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Polymer Chain Dimension from Rotational Angle Scaling of its Monomeric Units[#]

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Abstract

Motivation. This paper investigates the possibility of interpreting the usual scaling concept in polymer physics in terms of geometry alone. We proposed already to regard a macromolecule as a geometrical transition, where quantities defining the monomer shape are scaling with the length scale itself up to get to the polymer conformation.

Method. Here, square–well conformational energies of different widths and well–known rotational isomeric state of different statistical weights are taken into consideration to model the characteristic ratio as a circle map about torsional angle rotations. The macromolecular system chosen for the present investigation is the polyvinyl chain.

Results. The polymer chain characteristic ratio of has been described as it comes from torsional rotations on a circle located at the single unit scale.

Conclusions. The polymer size scaling is interpreted in terms of angular variables at the dimer scale and, more generally, polymer statistics is provided with a merely geometrical reading key.

Keywords. Polyvinyl chain; characteristic ratio; RIS and SW approximations; geometrical scaling laws; circle map.

Abbreviations and notations

GSL, geometrical scaling law
SW, square–well (conformational landscape)
BR, Brownian relativity
RIS, rotational isomeric state

1 INTRODUCTION

Despite the progresses in molecular modeling of small molecules based on realistic force field and even on *ab initio* computational studies [1], large polymer chains and long–range interacting systems continuously offer incommensurable difficulties and elude similarly accurate descriptions of statistical and dynamical properties at atomistic level [2,3]. Current research undergoing in several laboratories exploits new formalisms and innovative computational approaches [4–6]

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providing routes that may overcome such difficulties. A fruitful synergy of modeling algoritms and structural descriptors is highly desirable as common practice in the interdisciplinary research (see for instance in this journal Refs. [7–9]).

One fundamental and easily accessible polymer property that seems suitable for assessing the workability of new ideas is the size itself of a polymer chain and the way it may be produced and predicted from the atomistic description of its reduced units. To quantify and compare any polymer size to each other, it is matter of routine to resort to the familiar concept of characteristic ratio (C_∞), which evaluates the chain length displacement from the unitary Gaussian value [10]. As to calculating realistic characteristic ratios, the reader is strongly recommended to step back to ref. [10] and to the vast literature on this subject, where C_∞ is always calculated up to given approximation degrees of the potential energy surface (force field). Over the years, polymer scientists improved the accuracy of their predictions by ever more ingenious approximations and analysis of the long range interactions case–by–case involved [11]. The best way of modeling real macromolecules, however, consists in general of exploiting numerical chain generations that employ real parameters. In a first, molecular mechanics step, contour energy diagrams are calculated numerically, upon varying the small scale interactions with respect to torsional rotations of the building units [11–12]. Snapshots of large molecules are afterwards simulated by Monte Carlo (or equivalent) probabilistic sequence of dihedral angles, relying on the partition function actually implied [13].

Following a research program in progress in our laboratory, this work presents some new ideas in attempting a novel approach to statistical physics in general, with special attention paid to polymers and liquid media. It could be termed as the geometrical scaling program, and has been extensively drawn by several former investigations (see, for instance, Refs. [14–17]). Here, we will focus on modeling the polyvinyl (PV) chain size in light of two objectives, (*i*) understanding if chain conformations may be described analytically, from their molecular energy profiles and, particularly, (*ii*) investigating on some direct relation that gets the macromolecular dimension from conformational space features. PV is then simple enough to apply the rotational isomeric state approximation (RIS) and compare it with the corresponding results that come from the geometrical view formerly proposed.

In terms of points (*i*)–(*ii*), this study wishes to further contribute to these tasks: to replace numerical chain generations by a suitable analysis of the starting energy profile, and seeking a closed–formula for the (torsional) characteristic ratio. At this preliminary research stage, we are obviously required to control the high complexity underlying any numerical analysis and can take advantage of two straightforward methodologies: the RIS approximation and the use of square–well (SW) conformational energies. In the RIS approximation each molecule is regarded like only existing in discrete states around its energy minima [11], whereas SW landscapes are only functions of the angular width. From the modeling viewpoint only, and apart from the need of producing realistic data, RIS and SW applications have here in common that both will focus on one relevant statistical parameter only. To change the number of accessible states in RIS, it simply suffices in fact varying the energy depth, while SW basically represents an average over the allowed conformational angle range.

