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Strongly adsorbed comb copolymers with rigid side chainsRoman Stepanyan,¹ Andrei Subbotin,^{1,2} and Gerrit ten Brinke¹¹*Laboratory of Polymer Chemistry and Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands*²*Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow 117912, Russia*

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We study the conformational behavior in a plane of a comb copolymer molecule, consisting of a semiflexible backbone and rigid side chains interacting via a van der Waals potential. Using a mean-field approach, two different regimes are distinguished depending on the strength of the attraction between the side chains. In the weak attraction limit the side chains are oriented preferably perpendicular to the backbone. The persistence length λ of the comb copolymer molecule scales as the second power of the length of the side chain L : $\lambda \propto L^2$. In the strong attraction limit all side chains become strongly tilted and the persistence length scales as $\lambda \propto L^4$. The nonlinear bending regime is also studied and characterized by a change in structure and a decreasing moment of bending force as a function of curvature, i.e., bending becomes easier.

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I. INTRODUCTION

Comb copolymer molecules continue to attract considerable interest. It is usually implicitly assumed that comb copolymer molecules consist of a flexible macromolecular backbone densely grafted with flexible side chains. Due to the development of new synthetic methodologies, these systems are indeed currently attracting a lot of attention [1]. However, equally interesting representatives of this type of molecular architectures are side chain liquid crystal polymers, i.e., flexible backbones densely grafted with rigid side chains (usually via a spacer) [2,3], and hairy rod polymers, i.e., a rigid backbone densely grafted with flexible side chains [4]. Additionally, recent developments have demonstrated that comb-shaped polymer-amphiphile supramolecules, where the side chains are attached to the backbone (flexible or rigid) by physical interactions such as hydrogen bonding, ionic bonding, coordination complexation, etc., offer a unique concept to design functional polymeric materials [5–10].

The conformational characteristics of isolated comb copolymers consisting of a flexible backbone and flexible or rigid side chains have been studied in detail. In particular, the possibility to obtain cylindrical brushlike conformations in dilute solution has been addressed. Several theoretical and computer simulation papers discuss [11–17] the effective elasticity, induced by the steric repulsion between side chains. It was shown that the persistence length λ of a comb copolymer increases strongly as a function of the side chain length and grafting density. This induced stiffness is of interest because it could imply that for a suitable choice of parameters (e.g., side chain length, grafting density, solvent quality) a nematic solution might be obtained. The existing experimental data indicate that in practice [e.g., poly(methacrylate) backbone with oligo methacrylates side chains] indeed very stiff cylindrical brushlike structures are formed [19].

Atomic force microscopy studies of comb copolymer cylindrical brushes address the two-dimensional (2D) shape of the molecules [21,19]. As demonstrated by computer simu-

lations, this 2D confinement increases the stiffness of the molecule even further [15]. More excitingly, however, the 2D confinement was shown to lead to unexpected spiral-like conformations [22]. This problem was addressed theoretically [23] and by computer simulations [20] and a frozen asymmetric distribution of side chains was put forward as a possible explanation. Similar effects were examined a few years ago for linear chains, where as an intermediate state in the coil-globule transition [18] toroidal structures can be formed in 3D [24] or spirals if confined to a flat surface [25]. In this case attraction between the monomeric units was held responsible.

The possibility that attraction between side chains might also lead to spiraling of comb copolymers has not been considered in detail yet. The present work is a first attempt to study theoretically the influence of attraction between side chains on the conformational properties of comb copolymer molecules confined to a plane. To obtain a tractable model we restrict ourselves to a semiflexible backbone densely grafted with rigid side chains. The model should, however, equally well apply to the case of semiflexible side chains with a length not significantly exceeding their persistence length.

In Sec. II the effect of the strength of attraction between the side chains on their orientation will be discussed assuming a straight comb copolymer brush, i.e., a straight backbone. It is shown that a highly condensed state should appear for large attraction energies. In the subsequent section the flexibility of the backbone is introduced and the stability of the straight conformation with respect to bending is examined. Different regimes of persistence behavior are identified and the possibility of globulelike (folded, spiraled, etc.) conformations is discussed.

