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Statistics of Polymer Solutions from Scaling Concepts for Geometry and Relativistic Self-Diffusion in Liquids

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STATISTICS OF POLYMER SOLUTIONS FROM SCALING CONCEPTS FOR GEOMETRY AND RELATIVISTIC SELF-DIFFUSION IN LIQUIDS

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Basic results on conformational statistics of polymer solutions are derived from recent scaling concepts for geometry and a relativistic picture for Brownian self-diffusion in liquid media. Any chain conformation is interpreted as a geometrical state affected by its end-to-end dimension, which here denotes the mean deviation between geodesic paths diffusing in the relativistic liquid phase. Statistical polymer length distributions solve an undulatory equation in non-Euclidean manifolds for coil extension and shape. When length scale is vanishing, the size scaling is found again in terms of parallelism angle rotations. The characteristic chain ratio identifies instead an average metric coefficient, originating topologically from rotational degrees of freedom internal to single molecules.

Keywords: Polymer solutions; Conformational statistics; Geometrical scaling laws

INTRODUCTION

Macromolecules in liquid solution undoubtedly represent a challenging and relevant scientific discipline. Its remarkable importance in technology and industry aside, the variety of experimental and theoretical frames related draws an astonishing framework, rich of ingenious solutions, shortcomings, open questions and links to other fields, only apparently far away. For instance, while the suitability of universality and reptation paradigms [1] is not completely clarified yet (see, for instance [2]), chain molecules provide quantum gravity loops with effective representations [3] and exhibit quite general connections with topology, gauge fields and knot theory [4].

From a statistical viewpoint, folding patterns of polymer solutions have been described according to several approximation levels, dealing both with energetic and geometrical parameters (see the deep and general account given in [5]). In this direction towards conformational analysis, the schematic representation in Fig. 1 immediately shows some dominant step variable, determining shape and size of a

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Building a Long Molecule in a Liquid

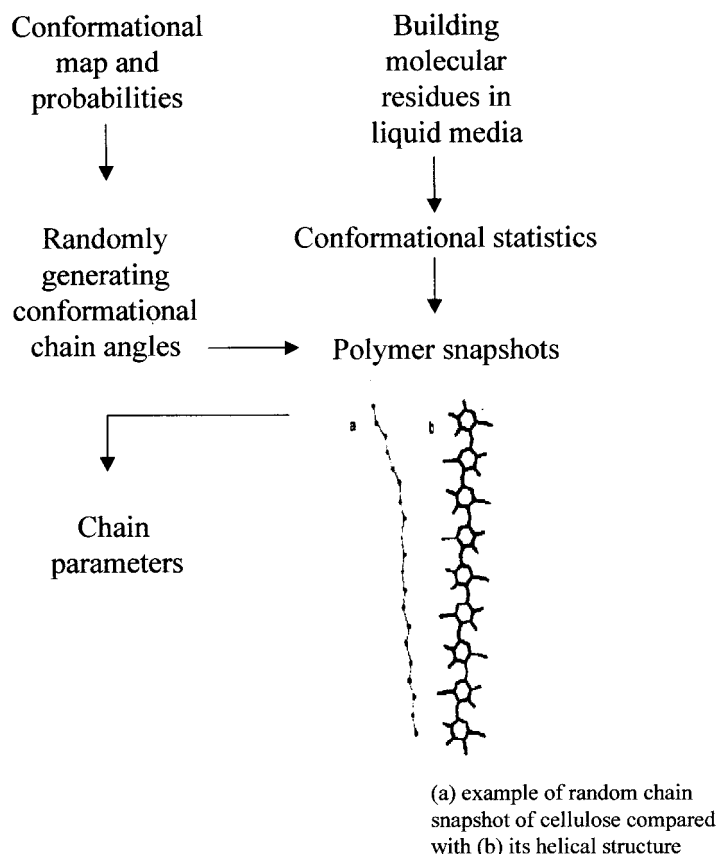


FIGURE 1 Summary of the conformational analysis of a long molecule immersed in a liquid.

polysaccharide molecule immersed in a liquid solution [6]. Conformational and dynamical properties of chains formed by n residues were then modelled upon specifying the geometry depicted by the $(n-1)$ sets of rotational angle pairs [7]. Molecules taking up regular helical conformations (like in crystallographic states) are easily identified by a single constant pair of values in the rotational angle map [8].