2 TEORETICAL SECTION

2.1 Brownian Relativity (BR)

This section briefly sums up the basic results achieved in the previous investigations [14–17], specially in Refs. [14,16], where a relativistic theory of Brownian movement for self–diffusion in liquids was formulated to derive the main scaling laws arising in polymer solutions. Resorting to the following Brownian space–time interval:

$$ds^2 = -g_{\mu\nu} dz^{\mu} dz^{\nu} \tag{1}$$

where $t \equiv z^0$ and diffusivity identifies $D = -g_{00}$, allowed us referring the previous equation to a fixed probability distribution set, and thus translating (polymer) statistics into geometry.

BR points first out a novel definition of macromolecule in a liquid. It identifies the curvature change caused by a local mobility variation produced into a diffusive space–time. The simplest example is provided by the Brownian special relativity against random walk, where lengths are contracted and time is dilated upon lowering the randomness of the host medium. It suffices starting from:

$$ds^2 = D\,dt - (\overline{dx^2} + \overline{dy^2} + \overline{dz^2}) \tag{2}$$

and locally decreasing mobility through $1 \rightarrow N$. For example, if one considers N liquid molecules collected in a linear tube of length $N\,a$ (a is the Kuhn step size) and merges them into a single chain, the Lorentz transformations associated (LT) provide a geometrical constraint ruling the transition between rod–like and curvilinear tubes, *i. e.*, from single molecules to a corresponding macromolecule in solution. In short, letting the new Lorentz factor be, $1 - \Delta D/D = D_N/D = \delta$ [14], the Brownian LT taking place give rise in the end to the following laws of time dilation and length contraction (TDLC):

$$\begin{aligned} dt' &= \delta^{-1}\, dt \\ \overline{dr'^2} &= \delta\ \overline{dr^2} \end{aligned} \tag{3}$$

yielding random walk size and Rouse time behaviors of ideal phantom chains, *i. e.*, without excluded volumes (or self–avoiding walks) [18]. For Rouse–like coils, $\delta \sim N^{-1}$ and therefore:

$$\begin{aligned} t' &= N^2 t_1 \\ \rho' &= N l^2 \end{aligned} \tag{4}$$

primes still denoting the polymer frame, t_1 being an intrinsic molecular time and $\rho \equiv \langle r^2 \rangle$.

Once BR takes curvature (or mass) into account, it may be exploited to deal with realistic systems. It so predicted the Flory radius and the Stokes formula for a suspended polymer particle, and a new scaling law, holding in the high concentration regime with and without chain entaglements [14].

Next section will deal with how exploiting BR to model conformational statistics of polymer chains, each conformation being regarded like a shape that scales geometrically with length. This will give us the notable advantage of concentrating on the molecular unit scale, where energy landscapes are playing the role of small scale–shapes reaching the macroscopic level in terms of statistical distributions and quantities related (in our case, the mean macromolecular size).

2.2 Geometrical Scaling Laws (GSL)

The former view led us also to an interesting geometrical analogy, having promising prospects in studying the nature of statistics in general [16,17]. BR suggests that universality originates from partially ordering (or shaping) the Brownian disorder where the coil embeds, according to a transformation like 1 → N. Reformulating the picture above in terms of simple geometry so returns a set of geometrical constraints (or geometrical scaling laws, GSL) that, in principle, may hold at any length scale. We so applied LT to a scalar shape (ϕ), which localizes a measure (λ) in some extended space (ρ) and, in the end, the relation achieved consisted of a simultaneous extension and shape contraction [16,17]:

$$\Phi_\Lambda(\rho') = \phi_\lambda(\rho) \tag{5}$$

The last relationship is maybe the simplest example of GSL, and corresponds to the well known time dilation and length contraction rules of special relativity where, since light plays there the role of an impassible limit of nature, space–time is no longer absolute but constrained instead to depend on the relative motion state. The diffusion coefficient invariance (BR) similarly resulted into scaling constraints ruling static and dynamic properties, including mean sizes and characteristic times. In this geometrical translation, the universal property turning out to scale is finally identified by the spatial probability (density). By the name of scaling law for geometry we so did and will denote a relationship among different statistical phenomena lying in distinct geometries, which can be joint through some common geometrical shape, to be opportunely defined.