II. STRAIGHT COMB COPOLYMER MOLECULE

We consider a comb copolymer molecule confined to a plane and model it as consisting of a semiflexible backbone with persistence length λ_0 and rigid side chains. The side chains are rigid rods of length L and width d , equidistantly grafted on both sides of the main chain, alternately pointing

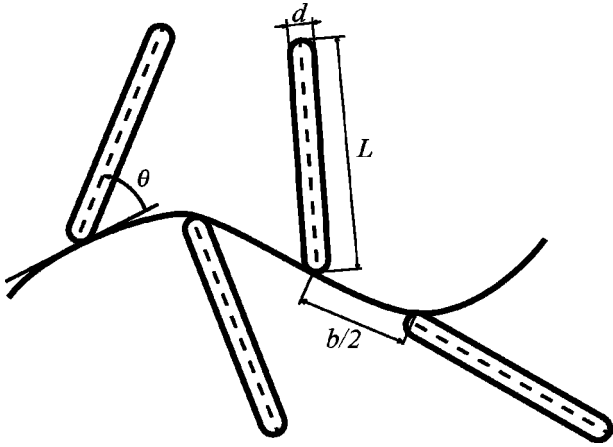


FIG. 1. Schematic representation of a 2D comb copolymer molecule.

“up” and “down” (Fig. 1), with a distance b between two consecutive rods at the same side of the backbone ($d < b \ll L$). We do not allow flipping over from one side of the backbone to the other. The effect of flipping will be discussed briefly in the Concluding Remarks. Two types of interaction between the rods are considered: steric repulsion and van der Waals attraction. The attraction potential *per unit length* is modeled by the inverse sixth power law (in units of $k_B T$)

$$u = -\epsilon \frac{d^4}{r^6}. \quad (2.1)$$

The energy parameter ϵ represents the energy of attraction between two small spheres of diameter d touching each other. If only steric interactions are important, the presence of many rigid side chains leads to a stiff cylindrical comb copolymer brush, particularly in 2D [15–17]. Therefore, we will restrict the discussion first to a straight backbone and devote the subsequent section to the bending elasticity of the molecule.

Generally, the free energy of this complex molecule can be written as a sum of three terms:

$$\mathcal{F} = F_{bb} + F_{sc} + F_{bb-sc}. \quad (2.2)$$

Here F_{bb} is the free energy of the backbone (i.e. of a semiflexible chain with persistence length λ_0), F_{sc} refers to the side chains and includes both an entropy part and the interaction between rods, and finally a cross term F_{bb-sc} representing the interaction between the backbone and the side chains. We will assume that $F_{bb-sc} \ll F_{sc}$ and henceforth the third term in Eq. (2.2) will be neglected.

We assume each rod to have complete rotational freedom, apart from excluded volume constraints, in the plane above or below the backbone. In practice, this can be realized by adding a spacer between the backbone and the mesogenic group representing the side chain [2,3].

We start our theoretical consideration from the *weak attraction limit* where steric repulsion plays the main role and the van der Waals attraction between the rods causes only

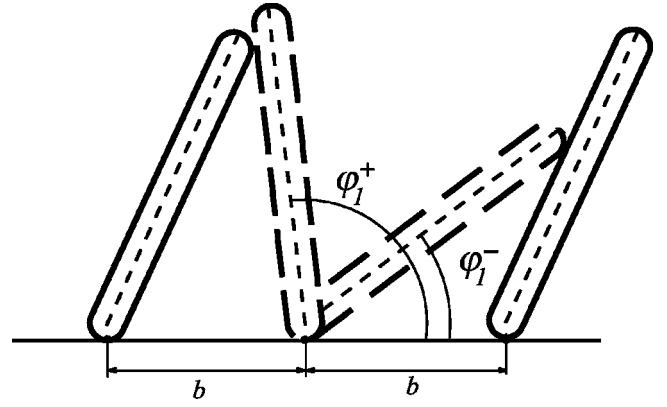


FIG. 2. Test rod and its nearest neighbors for a straight comb copolymer molecule.

small corrections to the system properties. Limits of applicability of this approximation will be discussed below.

Weak attraction limit. Let $f_i(\theta)$ denote the orientation distribution function of the side chain. Here $i=1,2$ denotes the two sides of the backbone and θ is the orientation angle in the plane of the molecule (see Fig. 1).