Along this cross-fertilizing research line, the present article continues some former work [9–12], generally proposed to relate statistics to geometry. Theoretical results, preliminary developed and discussed through the next Sections 1 and 2, aim at introducing the consequence of a recent relativistic picture of self-diffusion in simple liquids [9,13] and its geometrical analogy [10,12]. Here, they are helpful for linking geometry and energetics of single molecules to asymptotic chain features. Such predictions are normally carried out by means of Monte Carlo, or equivalent techniques [14]. They rely upon local contour energy diagrams, depending on significant degrees of freedom of the building block (normally, dihedral angles) and reproducing the monomer–monomer interactions mediated by the liquid [15]. In our

framework, suitable analysis of the starting energy landscape is expected to replace current numerical procedures.

1. BASIC CONCEPTS

1.1. Relativistic Self-diffusion in Liquids

A relativistic picture of self-diffusion in liquids allowed us to get the main scaling laws arising in polymer solutions (see [9] and references therein). If the bulk phase is structured relativistically with respect to diffusion, any macromolecule identifies the metric transformation induced by the local mobility (or diffusivity) change corresponding. Formally, the law of Brownian movement [16] was employed to introduce a 4-dimensional spacetime interval (σ^2) relying on mean square displacements ($\overline{x_k^2}$), time (t) and a limit diffusion coefficient value (D):

$$d\sigma^2 = Ddt - d\overline{x^2} - d\overline{y^2} - d\overline{z^2} \quad (1)$$

If a chain molecule forms by replacing N ($\sim D/D_N$) units, the invariance constraint joint to Eq. (1):

$$d\sigma^2 = d\sigma'^2 \quad (2)$$

allows one to account the overall spacetime scaling for. On this basis, laws of length contraction and time dilation originating from Lorentz transformations of special relativity [17] turn out corresponding to the scaling behaviour of end-to-end dimension and Rouse time belonging to ideal polymer coils [18]:

$$\begin{cases} \overline{r^2} \sim N \\ t \sim N^2 \end{cases} \quad (3)$$

where $\overline{r^2} = \sum \overline{x_k^2}$. Analogously to the original framework the ideal random coil, provided without mass, must lie in a flat manifold. Accounting for the mass distribution requires to introduce the space curvature. Particularly, curved and empty spaces have their analogy to single coils with excluded volume effects, while Einstein equations of general relativity [17] rather suit concentrated polymer systems. A new scaling law for average size ($\sqrt{\overline{r^2}}$), diffusion (D_N) and viscosity (η_N) coefficients of N -long chains:

$$D_N \sqrt{\eta_N \overline{r^2}} \sim \text{const} \quad (4)$$

was extrapolated as a weakly covariant transformation. It is quite satisfactorily fulfilled by universal exponents of both ideal and real polymer solutions, either in low and high molecular weight regimes (see discussion in [9]).

1.2. Scaling Concepts for Geometry

The previous picture suggest (a) looking at the scaling behaviour of macromolecules in solution as the consequence of partially ordering (or else, localizing, shaping, and so on) a space intrinsically disordered (i.e., a liquid) and (b) seeking some generalization in terms of basic geometry. We started from the simplest geometrical analogy, consisting of measuring a length (σ) in some extended space portion (ϱ), which is though as it was originally indistinguishable. This operation only requires introducing a scalar shape function (ϕ), for instance:

$$\varrho\phi = \sigma \quad (5)$$

and, similarly to the Brownian motion law $\sigma^2 \propto Dt$, tackling the last Eq. (5) relativistically. Formal details may exhaustively be found elsewhere [10,12]. Lorentz transformations for ϱ and ϕ returned a first example of scaling laws for geometry:

$$\phi_\ell(r) \propto \phi_\lambda(\varrho) \quad (6)$$

which can link shapes at two distinct scales (ℓ and λ). Further behaviours can be obviously determined on the basis of the initial geometrical constraint (Eq. (5)). In any case, when ϕ is thought as a spatial probability, statistical distributions in Brownian media turn out to scale accordingly. Equation (5) may also be considered like a uncertainty statement for geometry: measuring affects somehow extension and shape underlying. We will get back to this point just in the instance of polymer solutions (next section).

