline{r^2} \qquad (4)$$

while invariance of diffusional intervals between two observers O and O' reads

$$d\sigma^2 = d\sigma'^2 \qquad (5)$$

Notice $d\sigma^2(\bar{D}) = 0$ for any liquid molecule and/or portion having diffusion coefficient $\bar{D} = D$. More generally, the diffusivity value that implies the invariance condition in eq 5 will depend upon the diffusional features of the medium (see section ii-a).

Consider now N molecules radially disposed in O and collected in a tube[17,48] of length Na, a being the linear molecular size (see Figure 1a). Replacing such units with a single chain, having the same chemical nature as the original liquid system, turns out to be constrained by eq 5 (see Figure 1b). This operation can be investigated (i) by relating O and O' to each configuration (i.e., molecules in a tube and chain in a tube, respectively) and (ii) by calculating the relations between displacements and times coming from the so-called Lorentz transformations[29] (i.e., between times and between lengths) associated with eqs 2−5.

As concerning time, in a system linked to O', we must have[47]

$$d\sigma^2 = dt - d\overline{r^2} = d\tau \qquad (6)$$

or else

$$d\tau = \left(1 - \frac{d\overline{r^2}}{dt}\right) dt \qquad (7)$$

The derivative on the right depends on the relative motion between O and O' (see Figure 2a,b) and so on the difference between molecular and chain diffusivities, i.e., $D - D_N$. In $6D$ unit, it turns out that

$$d\overline{r^2}/d\tau = \chi \equiv 1 - D_N \qquad (8)$$

(instead of $\chi = 1 - (D_N/D)$) and the Lorentz transformation governing timelike systems takes the form:

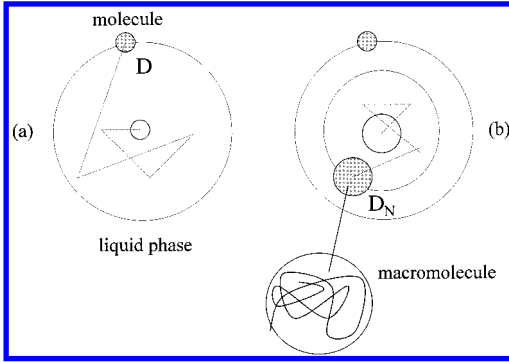$$d\tau = \frac{dt}{1 - \chi} \qquad (9)$$

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Figure 2. Scheme of the Brownian movement of (a) a single liquid molecule with diffusion coefficient D and (b) a chain molecule with diffusivity D_N.

where $\chi^{1/2}$ is here the analogy to the so-called Lorentz factor ($\beta = v/c$). To get the result for the modified mean square displacement, a comparison between spacelike intervals returns:

$$\overline{dR^2} = (1 - \chi)\,\overline{dr^2} \tag{10}$$

Notice, since $\chi = 0$ and $\chi = 1$ lead respectively to $D_N = 0$ and $D_N = 1$, the analogies made in eq 1 are consistent with eqs 8−10.

To proceed further, recall (i) the overall mobility of the single chain scales as[49] $1/N$, so that $D_N \sim 1/N$ (i.e., D/N in real units), and (ii) for an ideal system the proper quantities in O are additive in the typical length and time of single molecules,[50] say, a (the Kuhn step size for the chain) and t_0. We thus have $1 - \chi \sim 1/N$, $\overline{r^2} = (Na)^2$, $t = Nt_0$, and, after having integrated both sides of eqs 9 and 10,

$$\overline{R^2} = Na^2 \tag{11}$$

together with

$$\tau = N^2 t_0 \tag{12}$$

The last equations reproduce the classical results respectively for the end-to-end distance (i.e., random walk) and the global relaxation time (see the Kuhn-Rouse model, under the assumption of additive frictional properties of the chain) of an ideal coil.[51] The conceptual correspondence between ideal chain and ordinary random-walk without the excluded volume effect[52] makes then eqs 11 and 12 consistent with the use of a flat space (see SR), where each point is indistinguishable from each other and provided with no mass.[53] Note that the proposed approach is also suitable to describe a macromolecule that is restricted. In this case, when all bond angles (α_i) between adjacent monomers are not equally probable (say, $\overline{\cos \alpha} \neq 0$), it is possible to show eq 11 transforms into the Eyring equation, $\overline{R^2} = Na^2 f$, provided the chain diffusivity takes into account the so-called correlation factor f ($= (1 + \overline{\cos \alpha})/(1 - \overline{\cos \alpha})$) through the position $D_N \to f D_N$.[54]