As a matter of fact, whenever shape is regarded like some probability (density) or, equivalently, some uncertainty source, it may join statistics defined at two different scales, λ and Λ, see Eq. (5). In this way, we are now ready to work out the concept of characteristic ratio, defined as:

$$c_{\infty} = \lim_{N} c_{N} \tag{6}$$

where $c_j \equiv \langle r_0^2 \rangle / (j\, L^2)$ is the mean square end–to–end dimension of the unperturbed coil in virtual bond (or Kuhn step) unit. GSL identifies the former equation by a relationship of the form:

$$F\,(c_{\infty}; l\arg e\, scales) = f\,(\Phi_0; small\, scales) \tag{7}$$

where Φ_0 denotes a set of parameters defined within the single unit, and therefore accounting basically for coordinates and metric. In BR instead, as Eqs. (3)–(4) originally corresponded to:

$$rod - like\, tube\,(liquid) \rightarrow rand\,\mathrm{om}\, coil\,(c_{\infty} = 1) \tag{8}$$

we may apply the most general transformation class, leading the ideal coil to possess any arbitrary conformation, or shape:

$$rand\,\mathrm{om}\, coil \rightarrow any\ conformation\,(c_{\infty} \geq 1) \tag{9}$$

which, in formula, reads:

$$Nl^2 = g_{\rho\rho}\, \rho$$

Moreover, the latter implies $1/c_\infty = F$ and thereby:

$$q_{\infty} = f\,(\Phi_0) \tag{10}$$

with $q_\infty \equiv 1/c_\infty$. In this paper, the (analytical) dependence of c_∞ will be explored as a function of the most relevant degrees of rotational freedom, that is, the dihedral dimeric angles. As to the small scale function (*f*), it is rather natural setting it to a circle map, which will equal topologically to circular rotations performed at the molecular scale. From the practical viewpoint, we may set out two preliminary tasks, *i.e.*, addressing the connection between chain configurations and energy landscape behaviors, and studying the influence of molecular microstructure on the circle map parameters, employed in best fitting the characteristic ratio. Since these tasks certainly require extensive numerical analysis before getting to somewhat general conclusions, we are forced for now to choose either convenient approximation, by which the complexity of usual numerical calculations are better handled, or molecular structures that are simple enough. Here, as said already, we will focus on the PV system that is straightly described by means of SW and RIS methods.

2.3 Characteristic Ratio as a Rotation Map

BR suggests that the characteristic ratio of a polymer chain may be expressed in our case like the inverse of some topological map, accounting for angle displacements evaluated *analytically* at the scale of single monomers. The main insight suggested by Eq. (10) is the average size of statistically significant chain ensembles can be determined from mapping the angular degrees of freedom of single molecules according to suitable topological transformations, reasonably equivalent to simple rotation super–positions. To proceed with modeling the three numerical date sets obtained, we will so employ a sine–like circle map (φ_S). It represents one of the simplest examples of rotation maps describing 1–dimensional sequences bounded to a circle, which generally read:

$$\varphi\ (z+n)=\varphi\ (z)+n\ \ n\in Z \tag{11}$$

and particularly, if the periodic behavior is that of a sine function, reduce to:

$$\varphi_S\ (z)=z+\omega+\sum_k q_k\ \mathrm{sen}\,(2\,m_k\pi\,z) \tag{12}$$

still with $m_i \in Z$ and q_i, $\omega \in \Re$. The quantity ω identifies a constant driving force (frequency), whilst each q_i is the non–linear coupling strength belonging to the mode *i*. Everybody may argue that, depending on the mutual relationship among the coefficients selected, the last equation is able to give rise to rich dynamical pictures, which go from elementary periodic motions, to quasi–periodic (and even chaotic) trajectories. This subject matter is rather ample and the reader wishing deepening it a little is strongly recommended better resorting to the current textbooks and literature (see, for instance, Ref. [19]).

Stepping back to our application, *z* will take here the value of the dihedral angle range that is accessible to molecular torsion, whereas any other parameter is expected being sensitive to the geometrical microstructure involved (*i.e.*, the specific chemical nature). As the (1–dimensional) rotational state density is simply $\sim \Delta/(2\pi)$, it may be convenient to re–scale the map width by $z = \Delta/(n\pi)$, *n* denoting some intrinsic molecular parameter. In such a way, the angle $n\pi$ plays a similar role of that assumed by the angular Kuhn step size *l* in the ordinary statistics. The only noteworthy difference, obviously, would be concerned with the nature of the equations where these quantities appear. The scaling concept underlying relationships like Eqs. (4) is certainly statistical, whilst the one that is present in Eq. (10) is deterministic. We could also say, as pictorially reported elsewhere [16], that passing from monomers to their polymers is basically relying upon GSL that conceptually equal geometrical dualisms among (small scale, mesoscopic) angles and (large scale, macroscopic) lengths. In this way, once again, any macromolecular size dilation would be directly corresponding to a dimeric torsion.