In the mean field approach the free energy per rod can be expressed as

$$F = \frac{1}{2} \sum_i \int d\theta f_i(\theta) \ln[f_i(\theta)] + \frac{1}{2} \sum_i \int d\theta f_i(\theta) U_i(\theta), \quad (2.3)$$

where $U_i(\theta)$ is the interaction energy. In the present model it comprises hard core repulsion and van der Waals attraction between a test rod and its nearest neighbors *fixed in their average positions* φ_i ($i=1,2$) as depicted in Fig. 2:

$$\frac{1}{k_B T} U_i(\theta) = \begin{cases} U_i^{attr}(\theta) & \varphi_i^- < \theta < \varphi_i^+ \\ \infty & \text{otherwise.} \end{cases} \quad (2.4)$$

From equations (2.3) and (2.4) we obtain the general expression for the free energy functional of a test rod in units of $k_B T$

$$2F = \int_{\varphi_1^-}^{\varphi_1^+} d\theta f_1(\theta) \ln f_1(\theta) + \int_{\varphi_2^-}^{\varphi_2^+} d\theta f_2(\theta) \ln f_2(\theta) \\ + \int_{\varphi_1^-}^{\varphi_1^+} d\theta f_1(\theta) U_1^{attr}(\theta) + \int_{\varphi_2^-}^{\varphi_2^+} d\theta f_2(\theta) U_2^{attr}(\theta). \quad (2.5)$$

The distribution functions $f_i(\theta)$ are found by minimization, $\delta F / \delta f_i(\theta) = 0$

$$f_i(\theta) = \frac{1}{Z_i} \exp[-U_i^{attr}(\theta)], \quad (2.6)$$

where Z_i is the normalization factor.

The free energy per rod follows from Eqs. (2.5) and (2.6) and can for ϵ small (weak attraction limit) be written as

$$F = \frac{1}{2}(F_1 + F_2),$$

$$F_i = -\ln(\varphi_i^+ - \varphi_i^-) + \frac{1}{\varphi_i^+ - \varphi_i^-} \int_{\varphi_i^-}^{\varphi_i^+} U_i^{attr}(\theta) d\theta. \quad (2.7)$$

As mentioned above, the attractive part of the potential is modeled as the well-known van der Waals attraction. In the simplest case of two dielectric spheres it scales as the sixth power of the distance. Also the interaction energy of two parallel infinitely long thin rods can be computed analytically. The intermediate case of finite nonparallel rods can be considered only asymptotically if their length strongly exceeds the distance separating their central axes. This requires the strong inequality $b \ll L$, which is assumed to be satisfied in the present model.

Here we are interested in the attraction between two neighboring side chains, grafted on a straight backbone (Fig. 2). The van der Waals attraction energy in this particular case has the relatively simple form [see Appendix (A5)]:

$$U_i^{attr}(\theta) = -\frac{3\pi\epsilon d^4 L}{8} \frac{1}{b^5} \frac{1}{\sin^5 \varphi_i} \frac{1}{8x_i} \left(\frac{1}{(1-x_i)^4} - \frac{1}{(1+x_i)^4} \right) \quad (2.8)$$

with

$$x_i = \frac{L \sin(\theta - \varphi_i)}{b \sin \varphi_i}.$$

In Eq. (2.8) end effects are neglected and the potential therefore decreases as the fifth power of the distance (see Refs. [26,27]).

Next, the function $U_i^{attr}(\theta)$ will be expanded in a series around the point φ_i

$$U_i^{attr}(\theta) = U_i^{attr}(\varphi_i) + \frac{1}{2} \frac{\partial^2 U_i^{attr}(\varphi_i)}{\partial \theta^2} (\theta - \varphi_i)^2 + \dots, \quad (2.9)$$

where the first derivative term is absent because $\partial U_i^{attr}(\varphi_i)/\partial \theta = 0$ by definition of φ_i . Substituting Eqs. (2.9) and (2.8) into the free energy (2.7) and taking into account that the angles φ_i^+ and φ_i^- for a straight backbone can be found from simple geometry (see Fig. 2)

$$\varphi_i^+ - \varphi_i = \frac{b}{L} \left(\sin(\varphi_i) - \frac{d}{b} \right),$$

$$\varphi_i^- - \varphi_i = -\frac{b}{L} \left(\sin(\varphi_i) - \frac{d}{b} \right), \quad (2.10)$$

we obtain the following expression for the free energy in the weak attraction limit

$$F_i = -\ln \frac{b}{L} - \ln \left(\sin(\varphi_i) - \frac{d}{b} \right) - \frac{3\pi\epsilon d^4 L}{8} \frac{1}{b^5} \frac{1}{\sin^5 \varphi_i}$$

$$\times \left[1 + \frac{5[\sin(\varphi_i) - d/b]^2}{\sin^2 \varphi_i} + \dots \right]. \quad (2.11)$$