On the other hand, eqs 4−10 admit a more rigorous generalization in terms of standard tensor algebra. Following the basic language of SR, we first need to define the infinitesimal interval $d\sigma$ in eq 4 as[55]

$$d\sigma^2 = dt_*^2 - d\rho^2 = -\eta_{\mu\nu} dx^\mu dx^\nu \tag{13}$$

with $x^i = (t_*, x, y, z)$, $t_* \equiv t^{1/2}$, $\rho^2 \equiv \overline{r^2} = x^2 + y^2 + z^2$ and where the quantity at the right side is a sum written in the usual Einstein

notation (sum from μ, $\nu = 0$−3 over repeated indexes). The tensor specified by $\eta_{ii} = (-1, 1, 1, 1)$ and $\eta_{i \neq j} = 0$ represents the Minkowskian metric for the flat geometry.

Although stating mathematically a relativistic theory for the problem under consideration is not the task of the present work, Appendix II reports a first extension of eqs 4−10 according to a more general writing of the spacetime transformations involved. Other formal details can be exhaustively found elsewhere.[47,53,55]

(ii) General Relativity and Real Chain. *(a) Single Chain.* To deal with real macromolecules, where each segment has its own finite volume (see the excluded volume effect), the hypothesis of a flat space taken from SR is no longer applicable. Following the basic concepts of GR, we can describe the excluded volume effect for a single coil as a spacetime curvature and therefore employ the relativistic equations in the limit of a curved and empty space. To this end, recall first the mathematical form of the Einstein equation in GR (see Appendix III):[33−35,47,55,56]

$$R_{\mu\nu} - \frac{g_{\mu\nu} R}{2} = \phi\, T_{\mu\nu} \tag{14}$$

where $R_{\mu\nu}$ denotes the components of the Ricci tensor, $g_{\mu\nu}$ is the metric for the Riemannian geometry, R is the curvature scalar, ϕ is a constant value ($= -8\pi G$ in GR, G being the gravitational constant), and $T_{\mu\nu}$ is the matter tensor, namely, the terse summary of the interaction-momentum densities and currents in a material medium.

In investigating a real system, we take into consideration an isotropic chain. Accordingly, the most general metric tensor in polar coordinates (ρ, θ, φ) that can be adopted is[55]

$$d\sigma^2 = b(\rho)\, dt_*^2 - a(\rho)\, d\rho^2 - \rho^2 (d\theta^2 + \sin^2 \theta\, d\varphi^2) \tag{15}$$

where the radial coordinate stands now for the root mean square (see eq 13). The dependences $a = a(\rho) \equiv g_{\rho\rho}$ and $b = b(\rho) \equiv -g_{tt}$ follow from the implied relativistic equations and, when an empty space is considered, i.e., $T_{\mu\nu} = 0$ and $R/\phi \equiv T^\mu{}_\mu = 0$, it is well-known eq 14 reduces to[53]

$$R_{\mu\nu} = 0 \tag{16}$$

Appendix II illustrates the main mathematical developments leading to the so-called Schwarzschild solution of eq 16, which here is specified by[55]

$$b(\rho) = 1 + C/\rho \tag{17}$$

where C is a constant value and b obeys

$$a(\rho)b(\rho) = 1 \tag{18}$$

To proceed, consider the analogies in eq 1. First, replacing the chain by liquid molecules implies $D_N \to D$ and so the condition $g_{\mu\nu} \to \eta_{\mu\nu}$ (here equivalent to $a = b \equiv 1$) must hold. Second, when $D_N \to 0$, the Schwarzschild solution predicts that a has to diverge.[55,56] Such requirements are satisfied by (in real unit) $a \sim D/D_N$, so that

$$D_N \to D \leftrightarrow a \to 1$$

$$D_N \to 0 \leftrightarrow a \to \infty \tag{19}$$

The other component follows from eq 18

$$b(\rho) \sim D_N \tag{20}$$

and points out a constraint for average size and diffusivity of the chain, i.e., from eq 17

$$\rho(D_N - 1) = C \qquad (21)$$

Considering eq 21 in the limit of $D \ll D_N$ returns $\rho D_N \simeq C$, which is the original Stokes−Einstein law,[45] provided $C = (k_B T)/(6\pi\eta_l)$, where k_B is the Boltzmann constant, T the absolute temperature, and η_l the viscosity of the simple liquid.