1.3. Length–Temperature Equivalence

The former geometrical picture point then out a length-temperature equivalence [11]. Briefly, any thermal statistics would correspond to a geometrical transformation at smaller length scales:

$$\varepsilon = \ell(\mu) \quad (7)$$

where $\varepsilon = E/k_B T$ and $\mu = \varrho/L$ stand respectively for energy and length in Boltzmann and Bolyai–Lobachevskij (BL) unit. The last quantity is univocely specified by the BL formula:

$$e^{-\mu} = \tan \frac{\alpha}{2} \quad (8)$$

connecting parallelism angle (α) to distance (ϱ) in non-Euclidean spaces through the BL length (L) [19]. The Euclidean case is obviously approached in the limit of $L \rightarrow \infty$ ($\alpha = \pi/2$). By doing so, the most general problem becomes rewriting statistical thermodynamics results in terms of geometry (at smaller scales). We may consider, for

instance, the geometrical partition function specified by Eq. (7):

$$Z = \sum_k e^{-\ell_k} \quad (9)$$

When ℓ is a linear map, it returns the following average size equation (in L unit):

$$\Lambda_L = \left(\frac{\partial \ln Z}{\partial \ln L} \right) \quad (10)$$

which was applied to model swelling of polymer chains in liquid solutions and micellar growth in dilute microemulsions [11]. The so-called packing parameter was modelled as a length contraction–dilation of the liquid space that hosts single surfactant molecules.

Before proceeding, it is worth to summarize the two-folded significance which the end-to-end dimension would take in the framework aforesaid. From the relativistic picture for self-diffusion in liquids, it denotes a geodesic path lying in a Lobachevskij manifold, where length contraction and time dilation establish as intrinsic spacetime features. The scaling concepts for geometry more generally suggest looking at polymer coils as representative of geometrical states, undetermined by the observation scale itself (i.e., just the average end-to-end distance). We get so motivated explaining statistics of polymer solutions in terms of geometry alone.

2. CHAIN STATISTICS FROM GEOMETRY

2.1. Size Scaling from Parallelism Angle Rotations

Here, we set out to translate the polymer size scaling into angular rotations. The ideal limit of vanishing scales is the first point to face before concentrating ourselves on the level of single molecular residues.

Consider so the Lobachevskij geometry generated through parallelism angle rotations linked to a polymer coil with Kuhn step size l . For the sake of simplicity, we will restrict our analysis to the freely rotating chain model [20], characterized by fixed bond angle supplements (θ) and rotation angles that are free to vary. To describe the spatial coil evolution, the BL formula can be adopted upon mapping, for instance, $L \rightarrow l$ and $\alpha \rightarrow \theta$ (see Eq. (8) and Fig. 2(a)). The classical results base on the ordinary random-walk diffusion laws. Let c_∞ be the so-called characteristic ratio, the asymptotic end-to-end distance $\Lambda = \sqrt{r^2}$ is (in unit of l):

$$\Lambda^2 \sim c_\infty N \quad (11)$$

with $c_\infty = (1 + \cos \theta)/(1 - \cos \theta)$, or else:

$$\Lambda^2 \sim \bar{L} \quad (12)$$

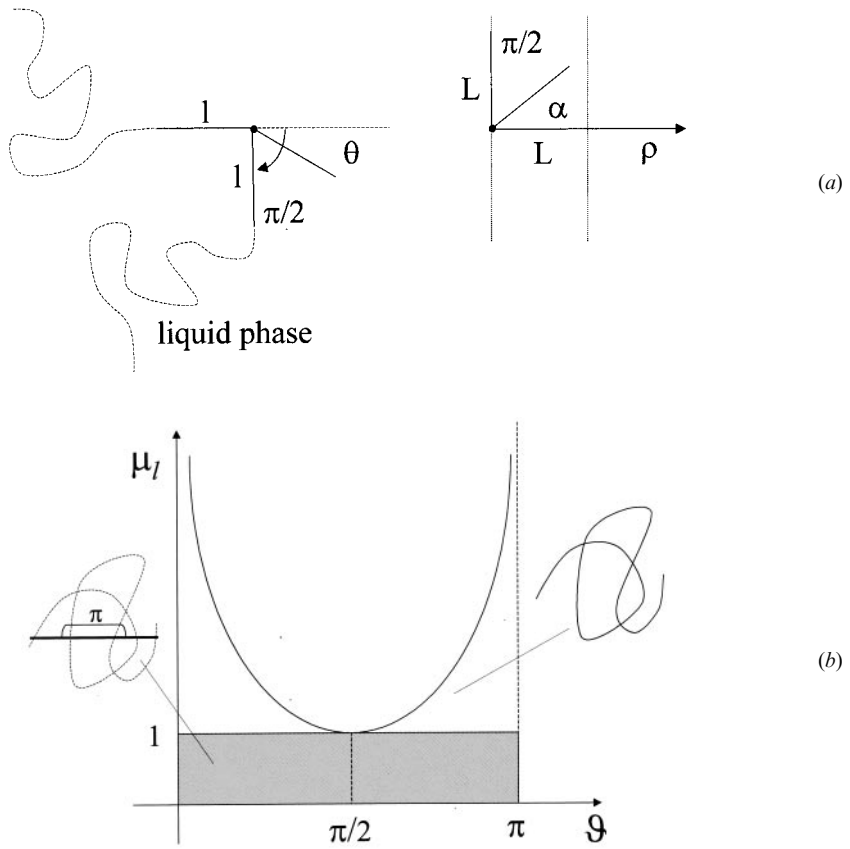


FIGURE 2 (a) Modelling the polymer chain conformation by the BL formula. (Eq. (8)); (b) Sketch of $\mu_l = \mu_l(\theta)$ and net parallelism angle scaling (Eq. (13)).

$\bar{L} \sim N$ being the contour length. To proceed, consider the angular dependence of $\mu_l \equiv \varrho/l$ along the end-to-end direction, $\varrho \rightarrow \varrho \cos \theta$:

$$\mu_l(\theta) = -(\cos \theta)^{-1} \ln \tan \frac{\theta}{2} \tag{13}$$

Its integral evaluates the net angular excursion that results from moving along the contour length, and reads (Appendix I):

$$\int_0^\pi \mu_l(\theta) d\theta = \frac{\pi^2}{2} \tag{14}$$

Thereby, as:

$$-\ln \tan \frac{\theta}{2} = \sum_k \frac{\cos^k \theta}{2k+1} = \cos \theta + O(\cos^3 \theta) \tag{15}$$

the same quantity calculated along any radial path approaching the Euclidean manifold ($\theta \rightarrow \pi/2$) must obviously equal π , or else the rectangle with width π and height $\mu_l(\theta \rightarrow \pi/2) = 1$ (Fig. 2(b)). Expressing the obtained results as:

$$\begin{cases} \bar{L} \sim \pi^2 \\ \Lambda \sim \pi \end{cases} \tag{16}$$

reproduces the scaling law for a random-walk, where lengths are mapped into angles, say $\bar{L} \sim N \rightarrow \pi^2$. Appendix II proves lastly the characteristic ratio in Eq. (11) follows from the constant arc length ratio between two coaxial horocycles [19] that are distant by two unit length:

$$c_\infty \sim e^{2/L} = \frac{1 + \cos \theta}{1 - \cos \theta} \tag{17}$$

Real asymptotic mean square displacements and ideal random-walk end-to-end dimensions can be therefore related by merely geometrical means (see also Fig. 3). Observe that the excluded volume effect (here, $\alpha \neq \pi/2$) equals curving the space again ($L \neq \infty$).

