Eur. Phys. J. Special Topics **225**, 1663–1671 (2016) © EDP Sciences, Springer-Verlag 2016 DOI: 10.1140/epjst/e2016-60017-5

Review

THE EUROPEAN PHYSICAL JOURNAL SPECIAL TOPICS

Understanding the stiffness of macromolecules: From linear chains to bottle-brushes

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Received 1 February 2016 / Received in final form 7 June 2016 Published online 18 July 2016

Abstract. The intrinsic local stiffness of a polymer is characterized by its persistence length. However, its traditional definition in terms of the exponential decay of bond orientational correlations along the chain backbone is accurate only for Gaussian phantom-chain-like polymers. Also care is needed to clarify the conditions when the Kratky-Porod wormlike chain model is applicable. These problems are elucidated by Monte Carlo simulations of simple lattice models for polymers in both d = 2 and d = 3 dimensions. While the asymptotic decay of the bond orientational correlations for real polymers always is of power law form, the Kratky-Porod model is found to be applicable for rather stiff (but not too long) thin polymers in d = 3 (but not in d = 2). However, it does not describe thick chains, e.g., bottle-brush polymers, where stiffness is due to grafted flexible side-chains, and the persistence length grows proportional to the effective thickness of the bottle-brush. A scaling description of bottle-brushes is validated by simulations using the bond fluctuation model.

1 Introduction

The stiffness of macromolecules is a central parameter that influences many properties of macromolecular materials [1-3]. Semiflexible polymers are building blocks for liquid crystalline devices [4] and play a role in living matter (biopolymers such as double-stranded (ds)DNA, actin etc. are fairly stiff [5]). While in many cases stiffness is an intrinsic chain property (e.g., controlled by bond angle and torsional potentials [1]), in the very important class of polyelectrolytes chain stiffness is controlled by the interplay with the counterions in the polymer solution [6–13], and this led to problems with an unambiguous quantitative characterization of the stiffness of these polymers (see, e.g., [10,12]). We will come back to this point in Sect. 4.

To characterize the stiffness of macromolecules quantitatively, the notion of "persistence length" is introduced, with the statement [2] "the directional correlation of

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two segments of a macromolecule diminishes exponentially with the growth of the chain length separating them". So if a bond vector \mathbf{a}_i between two repeat units at positions \mathbf{r}_i , $\mathbf{r}_{i+1}(\mathbf{a}_i = \mathbf{r}_{i+1} - \mathbf{r}_i)$ is projected on a bond vector \mathbf{a}_j s steps along the contour apart, the contour length between the bonds is $s\ell_b = (j-i)\ell_b$ with $\ell_b = |\mathbf{a}_i|$ and hence

$$\langle \cos \theta(s) \rangle = \langle \boldsymbol{a}_i \cdot \boldsymbol{a}_j \rangle / \ell_b^2 = \exp(-s\ell_b/\ell_p),$$
 (1)

where ℓ_p is the persistence length of the macromolecule. Often it is convenient to disregard the fact that a macromolecule is a sequence of discrete monomeric units, and treat it rather by a continuous curve r(s), s being then the curvilinear coordinate along the chain contour. The Hamiltonian of the chain then is [14]

$$\mathcal{H} = \frac{\kappa}{2} \int_{0}^{L} \left(\frac{\partial^2 \boldsymbol{r}(s)}{\partial s^2} \right)^2 ds , \quad \kappa = \begin{cases} k_B T \ell_p & (d=3)\\ 2k_B T \ell_p & (d=2) \end{cases}$$
(2)

while L is the contour length of the chain $((L = (N - 1)\ell_b \text{ in the discrete case when the "chain length", the number of repeat units, is N). From Eq. (2) one finds the mean square end-to-end distance <math>\langle R_e^2 \rangle$ as [14]

$$\langle R_e^2 \rangle = 2\ell_p L \left\{ 1 - \frac{\ell_p}{L} \left[1 - \exp\left(-L/\ell_p\right) \right] \right\}.$$
(3)

For very long chains, $L \gg \ell_p$, Eq. (3) reduces to the standard result for polymers obeying Gaussian statistics, $\langle R_e^2 \rangle = \ell_k L$ ($\ell_k = 2\ell_p$ then is the Kuhn step length). For $L \ll \ell_p$ one simply recovers the behavior of rigid rods, $\langle R_e^2 \rangle = L^2$.