To apply Eq. (10) like a best fit function where the number of fit parameters are mostly reduced (and thus the fitting selectivity correspondingly increased), we set $\omega = 0$, every m_i to the lowest integer compatible with the numerical data (the largest mode, or wave number) and each coupling coefficients bringing non–linearity to take the same value, $q_k = q$ for any $k > 1$. Therefore, the final equation we used in our interpolations took the following form:

$$q_\infty = \varphi_S\,(z) \tag{13}$$

where the heuristic coefficients to extract are m_i, *q* and *n* and, consistently, a further asymptotic constraints holds, $q_\infty\ (\Delta/n \to 0) = 0$ (*i.e.*, helical coils tend to get highly extended). Note also that its suitability to interpret polymer size data was already discussed in another preliminary investigation, performed on the cellulosic chain [20].

3 MODEL AND RESULTS

3.1 Choice of Models

As mentioned in the introduction, we want to investigate both general and quantitative aspects of the chain dimension dependence upon varying energetic and geometrical constraints of its monomeric unit. It is thus mandatory to investigate a simple chain model that involves as many conformational variations as possible. The most natural choice is that of vinyl polymer chains, already described in detail in the literature. The schematic representation of the chain fragment depicted in Figure 1 show the backbone torsional freedom parameters (conformational angles ϕ_i and ϕ_{i+1}) of the chain and the constraints (bond lengths and bond angles) which, together with the symmetry operation, generate the chain geometry. Several approximations, duly treated in the literature, can be introduced in the model, spanning from the fully accessible rotational space (freely rotating chain, FRC) to the interdependent rotational model with realistic potentials.

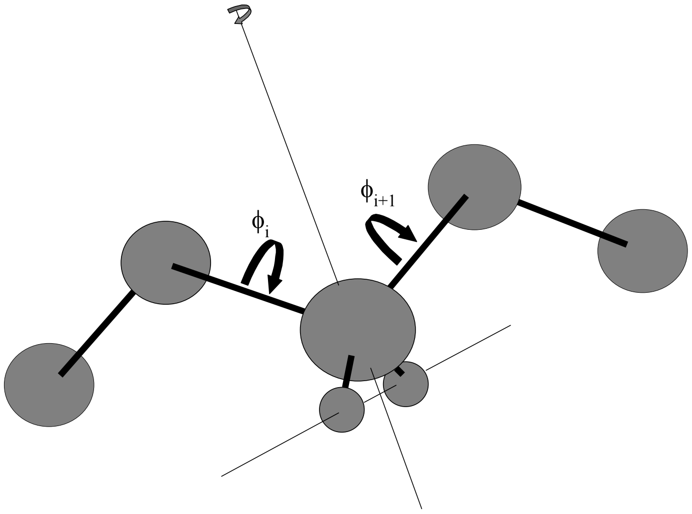

Figure 1. Schematic structure and torsion angles of the polyvinyl (PV) chain segment employed in the RIS and SW approximations.

The simple polymethylene molecular structure implies for each angle ϕ_i a symmetric energy profile with three conformational minima located at 60° (g^+), 180° (t) and 300° (g^-), the lowest energy being centered at 180°. Evaluation of (even) approximated conformational energy of chain segment of Figure 1 clarifies the mandatory choice of a minimum representative unit with two consecutive rotational angles (Figure 2 shows the 3D energy landscape for the RIS model of the chain). This energy landscape provides nine conformational states that have been grouped in Figure

3 according to symmetry operations. Non–symmetric substituents in vinyl polymer chains contribute a distortion to energy landscape which, in some cases, may even displace the minimum energy out of the *tt* state.