2.2. Chain Conformation as Indetermined by the End-to-End Dimension

The second purpose is recovering the ordinary polymer statistics through the same conceptual background underlying the previous paragraph. We should only consider finite length scales, and recall the uncertainty relation associated with Eq. (5):

$$\delta\phi \delta\varrho \sim \sigma \tag{18}$$

The (classical) limit, $\sigma \rightarrow 0$, brings us back to the instance just developed, angle rotations taking the place of length displacements. As soon as a macro-molecule

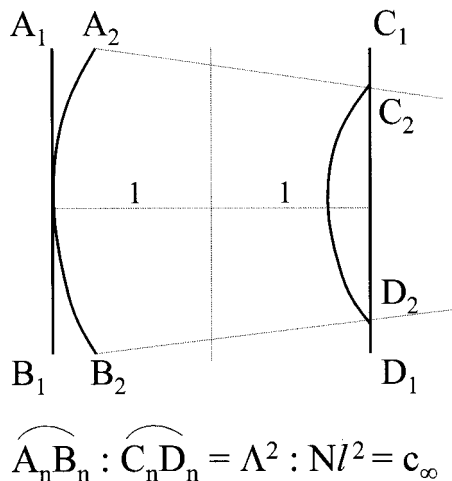


FIGURE 3 Characteristic ratio from the arc length ratio of two coaxial horocycles.

forms, i.e. $\sigma \neq 0$, we need a stochastic-causal (or quantum-like) description [21], where any chain conformation be representative of some indetermination state for polymer extension and shape. The most straightforward way to proceed is certainly modelling the statistical distribution of end-to-end separation distances by means of an ondulatory approach. Now, the simplest Schrodinger equation [22] when the Planck constant $\hbar \rightarrow \sigma$ and the manifold is curved [17] is:

$$-\frac{\sigma^2}{2\sqrt{g}}\partial_\mu(\sqrt{g}g^{\mu\nu}\partial_\nu\Upsilon_k) + v_k(\varrho^k)\Upsilon_k(\varrho^k) = \mu_k\Upsilon_k(\varrho^k) \quad (19)$$

where $\{\varrho^k\}$ is the coordinate set, v_k is the potential function in the ϱ^k representation, $g^{\mu\nu}$ specify the (contravariant) elements of the metric tensor with determinant $g = \det g_{\mu\nu}$ and $\partial_k \equiv \partial/\partial\varrho^k$. Note that information on chain statistics is carried by Υ_k and μ_k . The former denotes a wavefunction concept for geometry, termed hereinafter as Lobachevskij wave (LW), while the latter is the eigenvalue for the geodesic arc length. As ϕ depends on metric, however, a mean field description is only allowed by Eq. (18) [23]. To this aim, some average Gaussian curvature ($k_L \sim L^{-2}$) and metric coefficient (\bar{g}^{kk}) can be conveniently employed. Introducing in fact the curvature scalar, $R/2$ ($\sim -k_L$) [24]:

$$v_k \sim \frac{|k_L|}{2}\varrho^{k^2} \quad (20)$$

yields:

$$-\sigma^2\bar{g}^{kk}\partial_k^2\Upsilon_k + |k_L|\varrho^{k^2}\Upsilon_k = 2\mu_k\Upsilon_k \quad (21)$$

It is solved evidently by discrete harmonic eigenfunctions and spectra and, letting the variable transformation $x^k = \bar{g}^{kk}\varrho^k$, they are:

$$\begin{cases} \Upsilon_{k,n}^2 = a_n e^{-(x^{k^2}/2s^2)} H_{k,n}^2\left(\frac{x^k}{\sqrt{2s}}\right) \\ \mu_n = \frac{s^2}{L^2}\left(n + \frac{1}{2}\right) \end{cases} \quad (22)$$

Here, $s^2 \sim \sigma L$ is the total distribution variance (the uncertainty on the coil extension), $H_{k,n}$ denotes the n th Hermite polynomial along x^k and $a_n = 1/(2^n n! \sqrt{2\pi}s)$. Results are formally independent of shifting the average chain baricentre, $\varrho^k \rightarrow \varrho'^k = \varrho^k - \bar{\varrho}^k$.