Note that the monomer diameter (or the diameter of the rigid rods, d_r) does not show up in Eqs. (1) and (3), and actually it is tacitly assumed that the chain molecule is an infinitely thin phantom chain ($d_r = 0$), no interaction between monomeric units whatsoever is included. Therefore, the validity of Eqs. (1)–(3) is rather restricted (although this fact often is ignored in the literature, taking the Kratky-Porod wormlike chain model as something like the "gold standard" when one deals with semiflexible polymers).

The outline of this paper now is as follows: In Sect. 2, we discuss Monte Carlo results for a simple lattice model, namely the self-avoiding walk (SAW) on square and simple cubic lattices with an energy penalty ε_b when the SAW makes a kink [15–17]. While this model describes polymers in a very good solvent, also results for the standard SAW model under Theta point conditions [18] will be included. It will be seen that Eq. (1) always fails, while Eq. (3) fails in d = 2, but can be used in d = 3 for very stiff (and thin) chains of intermediate length. Section 3 gives an interpretation of these results, summarizing also Flory-type arguments [17, 19–21]. Section 4 then briefly discusses Monte Carlo simulations of bottle-brush polymers [18] using the bond fluctuation model [28] and their interpretation [15, 21, 22], while Sect. 5 summarizes our conclusions.

2 Monte Carlo test of the Kratky-Porod model

Using the pruned-enriched Rosenbluth method (PERM) [23], very precise data for SAW's on square and simple cubic lattices have been generated, varying the Boltzmann factor $q_b = \exp(-\varepsilon_b/k_BT)$ over two decades and using N up to N = 50000 [15–17]. Figure 1 gives plots of $\langle \cos \theta(s) \rangle$ vs. s, both in the form of semi-log plots (on which Eq. (1) would be a straight line) and as log-log plots, for both d = 2 and d = 3. The parameter q_b controlling chain stiffness varies from $q_b = 1$ (i.e., flexible chains)

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Fig. 1. (a) Semilog plot of $\langle \cos \theta(s) \rangle$ versus *s* for d = 2 (left) and d = 3 (right), showing three choices of q_b , namely 0.005 (red diamonds), 0.01 (green stars), and 0.05 (blue circles). Data are taken for N = 50000 (d = 3) and 25000 (d = 2). Straight lines indicate Eq. (1), with $\ell_p \approx 12$ (d = 2) and 5.7 (d = 3) for $q_b = 0.05$. (b) Log-log plot of $\langle \cos \theta(s) \rangle$ versus *s* for d = 2 (left) and d = 3 (right), showing three choices of q_b , namely 0.05 (magenta x), 0.2 (cyan triangles), and 1.0 (violet crosses). Straight lines indicate Eq. (5). In all legends, the values for the respective persistence lengths are given. {Adapted with permission from H.-P. Hsu, W. Paul, K. Binder, Europhysics Lett. **92**, 28003 (2010) and **95**, 68004 (2011).}

to $q_b = 0.005$ (very stiff chains: then $\ell_p \approx 118$ in d = 2 and $l_p \approx 52$ in d = 3, choosing $\ell_b = 1$ as our length unit here). It is seen that in d = 2 systematic deviations from Eq. (1) start already when $\langle \cos \theta(s) \rangle$ has decayed down to about 0.5, while in d = 3 Eq. (1) seems to hold down to about $\langle \cos \theta(s) \rangle \approx 0.02$, for rather stiff chains, but then also systematic deviations set in. For more flexible chains, Eq. (1) does not work at all, but rather there is clear evidence for a power law decay [24]. But in all cases one way to define a persistence length ℓ_p is to extract it from the initial slope of these curves, i.e. from $\langle \cos \theta(s = 1) \rangle$, via