On the other hand, the metric tensor change $\eta_{\mu\nu} \to g_{\mu\nu}$ induced by the transition from ideal to real coils can be related to the energy in the four-dimensional space. Observing that two spacelike observers, $d\theta = d\varphi = dt_* = 0$, are joined by $d\rho^2 = g_{\rho\rho}d\rho'^2$ and the elastic energy depends on ρ^2 allows to define the energy density associated with the radial direction as $\epsilon_\rho \sim \rho^2/\rho'^2 \sim g_{\rho\rho}$.[43] Then, the analogous quantity for the temporal dimension takes the form $\epsilon_t \sim t^2/t'^2 \sim g^2_{tt}$, since the timelike transformation is[56] $dt_*^2 = g_{tt}dt_*'^2$ and $t_* = t^{1/2}$. If one applies the condition required by the Schwarzschild solution in equation 18, the total quantity $\epsilon = \epsilon_\rho + \epsilon_t$ reads

$$\epsilon = g_{\rho\rho} + g_{\rho\rho}^{-2} \qquad (22)$$

so that, substituting the actual macromolecular size, ρ, and the end-to-end distance of an ideal coil, $\rho' = N^{1/2}a$, yields

$$\epsilon(N, \rho) \sim \frac{\rho^2}{Na^2} + \frac{N^2 a^4}{\rho^4} \qquad (23)$$

The first term on the right identifies the usual elastic energy (in $k_B T$ unit) that can be derived from the ideal chain result (see eq 11).[54] The other contribution descends from the chain reality, here represented by the curved space, and is formally equal to the repulsive energy coming from the excluded volume effect in a real coil. In fact, the energy minimum given by $(\partial\epsilon/\partial\rho)_N = 0$ is equivalent to set the following scaling law:

$$\rho \sim N^{1/2} \qquad (24)$$

which coincides with the radius of a real chain in a four-dimensional space predicted by the Flory formula.[1,31]

(b) Concentrated Polymer Solutions. In this case $T_{\mu\nu} \neq 0$ and the equations to solve do not take a simplified form:

$$R_{\mu\nu} - \frac{g_{\mu\nu}R^2}{2} = \phi T_{\mu\nu} \qquad (25)$$

It can be shown (see Appendix III, with $\phi \equiv 1$) that the relation between the metric elements a and b turn out to be

$$b'' = \frac{b'}{2}(\psi_b + \psi_a) + \frac{b'}{\rho}\left(\frac{\psi_a}{\psi_b} - 1\right) \qquad (26)$$

provided with

$$\psi_a = \frac{2T_{\rho\rho} + \rho T'_{\rho\rho} + \psi_b/\rho + \psi'_b}{\rho T_{\rho\rho} + 1/\rho + \psi_b} \qquad (27)$$

where

$$*' \equiv \frac{d*}{d\rho}$$

and

$$\psi_* \equiv \frac{d \ln *}{d\rho}$$

Equation 26 can be reduced first by introducing the variable $z(\rho) = \psi_b$

$$2z' = \psi_a(\rho) z - z^2 + \frac{2}{\rho}(\psi_a - z) \qquad (28)$$

and then using the position $z\xi = 1$

$$\xi' = \left(\frac{1}{2} + \frac{\xi}{\rho}\right)(1 - \psi_a\xi) \qquad (29)$$

In the following, the limit of large ρ values will be taken into consideration. Accordingly, we neglect ξ/ρ

$$\xi' \simeq \frac{1}{2}(1 - \psi_a\xi) \qquad (30)$$

and set, from eq 27,

$$\psi_{a\infty}(\rho) \equiv \lim_{\rho\to\infty} \psi_a(\rho) = (\ln T_{\rho\rho})' \qquad (31)$$

Let

$$\mu(\rho) = e^{(1/2)\int\psi_a d\rho'} \qquad (32)$$

and C' an arbitrary constant value, eq 30 can be rewritten as

$$\mu \, \xi(\rho) = \frac{1}{2}\int\mu \, d\rho' + C' \qquad (33)$$

so that

$$\frac{z}{2} = \frac{\mu}{C'' + \int\mu(\rho')\,d\rho'} \qquad (34)$$

with $C'' \equiv 2C'$. Choosing $|C''| \gg |\int\mu \, d\rho'|$ and making use of eq 31 implies

$$\mu(\rho) \sim T_{\rho\rho}^{1/2} \qquad (35)$$

and, from eqs 32 and 34, one gets

$$b(\rho) \propto e^{c''\int T_{\rho\rho}^{1/2} d\rho'} \qquad (36)$$

Since $c'' = 2/C''$ and $|c''\int T_{\rho\rho}^{1/2}d\rho| \ll 1$, we can expand the right side of eq 36 to first order in c'':

$$b(\rho) \propto 1 + c''\int T_{\rho\rho}^{1/2}\,d\rho' + O(c''^2) \qquad (37)$$