At this point we should discuss the range of applicability of the expansion (2.11). In order that it can be truncated after the first term, $\sin(\varphi_i) - d/b$ should be small. This condition can be satisfied if we assume that $d/b = 1 - \delta^2/2$, where $\delta \ll 1$ is a dimensionless small parameter. In this case the angles φ_i should be close to $\pi/2$, which implies that

$$\sin \varphi_i = 1 - y_i^2 \frac{\delta^2}{2}, \quad (2.12)$$

where y_i ($-1 \leq y_i \leq 1$) is a new parameter. Now, the second term between square brackets in Eq. (2.11) is proportional to δ^4 and can be omitted in a theory with accuracy up to δ^2 .

For the straight symmetric brush both sides of the backbone are equal implying that $\varphi_1 = \varphi_2$ (or $y_1 = y_2$). Therefore, combining this fact with Eqs. (2.12), (2.11), and (A6) one obtains the final expression for the free energy of the straight comb copolymer molecule

$$F_0 = -\ln \frac{b\delta^2}{L} - \ln(1 - y^2) - \frac{3\pi\epsilon d^4 L}{8} \frac{1}{b^5} [1 + \frac{5}{2} y^2 \delta^2]. \quad (2.13)$$

The behavior of F_0 can be studied by finding its minima. Depending on the magnitude of ϵ one or two minima are present. The minimum at $y=0$ is important in the region $\epsilon < \epsilon^*$ (*weak attraction*), where

$$\epsilon^* = \frac{8}{15\pi} \frac{b}{L(1-d/b)}. \quad (2.14)$$

It corresponds to all rods oriented preferably perpendicular to the main chain.

The existence of ϵ^* clarifies the exact meaning of the weak and strong attraction limits. For $\epsilon < \epsilon^*$ attraction can only shift slightly the quantitative characteristics of the molecule whereas qualitatively (scaling laws, conformations, etc.) they remain similar to the corresponding comb copolymer molecule with steric repulsion only. For $\epsilon > \epsilon^*$ (strong attraction limit) the picture changes qualitatively. Figure 3 presents y found from minimization of Eq. (2.13) as a function of ϵ . The result is a second-order phase transition at $\epsilon = \epsilon^*$ and a strong decrease in tilting angle (strong tilting toward backbone) for larger values of ϵ .

Since we are dealing with a one-dimensional model with local interactions (we used the van der Waals interaction only between nearest neighbors), the mean field approach does not work in the vicinity of the transition point and we will always have $y=0$ without phase transition at $\epsilon = \epsilon^*$. However, the way this is accomplished in the strong interaction regime is by having alternating domains of oppositely tilted side chains. Geometrical considerations show that the

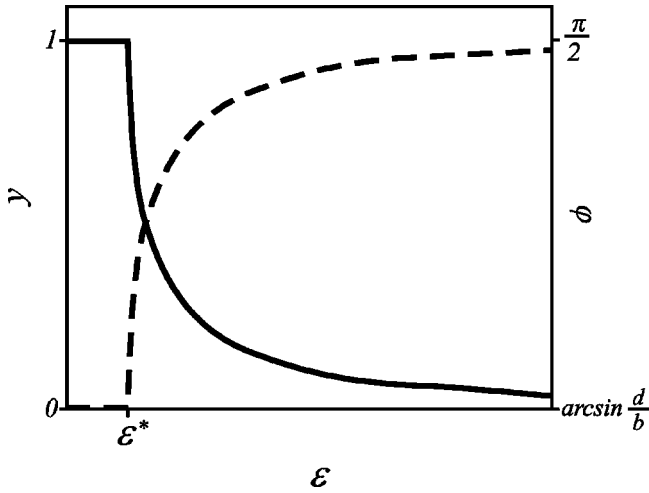


FIG. 3. Behavior of tilting parameter γ (dashed line) and tilting angle φ (solid line) as a function of the interaction strength ϵ .

defect zone between these domains has to be large. Hence the extra free energy associated with a defect zone is large and consequently the domains with side chains strongly tilted in one direction will be large. For a real comb copolymer of finite size this would almost certainly imply a tilting of all side chains at one side to the same direction.