$$\ell_p/\ell_b = -1/\ln(\langle\cos\theta(s=1)\rangle),\tag{4}$$

even in cases where most of the data fall in the regime where a power law holds,

$$\langle \cos \theta(s) \rangle \propto s^{-\beta}, \quad 1 \ll s \ll N, \quad \beta = 2 - 2\nu,$$
(5)

where ν is the Flory exponent for SAW's, $\langle R_e^2 \rangle \propto N^{2\nu}$, with $\nu \approx 0.588 \ (d=3) \ [25]$ and $\nu = 3/4 \ (d=2) \ [2]$.

One might think that the problem that Eq. (1) for large s always fails is a consequence of the excluded volume interactions prevailing in dilute solutions under good solvent conditions only. However, this is not the case: also for both dense melts [26] and dilute solutions at the Theta temperature [18,27] Eq. (1) fails and there occurs a power law decay, but the decay is faster, described by an exponent $\beta = 3/2$ in both cases. Thus there is no contradiction with the result that with respect to distances



Fig. 2. Log-log plot of $\langle \cos \theta(s) \rangle$ vs. s, for the standard SAW's on the simple cubic lattice for isolated long chains at the Theta temperature, $T = \theta = 3.717\varepsilon/k_B$. Three choices of N are included, as indicated. {Adapted from H.-P. Hsu, W. Paul, K. Binder, Macromolecules 43, 3094 (2010), Copyright ACS (2010).}



Fig. 3. Log-log plot of $\langle R_e^2 \rangle / (2L\ell_p)$ vs. L/ℓ_p , for d = 2 (a) and d = 3 (b). In (a) both data from a bead-spring model, simulated by Molecular Dynamics [29] (MD) and square lattice Monte Carlo data (MC), taken from [16], are included. Three choices of ℓ_p/ℓ_b for the MC data are indicated, while the MD data were taken for a wide range of ℓ_p/ℓ_b , $2 < \ell_p/\ell_b < 533$, but using only N = 400. Adapted from A. Huang, H.-P. Hsu, A. Bhattacharya, K. Binder, J. Chem. Phys. **143**, 243102 (2015) with permission of AIP publishing. In case (b) the wormlike chain (WLC) model prediction, Eq. (3), is included, and L is normalized by ℓ_p . A wide range of choices for ℓ_p is included, as indicated.

between monomeric units Gaussian statistics holds, $\langle R_e^2 \rangle = 2\ell_p L$ applies for large ℓ_p and $L \gg \ell_p$. Remember that we can write the end-to-end vector \mathbf{R}_e as a sum over all the successive bond vectors. Hence $\langle R_e^2 \rangle$ can be written as a sum over all bond vector correlations $\langle \mathbf{a}_i \cdot \mathbf{a}_{i+s} \rangle$. For $\beta < 1$ this sum diverges, and therefore the exponents β and $\nu > 1/2$ are related. For $\beta > 1$ the sum is convergent, however, and of order N. In fact, for no real polymers does Eq. (1) describe the asymptotic decay. Figure 2 illustrates the behavior at the Theta point, using Monte Carlo results [18] for the standard SAW model where an energy ε occurs if two monomeric units are nearest neighbors, and $\varepsilon = k_B T \ln q_\theta$ with $q_\theta = 1.3087$ to reach θ -conditions [23].

Figure 3 presents a test of the basic result of the wormlike chain (WLC) model for the end-to-end distance of semiflexible chains, Eq. (3). One always finds for $L/\ell_p < 1$ the trivial rod behavior, $\langle R_e^2 \rangle/(2L\ell_p) = (L/\ell_p)/2$. However, for $L > \ell_p$ in d = 2(Fig. 3(a)) an immediate crossover to the SAW-like behavior $\langle R_e^2 \rangle \propto \ell_p^{1/2}L^{3/2}$ sets in: recall that $\nu = 3/4$ in d = 2; hence the horizontal plateau at $\langle R_e^2 \rangle/(2L\ell_p) = 1$ predicted by the WLC model is not seen at all, unlike the case of d = 3 (Fig. 3(b)). In d = 3, ultimately also a crossover to the SAW result $\langle R_e^2 \rangle/(2L\ell_p) \propto L^{2\nu-1}$, occurs but when ℓ_p is very large the data follow the WLC prediction over some range, before the SAW behavior sets in.