When a concentrated solution of chain molecules replaces the simple liquid, the invariance condition for intervals in eq 5 becomes, referring to a medium that has diffusion coefficient equal to D_N,

$$d\sigma^2(D_N) = 0 \qquad (38)$$

while the diffusivity of the whole medium $D*$ becomes the perturbation to D_N. This means we have to consider the positions pointed out by

$$D \to D_N \qquad D_N \to D* \qquad (39)$$

Let $\lambda = \lambda(n)$ be a monotonically increasing function of the polymer concentration n, i.e., $\lambda, n \in [0,1]$ with $\lambda(0) = 0$ and $\lambda(1) = 1$ and $D^* = nD_N + (1 - n)D$ be an ideal Darken law,[57] we can write

$$b(\rho) \sim \frac{D^*}{D_N} = \lambda + \frac{1 - \lambda}{D_N} \qquad (40)$$

A comparison between eqs 37 and 40 in the limit of $n \simeq 1$ (highly concentrated systems) allows us to conclude that, for any choice $\lambda = \lambda(n)$,

$$1/D_N \sim \int T_{\rho\rho}^{1/2} d\rho' \qquad (41)$$

once the proportionality constant in eq 36 is set to unity and, consistently with eq 37, $c'' \equiv 1 - \lambda \ll 1$. Note that eq 41 agrees with usual phenomenological considerations, since chain diffusivity and energy density are respectively expected to decrease and increase with increasing segment number N.

For evaluating $T_{\rho\rho}$, we restrict ourselves to the contribution coming from the viscosity η_N. In fact, since we are working in diffusion coefficient unit, $T_{\rho\rho}$ identifies the medium viscosity (instead of the medium pressure, see GR):[55]

$$T_{\rho\rho} \sim \eta_N \qquad (42)$$

By working out eq 41 and keeping in mind the time τ can be obtained from

$$\tau = \frac{\rho^2}{D_N} \qquad (43)$$

one can derive the scaling laws implied. The large segment number provides a good approximation to a continuous space.[31] Substituting the average size, $\rho \sim N^\nu$, the diffusion coefficient $D_N \sim N^\delta$ and the viscosity $\eta_N \sim N^\epsilon$, eq 41 reads

$$N^{-\delta} \sim \int N^{\epsilon/2} N^{\nu-1} dN \qquad (44)$$

or, equivalently,

$$\frac{\epsilon}{2} + \nu + \delta = 0 \qquad (45)$$

Let then $\tau \sim N^\sigma$, using eqs 43 and 45 gives us

$$\sigma = \frac{\epsilon}{2} + 3\nu \qquad (46)$$

Results and Discussion

Equations 45 and 46 provide new scaling behavior. The first relation can be considered a sort of modified Stokes-Einstein law, $\rho D_N(\eta_N)^{1/2} \sim 1$, while the second equation, $\tau \sim \rho^3(\eta_N)^{1/2}$, relates the mean size, time, and viscosity coefficient. Taking into account the universal exponents currently adopted to describe the behavior of a monodisperse linear polymer melt, one can find that eqs 45 and 46 are satisfied in both low and high molecular weight regimes, i.e., above and below some crossover critical value (N_c) at which scaling of transport coefficients changes dramatically (see entanglement effects). In fact, the theoretical values predicted by reptational theories are[1,21,48,58] $\epsilon = 1$, $\delta = -1$, and $\sigma = 2$ when $N < N_c$ and $\epsilon = 3$, $\delta = -2$, and $\sigma = 3$ for $N > N_c$. If we set[51] $\nu = 1/2$ (see eqs 11 and 24) eqs 45 and 46 are satisfied in both cases.

It is known, nevertheless, that the most important rheological theories are at odds with experimental measurements performed over a vast range of molecular weights. Real coefficients, extrapolated from scaling behaviors of many polymeric species when N exceeds the crossover value, seem instead to be ranging in[21,58] $\epsilon \simeq \sigma \simeq (3.3 \div 3.7)$, with $\langle\epsilon\rangle = 3.4$. Inserting these data in eq 46, we derive $\nu \simeq (0.55 \div 0.62)$ and $\langle\nu\rangle = 0.57$, which are in good agreement with experimental results coming from light scattering experiments[1] ($\nu \simeq 0.55 \div 0.57$) and with the values predicted by numerical simulations of real coils in three dimensions[52] ($\nu \simeq 0.588$) and by Flory[32] ($\nu = 0.6$). Substituting the obtained ν-range in eq 45 returns then $-\delta \sim (2.2 \div 2.5)$ and $\langle\delta\rangle \simeq -2.27$, whereas very recently, in contrast to the common belief that in a real melt $D_N \sim N^{-2}$ for $N > N_c$, it has been suggested $-\delta \simeq (2.2 \div 2.4)$ and $\langle\delta\rangle \simeq -2.28$.[22]