3. DISCUSSION

Note the proposed Eq. (21) resembles that for the so-called geodesic deviation, say:

$$\frac{d^2\xi^k}{d\tau^2} + k_L\xi^k = 0 \quad (23)$$

giving the relative acceleration which two geodesic paths, parametrically displaced by $\xi^k = \xi^k(\tau)$, undergo. It only suffices to map $\xi_k \rightarrow \Upsilon_k$ and modify the curvature contribution accordingly. Interpreting statistical length distributions like ondulatory geodesic deviations so leads into a couple of main remarks. Precisely, (i) generating a polymer conformation (shape) affects the length distribution in the form of statistics. Any conformational statistics, in other words, stands for the uncertainty to pay for creating chain conformations; (ii) wavefunctions in the extension representation denote stationary deviations between geodesic trajectories, which Brownianly diffuse inside the relativistic liquid phase (Fig. 4).

As expected from any ondulatory approach, the obtained statistical description does not reduce to a single eigenfunction only. Usual normal distribution functions [20], generally adequate to model long flexible chains, correspond here to ground state Lobachevskij waves ($n=0, H_{k,0}=1$):

$$\Upsilon_{k,0}^2(x^k) = \frac{1}{\sqrt{2\pi s}} e^{-(x^k/2s)^2} \tag{24}$$

Note that LW associated with higher, excited levels ($n \geq 1$), possess more than one relative maximum (i.e., see Fig. 5) and can therefore be used for describing non-Gaussian cases. Particularly, the method above may be useful to attempt some closed-form expression applicable to difficult instances, like statistics of short chains of any flexibility [25]. To do so, taking anharmonic contributions into account would surely make the approach more realistic. We also see the excluded volume effect is carried here by odd wavefunctions, i.e., those where Hermite polynomials are vanishing in zero. In any case, the single total eigenfunctions read the product of their orthonormal projections:

$$\Upsilon_n^2(x^k) = A_n \prod_{k=1}^d e^{-(x^k/2s)^2} H_{k,n}^2\left(\frac{x^k}{\sqrt{2}s}\right) \tag{25}$$

d being the manifold dimension and $A_n = a_n^d$.

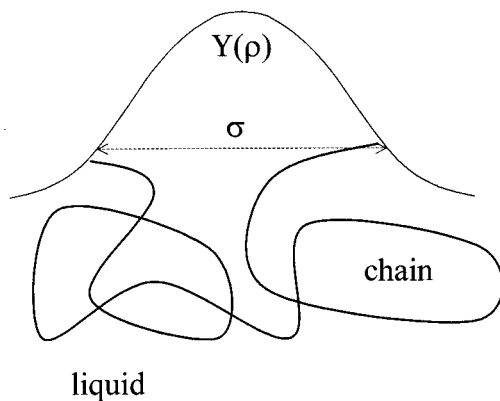


FIGURE 4 Statistical density of chain length displacements as average diffusive geodesic deviations.

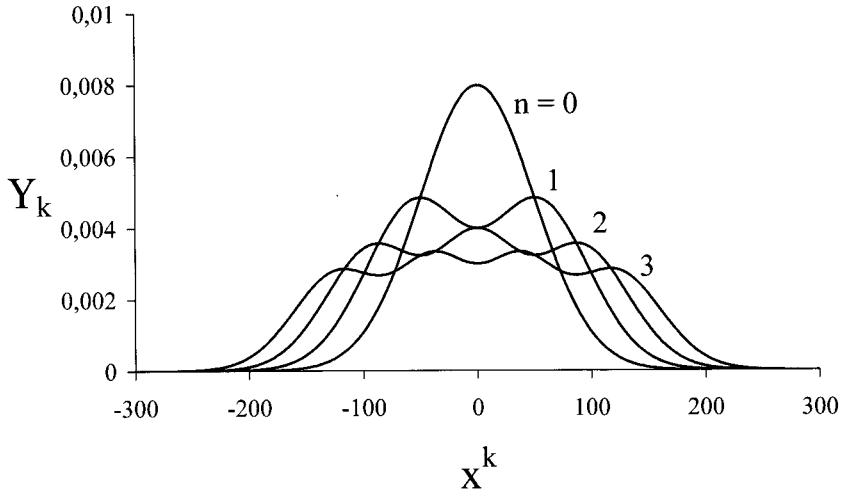


FIGURE 5 One-dimensional LW (Eq. (22)). The n value indicates the linear superposition of the first n eigenfunctions normalized to unity ($H_0=1$, $H_1=2r$, $H_2=4r^2-2$, $H_3=8r^3-12r$).