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The failure of the WLC result in d = 2 is also seen for a off-lattice model with a bond angle potential [29] $U_{\text{bend}}(\theta) = \varepsilon_b(1 - \cos\theta)$, where for large ε_b (then $U_{\text{bend}}(\theta) \approx \varepsilon_b \theta^2/2$) typical angles between subsequent bond vectors are very small, unlike the 90° kinks of the lattice model, which should theoretically make this chain model better representable by the Kratky-Porod model. Although the local chain conformations for the lattice and continuum models thus are very different, the global properties of the chains such as $\langle R_e^2 \rangle$ behave very similar. Figure 3(a) needs to be taken into account for the interpretation of AFM studies of stiff chains like DNA absorbed on planar substrates.

3 Crossover from Gaussian semiflexible chains to SAW's

The double crossover from rods to Gaussian coils and the SAW-like coils, swollen by the excluded volume interaction, is well-known experimentally [30]. However, in this work it was erroneously claimed (without support by the data!) that the crossover from Gaussian to swollen coils occurs universally at $L/\ell_p = 100$, irrespective how large ℓ_p is. This is obviously incorrect, as also Fig. 3(b) shows, and as also can be seen from simple Flory-type arguments [17, 19–21].

For this it is convenient to consider a somewhat different model of semiflexible polymers, describing them as freely jointed rods of length ℓ_p , and diameter d_r . The 2nd virial coefficient then is proportional to $v_2 = \ell_p^2 d_r$ (in d = 3). The free energy of a chain is written as a function of R_e as

$$\Delta F \propto R_e^2 / (\ell_p L) + v_2 R_e^3 [(L/\ell_p)/R_e^3]^2 , \qquad (6)$$

the first term being the elastic energy of the coil and the second term describes binary interactions (proportional to the square of the density $(L/\ell_p)/R_e^3$ of the rods), omitting all prefactors of order unity. For $L \to \infty$, minimization of ΔF with respect to R_e yields

$$R_e \propto (\nu_2/\ell_p)^{1/5} L^{3/5} \propto (\ell_p d_r)^{1/5} L^{3/5}.$$
(7)

Eq. (7) holds only, however, if L exceeds L^* , with

$$L^* \propto \ell_p^3/d_r^2$$
, or, $R_e > R_e^* = \ell_p^2/d_r$. (8)

In d = 2, however, $v_2 \propto \ell_p^2$, and a similar argument yields $R_e \propto \ell_p^{1/4} L^{3/4}$ and $L^* \propto \ell_p$, i.e. a direct crossover from rods to SAW's occurs (as seen in Fig. 3(a)). Eqs. (7), (8) imply $R_e^2/R_e^{*2} \propto (L/L^*)^{6/5}$ or $R_e^2/(2\ell_p L) \propto (L/L^*)^{1/5}$. This relation is tested in Fig. 4, but using empirical estimates for $L^*(q_b)$, which imply $L^* \propto \ell_p^{2.5}$, however. It is unclear whether the 20% discrepancy between this exponent 2.5 and the exponent 3 in Eq. (8) is meaningful; however, we recall that Flory theory also implies a 10% discrepancy between the exponent $2\nu - 1$ in Fig. 4 as well, as is well known [25].