In the end, the achieved covariant scaling laws turn out to be in good agreement with the basic phenomenology of polymer chemistry. Further developments of the proposed theory are now needed (i) to achieve a new scaling law completing eqs 45 and 46, (ii) to deal with other physical phenomena (i.e., thermal, dielectric, magnetic, etc.) and (iii) to investigate other concentration regimes (i.e., semidilute). This can be done by a better understanding of the invariance condition for D (i.e., eqs 2−5), whose weak character (in comparison with the invariance of c in SR, see postulate II in Appendix I) would point out another interesting consequence of the presented link, between relativistic field theory and polymer physics and chemistry.

Conclusions

1. Interpreting a simple liquid as a four-dimensional space ruled by a covariant Brownian movement and an invariant diffusion coefficient allows us to deal with a local diffusivity change based on a relativistic theory. Replacing liquid molecules with a macromolecular chain becomes a coordinate transformation that can be investigated by applying special (SR) and general (GR) theories of relativity, according to the geometrical nature of the space. The local nature of the proposed approach, which is geometrically well stated, can represent a promising way to describe microscopic transport properties of macromolecular solutions and other complex media.

2. Application of SR gives the end-to-end distance and global relaxation time of a single ideal chain. In this case, it turns out that the quantity $1 - D_N/D$ takes the place of the Lorentz factor in SR (i.e., v/c), so that $D_N \to D$ and $D_N \to 0$ yield the previously supposed conditions of nonrelativistic (i.e., simple liquid) and relativistic (i.e., polymeric fluid) spaces. The obtained results are consistent with the use of a flat space, where any molecule possesses no mass (i.e., with no excluded volume effect).

3. Describing the excluded volume effect as due to a spacetime curvature and applying the GR equations for a curved and empty space with a Schwarzschild metric imply the Stokes−Einstein law and the Flory formula for a four-dimensional real coil.

4. The general Einstein equations (namely, with non-null matter tensor) provide a new scaling behavior for the main quantities of a monodisperse linear polymer melt. It is satisfied, in both the low and high molecular weight regimes and for ideal and real behaviors, by universal exponents for the scaling laws of average size, characteristic time, diffusion, and viscosity coefficients. It then agrees with recent studies concerning highly entangled macromolecular solutions, which contradict the common belief that the chain self-diffusion scales as N^{-2}.

5. It is suggested that diffusional phenomena and scaling laws in polymer physics and chemistry can be recast as covariant laws in the framework of a weak relativistic field theory, where

the invariance constraint for D is not a limit condition, but a feature depending on the system under consideration.

Appendix I

We recall here the basic concepts of SR and the related Lorentz transformations.[29,46,47] In 1905 A. Einstein advanced two fundamental postulates: (I) The laws of physics are the same in all inertial frames of reference. (II) The velocity of light in vacuum has the same constant value in all inertial frames and is independent of the motion of the light source.

Consider two inertial frames $O = \{x, y, z, t\}$ and $O' = \{x', y', z', t'\}$ such that O' is moving along the positive direction of the common axis of the two frames, with a constant speed v relative to O. Suppose then a point source, fixed at the origin of O, emits a light pulse traveling in all directions with velocity c. At a time t, the Cartesian equation of the spherical wave front of radius ct and centered at the origin of O is

$$x^2 + y^2 + z^2 - c^2 t^2 = 0 \tag{47}$$

According to axioms I and II, the spherical wave front seen by an experimenter in O' must obey the equation

$$x'^2 + y'^2 + z'^2 - c^2 t'^2 = 0 \tag{48}$$

Linearity of the transformations between O and O' implies

$$x^2 + y^2 + z^2 - c^2 t^2 = \chi(v)\,(x'^2 + y'^2 + z'^2 - c^2 t'^2) \tag{49}$$

where χ may depend on v but does not depend upon space and time coordinates. Requiring that any movement along the x-axis does not change direction after the coordinate transformation, a simple calculation can prove that

$$x' = \chi\frac{x - vt}{(1 - \beta^2)^{1/2}}, \quad y' = \chi y, \quad z' = \chi z, \quad t' = \chi\frac{t - x\beta/c}{(1 - \beta^2)^{1/2}} \tag{50}$$

with $\beta = v/c$. To proceed further, we observe the frame O moves with a velocity $-v$ relative to O', and so we must have