Another point concerns the interpretation of the root mean squares met (σ , L , s). Taking advantage of the same unit in Section 2.1, $\sigma \sim \bar{L}$ and $L \sim l$, implies at once:

$$s^2 = Nl^2 \quad (26)$$

i.e., the scaling law for a random-walk again, along with its normal distribution:

$$\Upsilon_{r,0}^2(r) = \frac{1}{l\sqrt{2\pi N}} e^{-(r^2/2Nl^2)} \quad (27)$$

Following a second line, however, one may also think of the equilibrium state of a three-folded geometrical process, for measure, extension and shape (Fig. 6). Working out the equilibrium partition function with $s = L \rightarrow \sigma$, correctly constrains Λ and σ to possess the same scaling behaviour (Appendix III). As for the meaning of the constant metric tensor, we may come back to the actual coordinate set ($x^k = -\bar{g}^{kk} \varrho^k$) and distribution variance ($s_{kk}^2 = \bar{g}^{kk} Nl^2$) and write $c_\infty = \bar{g}^{kk}$ or, in covariant notation:

$$c_\infty \bar{g}_{kk} = 1 \quad (28)$$

Not surprisingly, the characteristic ratio is linked to an average metric coefficient, changing its unitary Euclidean value ($\theta = \pi/2$ in Eq. (17)) whenever geometry gets curved.

4. SUMMARY AND FUTURE RESEARCH LINE

The aforesaid can be summed up into an overall equation of the form:

$$F(c_\infty; \text{large scales}) = f(\Phi_0; \text{small scales}) \quad (29)$$

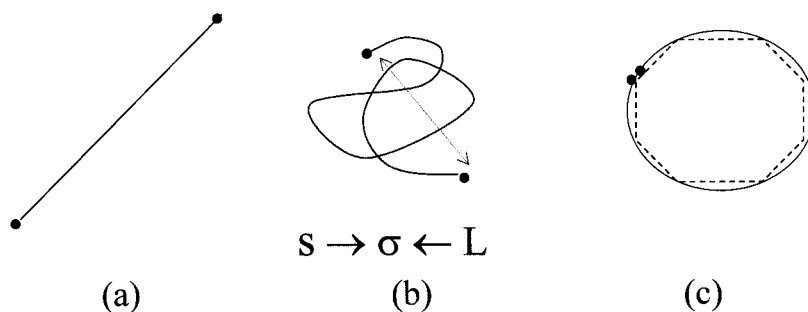


FIGURE 6 Scheme of (a) extension, (b) measure (equilibrium) and (c) shape-like states.

Φ_0 being a set of molecular parameters. Expressing the function on the right may take advantage of results in Section 2.1, where the characteristic ratio concept was translated in terms of rotational degrees of freedom in single residues (generally, dimmers). The large scale analysis joint instead the coil size to some average metric coefficient. Therefore, Eq. (28) simply transforms into:

$$c_\infty \varphi_0(\bar{g}_{kk}) = 1 \quad (30)$$

where φ_0 is a rotation map [26], basically a small scale perturbation of the ideal coil state ($c_\infty = 1$). Equation (29) thus becomes:

$$q_\infty = \varphi_0(g_{\mu\nu}, u_{\mu\nu}; x^\mu) \quad (31)$$

the right side generally connecting a set of internal coordinates (x), metric (g) and energy contributions (u) to $q_\infty \equiv 1/c_\infty$.