4 Thick, wormlike chains without Gaussian behavior

The archetypical example of thick polymer chains are bottle-brushes, i.e., macromolecules with a comb polymer chemical architecture, where side chains with N effective monomers are grafted (grafting density σ) to a flexible chain with N_b units, acting as backbone [31,32]. The excluded volume forces between the side chains cause an effective stiffening of the backbone, Varying σ and N, the persistence length of



Fig. 4. Log-log plot of $\langle R_e^2 \rangle / (2\ell_p L)$ vs. L/L^* for different choices of q_b and hence ℓ_p , as quoted in the key. The horizontal straight line is the WLC result (Eq. (3)), while the dotted line shows the SAW slope $2\nu - 1 = 0.176$ (rather than 1/5). Data with ordinate values below unity are affected by crossover to the rod regime. {Reproduced from H.-P. Hsu, K. Binder, J. Chem. Phys **136**, 024901 (2012) with permission of AIP publishing.}

these wormlike objects can be controlled. Hence they find much interest as building blocks for various applications in material science, as well as in biological contexts (e.g., aggrecan molecules in the articular cartilage are bottle-brushes [33]). However, extracting ℓ_p for bottle-brushes from scattering experiments encounters enormous difficulties: polydispersity of both backbone and side chains; the cross sectional density profile of the WLC is not known; the effective contour length of the "worm" L_{cc} is unknown, $L_{cc} < L$ since the actual backbone does not need to follow precisely the cylinder axis; etc. Thus, experimental results for ℓ_p are controversial (e.g. [34,35]).

Large scale simulations of bottle-brushes do not suffer from the above difficulties, and structural properties including the cross-sectional density profile are accessible [36] in arbitrary detail. Using the bond fluctuation model [28] and advanced algorithms [26], backbone chain lengths up to $N_b = 1027$ and side chain lengths $6 \leq N \leq 48$ were accessible. In this lattice model [28] each monomeric unit blocks all 8 sites of an elementary cube of the lattice from further occupation, and bond lengths can vary from 2 to $\sqrt{10}$ lattice spacings, so that $\ell_b \approx 2.7$ on average. A detailed mapping of the mean square gyration radius $\langle R_g^2 \rangle$ and the coherent structure factor S(q), q being the scattering vector, on corresponding experiments [37] shows that the model accurately reproduces the structure of the real bottle-brushes on mesoscopic scales.

In rough agreement with experiments [34,35], a scaling of the cross-sectional radius $R_{cs}(N) \propto N^{\nu}$ was found [15,18,21,22,37], and in contrast to theoretical predictions [38] no evidence whatsoever for a Gaussian regime ($\langle R_e^2 \rangle \propto N_b$) of the bottlebrushes was found. It is possible that for much longer $N(N > 10^3)$ and/or very high σ a stronger stretching of the backbone occurs and the Kratky-Porod WLC model would be validated [39], but for all practical purposes this is of no interest. Rather a simple scaling description in terms of blobs with diameter $2R_{cs}(N)$ was established (Fig. 5): from the mean square displacement between backbone monomer $\langle \Delta r^2(s) \rangle s$ steps apart along the contour we find $s_{blob}(N)$ from the condition $\langle \Delta r^2(s_{blob}(N)) \rangle^{1/2} = 2R_{cs}(N)$ (Fig. 5(a)). Rescaling then the mean square end-to-end distance of the backbone $\langle R_e^2 \rangle$ with its asymptotic behavior for large N_b , $\langle R_e^2 \rangle = 2\ell_b \ell_{p,R} N_b^{2\nu}$ where now $\ell_{p,R}$ is an "effective" persistence length extracted directly from these data, and rescaling N_b with $s_{blob}(N)$ we find all data for the different choices of N collapse on a master curve. If a Gaussian intermediate regime with $\langle R_e^2 \rangle \propto N_b$ would have been present, it would show up with a maximum exceeding unity and subsequent decrease towards unity in this plot. The absence of the Gaussian