In order to obtain manageable analytic expressions [e.g., Eq. (2.13)], we had to restrict the final discussion to the very dense grafting limit, $d/b \sim 1$. In practice, d/b will be usually considerably smaller. For this case the above analysis remains valid, except that numerical factors will change. Here precise results can only be obtained by numerical methods.

Strong attraction limit. In the strong attraction limit all conformational properties of the comb copolymer molecule are dominated by the attraction part of the free energy. It implies that the system will try to satisfy the condition of minimum attraction energy, which corresponds to the most densely packed state. All rods will lie down on the backbone as shown in Fig. 4. The energy per rod can be estimated from Eq. (2.8) as

$$E = -\frac{3\pi\epsilon L}{8} \frac{d}{b}. \quad (2.15)$$

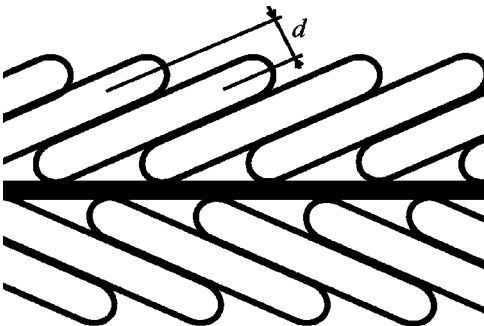


FIG. 4. Dense packing of rods in the straight molecule (the direction of tilting can also be opposite at opposite sides of the backbone).

However, this result is correct only when the temperature $T = 0$.

For $T \neq 0$ fluctuations will break the dense packing and conformations with some free space between the rods will appear, so that the orientation angle will be slightly larger than the minimal possible angle

$$\varphi = \arcsin \frac{d}{b} + \varphi'. \quad (2.16)$$

Here φ' is considered to be a small parameter that gives rise to a change in the attraction energy given by

$$E' \approx \frac{15\pi\epsilon L}{8d} \sqrt{\frac{b^2}{d^2} - 1} \varphi'. \quad (2.17)$$

This energy should be of the order of thermal energy $k_B T$ (note that $k_B T \equiv 1$ in the present paper). This allows us to find the value of φ' and associated with it the characteristic amplitude ψ of the fluctuations of the angle between two consecutive segments of the backbone of length b

$$\psi = \frac{b}{L} \sqrt{1 - \frac{d^2}{b^2}} \varphi' \approx \frac{8}{15\pi} \frac{d^2}{\epsilon L^2}. \quad (2.18)$$

III. BENDING ELASTICITY

So far we limited ourselves to the consideration of a straight comb copolymer brush. The objective of the present section is to analyze the bending elasticity characteristics of the molecule. This will be done by studying the behavior of the free energy as a function of the curvature of the backbone. As before, we will start with the weak attraction limit.

Weak attraction limit. To examine theoretically the elasticity, we should generalize the free energy (2.13) for the case of nonzero curvature. For our purpose we need an expansion of F as a function of $1/R$ up to the quadratic term only. In other words, the limiting angles φ_i^+ , φ_i^- and the attraction energy U_i^{attr} have to be recalculated for the case where the main chain is uniformly bent with a radius of curvature R ($R \gg L$).

The limiting angles can be found from simple geometrical arguments (see Fig. 5)

$$\begin{aligned} \varphi_1^+ - \varphi_1^- &= \frac{2b}{L} \left(\sin(\varphi_1) - \frac{d}{b} + \frac{L}{R} \right), \\ \varphi_2^+ - \varphi_2^- &= \frac{2b}{L} \left(\sin(\varphi_2) - \frac{d}{b} - \frac{L}{R} \right). \end{aligned} \quad (3.1)$$

The attraction energy for the bent brush is given by Eq. (A8) in the Appendix. Together Eqs. (3.1) and (A8) lead to the generalized expression for the free energy as a function of parameters y_1 and y_2