Two main steps to deal within the near future are so (i) concentrating on the relation between chain configuration and energy surface and (ii) studying the influence of molecular microstructure which maps φ_0 should account for. First practical goals are performing standard computer simulations (molecular force fields and Monte Carlo analysis) and to derive c_∞ as a function of relevant energy diagram parameters. Once this is done, one can check the suitability of rotation maps to model Eq. (31). Doing so, and better handling the complexity of numerical calculations, would surely benefit from adopting convenient approximations. We will therefore focus on statistics of rather simple systems, like polysaccharide molecules in liquid solutions with square-well potential barriers, only depending on two parameters (width and depth). For instance, sine-circle maps of the form:

$$\varphi(z) = z + \sin(2\pi z) + \text{const} \quad (32)$$

where proven already to describe the characteristic ratio (q_∞) in cellulosic solution [27]. The quantity z was related to the dihedral angle range accessible to cellobiose torsions (i.e., the energy barrier width).

CONCLUSIONS

Scaling and conformational statistics of macromolecules in solution are investigated by starting from a relativistic picture of self-diffusion in liquids and its geometrical analogy. Chain molecules are first defined through the curvature caused by locally lowering the mobility of the liquid bulk where they embed. Their conformation (shape) were then conceived as geometrical entities, scaling with length. Moreover:

1. Polymer conformations have been regarded as representative of geometrical states, for chain extension and shape, which are undetermined by the length scale of observation (i.e., the end-to-end dimension).
2. When length scale is vanishing, end-to-end separation and characteristic ratio follow, as intrinsic geometrical properties, from the parallelism angle scaling in the Bolyai–Lobachevskij manifold modelling the liquid.
3. In a stochastic causality description, chain statistics descends from a geometrical uncertainty. It is described by wave functions (LW) travelling in a curved geometry and solving an ondulatory equation for geodesic deviations. Usual normal distributions are found again as ground eigenstates.
4. At small length scales, the characteristic ratio can be expressed by rotations about molecular geometry coordinates. At finite scales, it points out the average metric coefficient of the space hosting the polymer coil.
5. Conformational polymer statistics is suggested being the counterpart of some small scale-geometry (i.e., monomer).

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- [29] It is simply meant here the universal exponent of Λ is γ if and only if $\sigma \sim N^\gamma$.

APPENDIX I

To work out Eq. (14), it suffices considering the variable change $x = \theta/2$:

$$\int_0^\pi \mu_l(\theta) d\theta = -2 \int_0^{\pi/2} (\cos 2x)^{-1} \ln \tan x dx \quad (33)$$

and recall [28]:

$$\int_0^{\pi/2} (\cos 2x)^{-1} (\ln \tan x)^{2n-1} dx = \left(\frac{1 - 2^{2n}}{2n} \right) \pi^{2n} |B_{2n}| \quad (34)$$

with $n = 1$ and $B_2 = 1/6$ (the second Bernoulli number).

APPENDIX II

The quantity $e^{1/L}$ equates the constant ratio between the arc lengths of two coaxial horocycles, separated by the unit length [19]. A horicycle is a circle with infinite radius, corresponding to the straight line concept in Euclidean geometry. Equation (17) thus descends from the BL formula:

$$e^{-1/L} = \tan \frac{\theta}{2} \quad (35)$$

and from:

$$\tan \frac{\theta}{2} = \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right)^{1/2} \quad (36)$$

with $\theta \in [0, \pi]$.

APPENDIX III

BBLE, combined with the spectrum in Eq. (22), reduces the equilibrium partition function to a geometric series in μ_n :

$$Z = \sum_n e^{-(\sigma/L)(1/2+n)} = \frac{e^{\sigma/2L}}{e^{\sigma/L} - 1} \quad (37)$$

The statistical definition of average coil size in L unit [11]:

$$\Lambda_L = \left(\frac{\partial \ln Z}{\partial \ln L} \right) \quad (38)$$

implies, from Eq. (10), that the scaling laws for Λ and σ equal [29]:

$$\Lambda_L = \frac{1}{2} \lim_{L \rightarrow \sigma} \left(\frac{e^{\sigma/L} + 1}{e^{\sigma/L} - 1} \right) \sim \text{const} \quad (39)$$