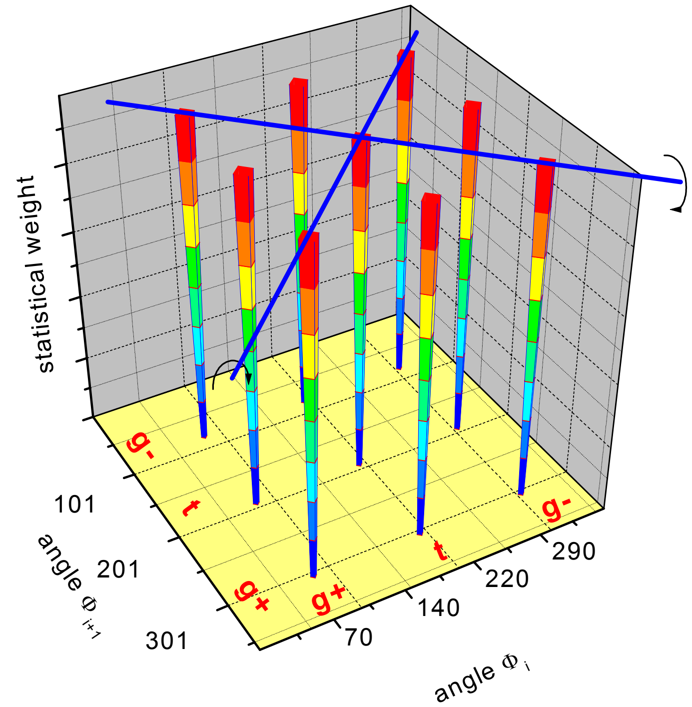

Figure 2. Three–dimensional conformational map building up PV chains. The third dimension wants visualizing the statistical weight value placed in the square RIS matrix of rank 3 (g = gauche, t = trans, other symbols as in Figure 1).

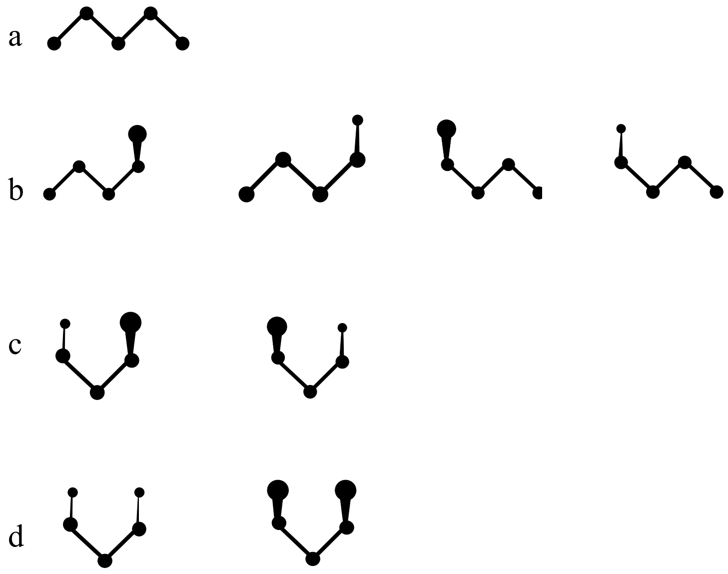

Figure 3. Scheme of the relevant minimum energy conformations employed in Figure (6): tt (a) tg^+, tg^-, g^+t, g^-t (b) g^+g^+, g^-g^- (c) g^+g^- and g^-g^+ (d).

Given these premises, exploitation of the approach illustrated in the previous chapter requires that the dimensional properties of the chain can be widely varied by exploring a full range of energy patterns, upon defining the statistical weight of the conformational states according the scheme depicted in Figure 4 for a single rotational angle.

Case (1). A family of vinyl chains with only one SW minimum and centered at 180°/180° (*i.e. tt*) is considered. Conformational freedom is artificially increased by increasing the width (Δ) of the well by a finite number of steps (grid).

Case (2). The family of chain model of case (1) is extended by moving the absolute minimum energy into each of the $3^2 - 1 = 8$ minima of the unit represented in Figure 1. Note that some asymmetric vinyl chains would fit into these cases.

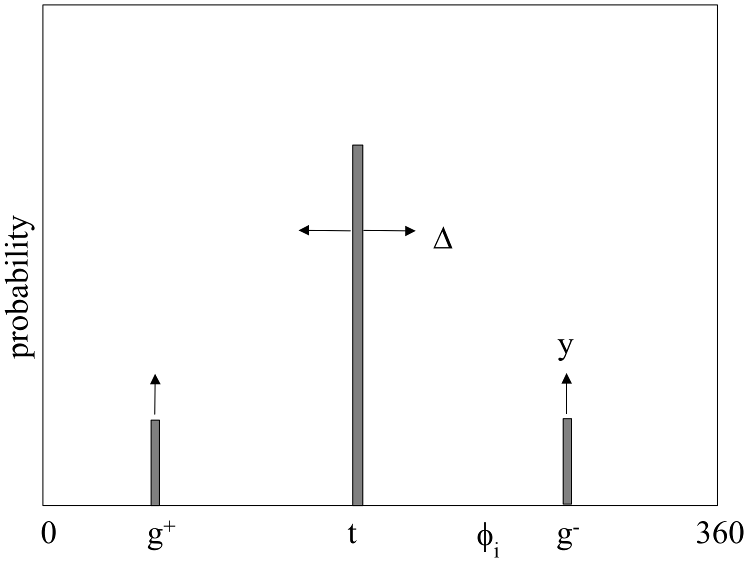

Figure 4. Scheme of the two antagonistic variables which this study bases on: the statistical weight (y, RIS) and the map width (Δ, SW).