$$\chi(-v)\,(x^2 + y^2 + z^2 - c^2 t^2) = x'^2 + y'^2 + z'^2 - c^2 t'^2 \tag{51}$$

or else

$$\chi(v)\chi(-v) = 1 \tag{52}$$

If the space is isotropic, χ can only depend on the magnitude of velocity and not on its direction, i.e., $\chi^2 = 1$ and $\chi = \pm 1$. For $v = 0$ and $t = 0$, the solution $\chi = -1$ returns $x'^2 = x^2$, which contradicts $x'^2 = x^2$, and so it must be rejected. The distance ds is defined by setting $\chi = 1$ in eq 49

$$ds^2 = dx^2 + dy^2 + dz^2 - c^2 dt^2 \tag{53}$$

which denotes the spacetime interval between two point in the four-dimensional space and is an invariant, i.e., $ds^2 = ds'^2$.

Lorentz contraction and time dilatation are now immediate consequences of eq 50 with $\chi = 1$. Consider a measuring rod which is at rest relative to O' and is placed parallel to the x'-axis. The end points of the rod have constant coordinates and

the length of the rod in O' is $l_0 = x'_2 - x'_1$. According to the first part of eq 50, the motion of the two end points relative to O is determined by

$$x'_2 = \frac{x_2(t) - vt}{(1 - \beta^2)^{1/2}}, \quad x'_1 = \frac{x_1(t) - vt}{(1 - \beta^2)} \tag{54}$$

and so

$$l = l_0 (1 - \beta^2)^{1/2} \tag{55}$$

where $l = x_2(t) - x_1(t)$. By a similar argument, we can show from the last part of eq 50

$$t = (1 - \beta^2)^{-1/2}\tau \tag{56}$$

where τ and t are respectively the proper time of a clock at rest in O' and the corresponding time interval measured by a clock located in O, moving with the velocity v relative to O'.

In section (i), the same basic concepts will be applied to the diffusion law in eq 2 according to the position $(r^2, t, v, c) \rightarrow (\bar{r}^2, t^{1/2}, D_N, D)$.

Appendix II

In all generality, a Lorentz transformation from $O \equiv \{x^\mu\}$ to $O'\ \{x^{\mu'}\}$ reads[53,55,56]

$$x^{\mu'} = \Lambda^\mu{}_\nu x^\nu + b^\mu \tag{57}$$

b^μ and $\Lambda^\mu{}_\nu$ being constant terms, the latter obeying

$$\eta_{\mu\nu} = \Lambda^{\mu'}{}_\mu \Lambda^{\nu'}{}_\nu\, \eta_{\mu'\nu'} \tag{58}$$

where $\eta_{\mu\nu}$ is the Minkowski metric in eq 13. Consider an event that is linked to O, i.e., $dx^\nu = 0$. For one observer O', which moves with different diffusion coefficient, eqs 57 and 58 imply

$$dx^{\mu'} = \Lambda^\mu{}_0\, dt^{1/2} \tag{59}$$

and

$$dt^{1/2'} = \Lambda^0{}_0\, dt^{1/2} \tag{60}$$

Dividing $dx^{\mu'}$ by $dt^{1/2'}$ gives us $\chi^{1/2}$ (see eq 8) and

$$\Lambda^\mu{}_0 = \chi^{1/2}\Lambda^0{}_0 \tag{61}$$

so that, as

$$\Lambda^\mu{}_0 \Lambda^\nu{}_0\, \eta_{\mu\nu} = -(\Lambda^0{}_0)^2 + \sum_1^3 (\Lambda^k{}_0)^2 = -1 \tag{62}$$

we have

$$\Lambda^0{}_0 = (1 - \chi)^{-1/2} \tag{63}$$

and

$$\Lambda^\mu{}_0 = \left(\frac{1}{\chi} - 1\right)^{-1/2} \tag{64}$$

The other elements $\Lambda^\mu{}_\nu$ are defined unless of an arbitrary rotation. However, one can set

$$\Lambda^\lambda{}_t = (1 - \chi)^{-1/2} \tag{65}$$

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and

$$\Lambda^0_t = \left(\frac{1}{\chi} - 1\right)^{-1/2} \tag{66}$$

which, together with eqs 63 and 64, represent the general transformation laws pointed out by eqs 9 and 10.