Fig. 5. (a) Log-log plot of the root mean square displacement of backbone monomers as function of the chemical distance s along the backbone contour, for $N_b = 1027$ and four choices of side chain length N, as indicated. At the ordinate, the independently determined estimates for $2R_{cs}(N)$ are shown and highlighted by horizontal broken lines. The vertical broken straight lines indicate how $s_{\text{blob}}(N)$ is extracted. (b) Rescaled mean square end-toend distance of bottle-brush backbones, $\langle R_e^2 \rangle / (2\ell_b \ell_{p,R} N_b^{2\nu})$, plotted vs. the rescaled chain length $N_b/s_{\text{blob}}(N)$. {Reproduced with permission from H.-P. Hsu, W. Paul, K. Binder, Europhysics Lett. **92**, 28003 (2010).}

regime simply is understood from the Flory treatment also: when $d_r \propto \ell_p$ in Eq. (8), $L^* \propto \ell_p$, and a direct rod-SAW crossover must occur. Thus, stiffness due to chain "thickness" leads to WLC's that are not described by the Kratky-Porod model.

At this point we want to pose the question, whether this behavior might not also be at the origin of the difficulties to identify a persistence length for polyelectrolyte chains in solution. These chains consist of a backbone surrounded by its counterion cloud. If we want to understand the bending stiffness of a polyelectrolyte, we would need to consider the free energy of the compound object of backbone and cloud, and not only the backbone, effectively leading to a description as a thick polymer. Such considerations have also been used to analyze the isotropic-nematic transition in solutions of rod-like polyelectrolytes [40–42]. The radial density distribution within the counterion cloud has been determined experimentally [43] along the same lines as discussed in [36]. Interestingly, it is qualitatively the same as the radial density of side chain monomers obtained in [15] and used to define the effective thickness of bottle-brush polymers. This would suggest that the correct coarse-grained picture of a polyelectrolyte chain (as for the bottle-brush polymers) would not be provided by the Kratky-Porod model but by a pearl-necklace model of blobs with a diameter given by the effective thickness of the chains, and the persistence length of the chains would be also given by their effective thickness.

5 Conclusion

By extensive Monte Carlo simulations and accompanying theoretical arguments, the applicability of the Kratky-Porod (K-P) wormlike model was clarified. It was shown that in d = 2 dimensions (i.e., for semiflexible polymers adsorbed on planar substrates) it fails completely, one has a direct crossover from rods to SAW's. In d = 3, if the chains are sufficiently thin $(d_r \ll \ell_p)$, there occurs a double crossover from rods to Gaussian-like chains, well described by the K-P WLC model, and only for very long chains $(L \gg L^*(\ell_p))$ SAW-type behavior sets in. We have shown that $L^*(\ell_p)$ is still incompletely understood. For bottle-brush polymers, where ℓ_p increases because $d_r = 2R_{cs}(N)$ increases with side chain length N, the Gaussian regime is absent, and again a single crossover from rod-like chains to SAW's occurs, even in d = 3 dimensions.

These considerations can be extended to the chain structure factor S(q) [44], to the problem of semiflexible chains under the action of stretching forces (e.g. [17,44,45], or under confinement (e.g. [29,46–49]). Also the adsorption transition of semiflexible polymers has been of longstanding interest (e.g. [50,51]) as well their nematic ordering in semidilute solutions (e.g. [52,53]). Dynamics of semiflexible polymers is an interesting issue (e.g. [54]), however, lack of space precludes a more detailed discussion. Nevertheless, we hope that the present concise review shows that the physics of semiflexible polymers still is a very active field, with many open problems, and provides a motivation to the reader to study these problems in more detail. Only a small selection of available results could be mentioned here, and we apologize to all colleagues whose interesting contributions could not be included.

Two of us (K.B. and W.P.) have profited in our understanding of polymers from several decades of fruitful collaboration and discussions with Kurt Kremer. H.-P. Hsu is grateful to him for his valuable guidance after getting the chance to join his group. The original research that is reviewed here was carried out in the framework of the collaborative research center SFB625/D3 of the Deutsche Forschungsgemeinschaft (DFG). We also thank Aiqun Huang and Aniket Bhattacharya for their fruitful cooperation (Ref. [29]) from which the MD results in Fig. 3(a) were taken.

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