Case (3). A family of symmetric vinyl chain (polymethylene–like) is investigated based on the three conformational isomeric states (for each torsional angle) but tuning their statistical weight (relative to the state *t*) by a factor y, with $0 \le y \le 1$.

The above described set of models offers a wide variation of conformational extension being the numerical results a demanding test for the approach here proposed. A subsequent step toward the realistic description of the chain can then be reached by differentiating the probability of consecutive rotations on the basis of the pairwise inter–dependent bond model and therefore disfavoring cross–interacting pairs g^+g^- and g^-g^+.

3.2 Calculation Procedures

Calculation of average chain geometrical properties requires essentially two steps: once an appropriate definition of the conformational energy is given for each selected conformation, a matrix containing the statistical weights is the only required input for the computer evaluation of end–to–end distance and other quantities derived from them; other input parameters, such as bond length and angles are kept constant. Algorithms are provided in literature as well as the computer software written in Fortran [11]. Therefore, the overall polymer chain dimensions can be described by the mean square backbone end–to–end distance and the mean square radius of gyration. The importance of the latter resides in the fact that it can be measured directly by scattering methods. However, the scrutiny of dimensional properties of a given polymer system is more efficiently done when the full range of molecular weight (or degree of polymerization) is analyzed. Under these circumstances, the average topological properties are comparatively well described through the chain–length dependence of quantities such as the characteristic ratio, persistence length and correlation function.

Whatever the chemical features and provided the molecular weight is very large (that is for a degree of polymerization n which approaches infinity), the distribution of end–to–end length is Gaussian and C_n equals an asymptotic characteristic ratio C_∞, *i. e.*:

$$\mathrm{C}_\infty = \lim_{n\to\infty} \frac{\left\langle r^2 \right\rangle_o}{nL^2} \tag{14}$$

where n is the number of monomer units, L the average virtual bond length, and $<r^2>_o$ is the mean square end–to–end distance under unperturbed conditions, *i. e.* θ–Flory solvent [10]. This relation is extremely important, in that any conformational expansion is intrinsically amplified in the chain dimension $<r^2>_0$ by the characteristic parameter C_∞, independently of the number of monomer units n; therefore, C_∞ represents a highly demanding test for the appropriateness of conformational calculations and, at the same time, is a discriminating factor for conformation–dependent solution properties. The values of C_∞ evaluated for each chain model (indicated in cases 1–3) can be therefore aligned to the functional dependence described in the theoretical section.

3.3 Results and Discussion

By using conventional computational procedures (Flory method) [11], several chain characteristics (numerical results) can be obtained for each chain model described in section 3.1. As an example of chain dimension results calculated from the aforesaid procedure, Figure 5 shows some data of C_n *vs.* n for a given SW family (case 2, where Δ ranges from 0 to 2π and the energy minimum is either centered at gg or $g^- g^-$).

Computational algorithms [11] provide the data points of C_n *vs.* n (as those of Figure 5), including the extrapolated value C_∞ for each models and structures, illustrated in Figures 3 and 4.

The limiting values C_∞ have been analyzed by plotting $q_\infty = 1/C_\infty$ as a function of Δ. Figure 6 reports the results for chain models investigated, each solid point representing the q_∞ values for a given starting geometry (Figure 3a–c) as a function of the square–well width Δ. The three data sets converge to the same limit upon $\Delta \rightarrow 2\pi$, where the whole conformational space is accessible, canceling the topological differences of the starting chain models. The continuous lines in Figure 6 represent, instead, the trends of q_∞ *vs.* Δ, which were deployed in the full torsional angle range, provided with the least number of lowest periodic modes, see Eqs. (12)–(13). Heuristic coefficients have been collected in Table 1. As to the model *d*, although standing for an interesting case by itself, it represents a physically unsustainable chain collapse at low Δ range and, being devoted to practical importance, will be neglected at this stage.