Appendix III

We recall now some basic notions of GR.[44,53,56,57] The fundamental postulate is the principle of equivalence of gravitation and inertia (EP), which states that "At every spacetime point in an arbitrary gravitational field, it is possible to choose a locally inertial coordinate frame such that, within a sufficiently small region of the point in question, the laws of nature take the same form as in unaccelerated Cartesian coordinate systems in the absence of gravitation". An alternative version of EP is known as the principle of general covariance. It postulates that a physical equation holds in a general gravitational field if two conditions are met: (1) The equation holds in the absence of gravitation, i.e., it agrees with the laws of SR when the metric tensor $g_{\mu\nu}$ equals the Minkowski tensor $\eta_{\mu\nu}$ and when the affine connection $\Gamma^\mu_{\nu\gamma}$ (see next eq 74) vanishes. (2) The equation is generally covariant; i.e., it preserves its form under a general coordinate transformation $x \rightarrow x'$.

The GR language is formulated within the frame of the non-Euclidean geometry and makes use of the tensor algebra. According to EP, there is always a free-falling coordinate system $\{\xi^i\}$ in which the motion equation is that of a straight line, and the proper time is given by

$$ds^2 = -\eta_{\mu\nu} \, dx^\mu \, dx^\nu \tag{67}$$

In a general arbitrary coordinate system $\{x^i\}$, we have

$$ds^2 = -g_{\mu\nu} \, dx^\mu \, dx^\nu \tag{68}$$

where

$$g_{\mu\nu} = \left(\frac{\partial \xi^\alpha}{\partial x^\mu}\right)\left(\frac{\partial \xi^\beta}{\partial x^\nu}\right) \eta_{\alpha\beta} \tag{69}$$

Briefly, the Einstein field equations can be derived from a principle of stationary action, i.e., $\delta I = 0$, and one obtains

$$\frac{1}{16\pi G} \delta \int g^{\mu\nu} R_{\mu\nu} (-g)^{1/2} \, d^4x = -\delta I_F \tag{70}$$

the term on the left side being the contribution of gravity (G is the gravitational constant) and I_F indicating the part of the action function due to all other fields. In the end, one obtains

$$R_{\mu\nu} - \frac{g_{\mu\nu} R}{2} = 8\pi G \, T_{\mu\nu} \tag{71}$$

where $R_{\mu\nu}$ denotes the components of the Ricci tensor:

$$R_{\mu\kappa} = \frac{\partial \Gamma^\lambda_{\mu\lambda}}{\partial x^\kappa} - \frac{\partial \Gamma^\lambda_{\mu\kappa}}{\partial x^\kappa} + \Gamma^\eta_{\mu\lambda} \Gamma^\lambda_{\kappa\eta} - \Gamma^\eta_{\mu\kappa} \Gamma^\lambda_{\lambda\eta} \tag{72}$$

R is the curvature scalar, given by the trace of the Ricci tensor

$$R \equiv R^\mu_{\ \mu} = g^{\mu\nu} R_{\mu\nu} \tag{73}$$

and $T_{\mu\nu}$ is the matter tensor. In eq 72, $\Gamma_{\mu\nu}$ specifies the elements

of the Levi−Civita tensor (or affine connection),

$$\Gamma^\lambda_{\mu\nu} = \frac{1}{2} g^{\lambda\rho} \left(\frac{\partial g_{\rho\mu}}{\partial x^\nu} + \frac{\partial g_{\rho\nu}}{\partial x^\mu} - \frac{\partial g_{\mu\nu}}{\partial x^\rho}\right) \tag{74}$$

while the Ricci tensor follows from the Riemann tensor ($R_{\lambda\mu\nu}$) according to $R_{\mu\nu} = g^{\lambda\iota} R_{\lambda\iota\mu\nu}$.

Appendix IV

Consider the Einstein eq 16 for the empty space. To express the elements of the Ricci tensor, we first need those of the affine connection and those of the inverse of $g_{\mu\nu}$. In this case the metric is diagonal, and so $g^{\mu\nu} g_{\mu\nu} = 1$, where, $g_{\rho\rho} = a$, $g_{tt} = -b$, $g_{\theta\theta} = \rho^2$, and $g_{\varphi\varphi} = \rho^2 \sin^2 \theta$ (see eqs 13 and 15). This returns the nonvanishing components given by

$$\Gamma^\rho_{\rho\rho} = \frac{1}{2}\psi_a \quad \Gamma^\rho_{\theta\theta} = -\frac{\rho}{a} \quad \Gamma^\rho_{\varphi\varphi} = -\frac{\rho \sin \theta}{a} \quad \Gamma^\rho_{tt} = \frac{b'}{2a} \tag{75}$$

$$\Gamma^\theta_{r\theta} = \Gamma^\theta_{\theta r} = \frac{1}{\rho} \quad \Gamma^\theta_{\varphi\varphi} = -\sin\theta\cos\theta \tag{76}$$