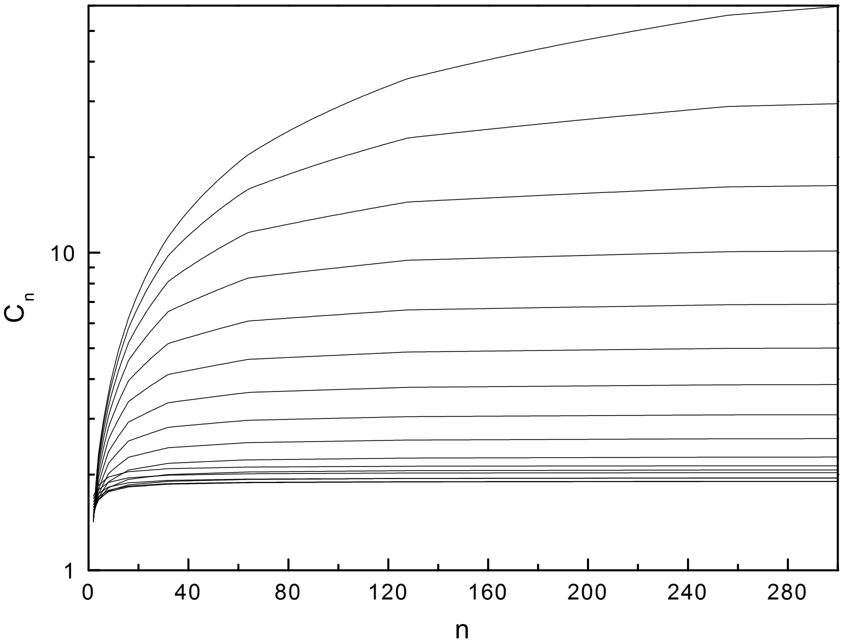

Figure 5. The locus points C_n against n derived to extrapolate their asymptotic values (whenever the limit $n \rightarrow \infty$ is well defined). Curves range from $\Delta = 360°$ (bottom curve) to $\Delta = 20°$ (upper curve) in steps of 20°.

Table 1. The heuristic circle map parameters (see Eqs. (12)–(13)) best fitting all of the trends reported in Figures (6)–(7).

SW initial state	n	k_1	m_1	k_2	m_2
tt	4.20	–0.14	1	0	0
tg	4.79	0	0	–0.053	2
gg	3.63	0.053	1	–0.093	2
g+g–	–	–	–	–	–

RIS model	n	k_i	m_i
indep	5.84	0.13	1
interdep.	15.50	0.07	3

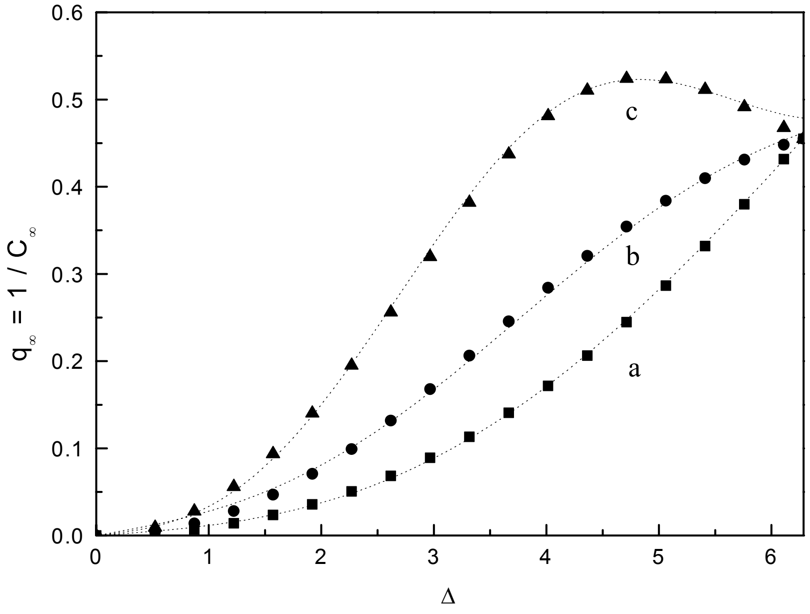

Figure 6. The locus points q_∞ against Δ, calculated from the RIS–SW approzimations applied to PV chains (solid points). The flat landscape was centered at each of the energy minima (a–c) specified by Figure (3). Lines reproduce the best fits based upon sine circle maps.