$$\Gamma^\varphi_{r\varphi} = \Gamma^\varphi_{r\varphi} = \frac{1}{\rho} \quad \Gamma^\varphi_{\varphi\theta} = \Gamma^\varphi_{\theta\varphi} = \cot\theta \tag{77}$$

$$\Gamma^t_{tr} = \Gamma^t_{rt} = \frac{1}{2}\psi_b \tag{78}$$

$*' \equiv d*/d\rho$ indicating the derivative along the ρ direction and $\psi_* \equiv d \ln */d\rho$. If one inserts eqs 75−78 in eq 72, then has

$$R_{tt} = -\frac{b''}{2a} + \frac{b'}{4a}(\psi_a + \psi_b) - \frac{b'}{\rho a}$$

$$R_{\rho\rho} = \frac{1}{2}\psi_{b'}\psi_b - \frac{1}{4}\psi_b (\psi_a + \psi_b) - \frac{1}{\rho}\psi_a$$

$$R_{\theta\theta} = \frac{\rho}{2a}(\psi_b - \psi_a) + \frac{1}{a} - 1$$

$$R_{\varphi\varphi} = \sin^2 \theta \, R_{\theta\theta} \tag{79}$$

and $R_{\mu\neq\nu} = 0$. On the basis of eq 79, it can be proved that the solution of eq 16 follows by coupling $R_{\rho\rho} = R_{\theta\theta} = R_{tt} = 0$ to

$$\frac{R_{\rho\rho}}{a} + \frac{R_{tt}}{b} + \frac{1}{\rho a} (\psi_a + \psi_b) = 0 \tag{80}$$

which requires, for a metric approaching the Minkowski tensor, i.e., $\lim_{\rho\to\infty} g_{\mu\nu} = \eta_{\mu\nu}$, the condition

$$a(\rho)b(\rho) = 1 \tag{81}$$

From the vanishing of $R_{\rho\rho}$ and $R_{\theta\theta}$, we obtain in the end

$$b(\rho) = 1 + \frac{C}{\rho} \tag{82}$$

C being a constant value.

Appendix V

To solve eq 14, we can adopt the components $R_{\mu\nu}$ developed in the previous Appendix II (see eq 79). Then, from eq 73, one has

$$R = \frac{\psi_b}{a}\left(\psi_{b'} + \frac{2}{\rho} - \frac{\psi_b}{2} - \frac{\psi_a}{2}\right) + \frac{2}{\rho}\left(\frac{1}{\rho a} - \frac{1}{\rho} - \frac{\psi_a}{a}\right) \tag{83}$$

and, let $G_{\mu\nu} \equiv R_{\mu\nu} - (1/2)g_{\mu\nu}R$, the first members on the left of eq 14 are

$$G_{tt} = \frac{b}{\rho}\left(\frac{1}{\rho a} - \frac{1}{\rho} - \frac{\psi_a}{a}\right)$$

$$G_{\rho\rho} = \frac{a-1}{\rho^2} - \frac{\psi_b}{\rho}$$

$$G_{\theta\theta} = \frac{\rho\psi_b}{2a}\left(\frac{\psi_a}{\psi_b} - 1 - \rho\psi_{b'} + \frac{\rho\psi_b}{2} + \frac{\rho\psi_a}{2}\right)$$

$$G_{\varphi\varphi} = \frac{(\rho \sin\theta)^2 \psi_b}{2a}\left(\frac{\psi_a}{\rho\psi_b} - \frac{1}{\rho} - \psi_{b'} + \frac{\psi_b}{2} + \frac{\psi_a}{2}\right) \quad (84)$$

with $G_{\mu\neq\nu} = 0$. Equating $G_{\mu\nu} = T_{\mu\nu}$ (here we set $\phi = 1$) and employing the limit of large ρ values, the equation system becomes equivalent to solve

$$b'' = \frac{b'}{2}(\psi_b + \psi_a) + \frac{b'}{\rho}\left(\frac{\psi_a}{\psi_b} - 1\right) \quad (85)$$

where we set $T_{\mu\neq\nu} = T_{\theta\theta} = T_{\varphi\varphi} = T_{tt} \simeq 0$ and with, from $G_{\rho\rho} = T_{\rho\rho}$:

$$\psi_a = \frac{2T_{\rho\rho} + \rho T'_{\rho\rho} + \psi_b/\rho + \psi'_b}{\rho T_{\rho\rho} + 1/\rho + \psi_b} \quad (86)$$

Note that $G_{\varphi\varphi} = 0$ is equivalent to $G_{\theta\theta} = 0$, while $\rho \to \infty$ implies $G_{tt} = 0$ identically.

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