The parameter Δ (cases 1 and 2) specifically measures the increase in the conformational freedom, a fact that, although indirectly, is similarly obtained upon increasing the variable y from 0 to 1 (case 3). Although both models produce a limiting value of $C_\infty \approx 2.2$, a fundamental difference exists for the rate of freedom increase and for the limiting case reached at Δ = 2π. (*i.e.*, the freely rotating chain) and the RIS model endowed with equiprobable states (y = 1). In the second instance, only three isomeric and representative conformational states are taken into account for each conformational angle (see Figure 2). To homogeneously represent the second data kind, we are clearly needed to translate model–1 (based on SW) into model–3 (based on discrete RIS), that is, to find the angular width (Δ^*) corresponding to a given statistical weight for the trans state (y). From the statistical viewpoint this may be unambiguously done through the fundamental partition function concept (Z), which expresses the width of the accessible conformational space. Chain partition function (and therefore, average monomer conformational entropy) is numerically evaluated in the same computational procedure used to calculate chain dimensions. A (linear) plot can be easily made of $(\log Z/N)_{sw}$ as a function of $\log(\Delta/\Delta_{max})_{sw}$ for the SW model and the corresponding (non–linear) locus point of $(\log Z/N)_y$ as a function of y/y_{max}. In this way, the isoentropic transformation identifies the value of Δ* for each y value.

By doing so, the values of y becomes statistically equivalent to a torsional SW rotation in circle angle unit, and we are finally able to draw the plot in Figure (7), which is now comparable to the first data set, coming directly from SW–like chains. Note also that, to usefully ensure the straight mapping $0 \le y \le 1 \leftrightarrow 0 \le \Delta^* \le 2\pi$, the SW ground energy was fixed to zero. Coefficients of these curves have been also added to Table 1.

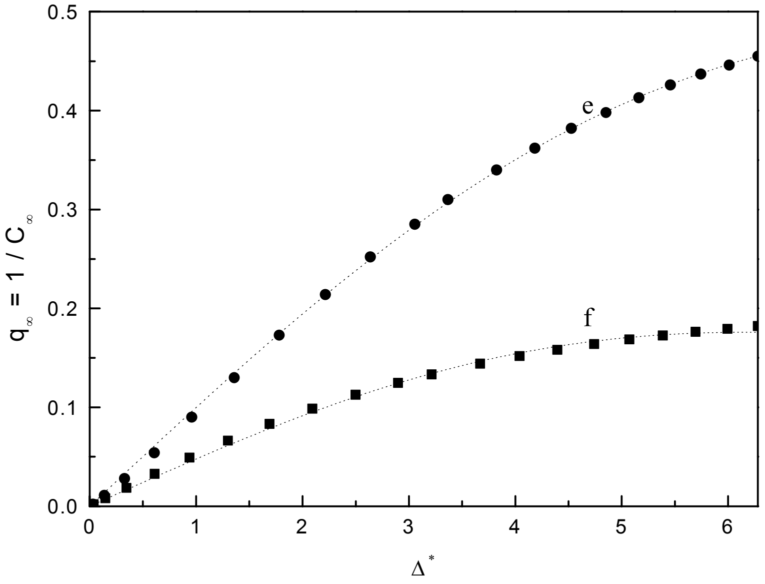

Figure 7. The locus points q_∞ against Δ^*, the latter denoting an apparent map width extracted from the statistical weight *y*, for the independent state model (e) and the interdependent state model (f).

It is worth mentioning at this point that the kind of data reported in Figure 6 (and in part also in Figure 7) shows the rate of changes in the dimensional properties of a polymer upon increasing and mixing several conformational states. Here, only a mechanicistic “mixing rule” has been employed, but a coherent interpretation emerges on the role of “open” and “closed” conformational states depicted in Figure 3a. The actual meaning of curve coefficients and correlation of these coefficients with atomistic features, that is, generating chain conformations from the geometrical scaling of its inner unit shape, need now both more data and conceptual elaboration.

4 CONCLUSIONS

1. Polymer chains were interpreted like geometrical scaling laws from the monomer scale, energy landscapes playing the role of a distortion profile of some inner molecular shape.

2. The characteristic ratio is suggested to descend from rotations on a circle which is set at the chain unit scale, where an elementary step angle may be introduced in analogy to the molecular diameter (or else, the Kuhn step size).

3. A simple parametric investigation of poly–vinyl chains is worked out with conformational square–well energies and the rotational isomeric state method. Poly–vinyl dimensions were calculated as a function both of the angular square–well width (Δ) and the relative state probability (defined by the parameter *y*) and the gotten data turned out being well modeled by sine–like rotations on a circle.

4. A proper mixing of probabilities tuned over the whole accessible conformational space needs

further elaboration along these preliminary lines.

5. To interpret a macromolecule like a geometrical scaling opens new prospects in understanding polymer chain statistics, and statistics in general. Passing from small to large scales by means of straight geometry arguments might yield with time some novel methodology allowing a direct relationship between monomer and polymer assessments. Stressing this viewpoint further, usual numerical methods simulating disorder in polymeric fluids may be even replaced by geometrical problems alone.

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