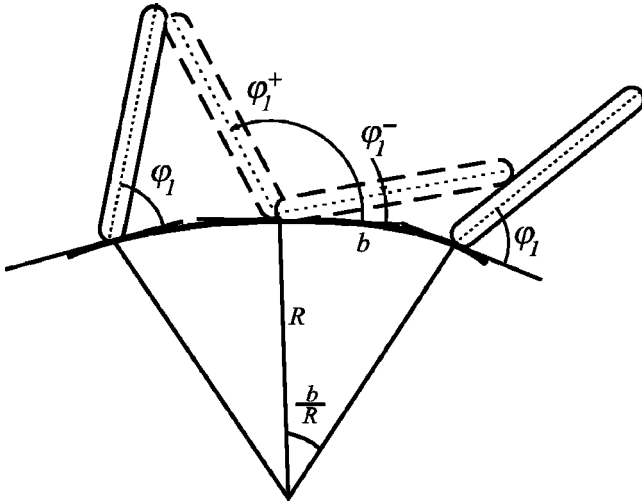


FIG. 5. The test rod and its nearest neighbors for a bent comb copolymer molecule.

$$F = -\ln \frac{b\delta^2}{L} - \frac{1}{2} \ln \left[1 - y_1^2 + \frac{2L}{\delta^2 R} \right] - \frac{1}{2} \ln \left[1 - y_2^2 - \frac{2L}{\delta^2 R} \right] - \frac{3\pi\epsilon d^4 L}{8 b^5} \left[1 + 5 \frac{L^2}{R^2} + \frac{5\delta^2}{4} (y_1^2 + y_2^2) \right]. \quad (3.2)$$

The equilibrium values of the angles (i.e., y_i) are found from minimization of the free energy.

First we focus on the solution for $\epsilon < \epsilon^*$ where the only stable value of the tilt angle corresponds to $y_{1,2} = 0$. In this limit the free energy has a very simple form

$$F = F_0 + \left(\frac{2}{\delta^4} - \frac{15\pi\epsilon L}{8b} \right) \frac{L^2}{R^2}, \quad (3.3)$$

where F_0 is the free energy of the straight brush. The main contribution is due to the repulsive part of the potential. The attraction contribution is negative and reduces the stiffness of the comb copolymer molecule. The persistence length of the molecule can be calculated on the basis of the general relation

$$\Delta F = \frac{\lambda b}{2R^2}, \quad (3.4)$$

where λ is the persistence length of the complex. Hence, it is given by

$$\lambda = \lambda_0 + \frac{L^2}{b} \left(\frac{1}{(1-d/b)^2} - \frac{15\pi\epsilon L}{4b} \right). \quad (3.5)$$

Here λ_0 is the persistence length of the bare backbone. The correction to λ_0 scales as L^2 and it is interesting to note that it decreases with increasing attraction strength.

Strong attraction limit. A qualitatively different behavior can be expected in the region of large attraction parameter $\epsilon \gg \epsilon^*$. As stated in the previous section, the attractive part of

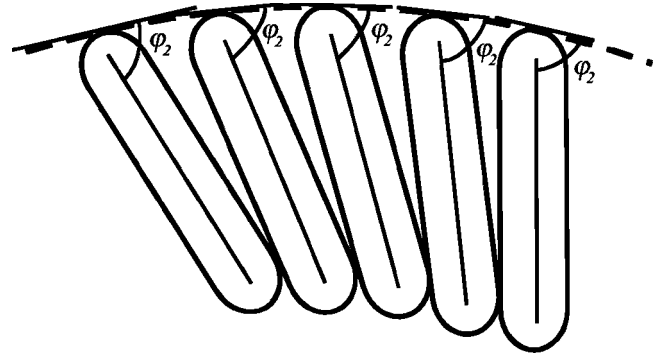


FIG. 6. Ordering of side chains in the concave part of the molecule in the strong attraction limit.

the potential dominates in this regime. For small bending the fluctuations are very important and this case cannot be described by the mean field approach. Therefore we use the scaling approach described in [18] and estimate the persistence length for small ψ by

$$\lambda \approx \frac{2b}{\psi^2}. \quad (3.6)$$

Here ψ is given by Eq. (2.18). This leads to the following expression for the persistence length

$$\lambda \approx \frac{225\pi^2}{32} \frac{\epsilon^2 b L^4}{d^4}. \quad (3.7)$$

It strongly depends on the energy parameter ϵ . The scaling dependence on L also differs from Eq. (3.5) and is much stronger. In the limit $T \rightarrow 0$ (or $\epsilon \rightarrow \infty$) the molecule is densely packed and the persistence length (3.7) becomes infinitely large.

Now we can estimate the characteristic radius of curvature separating the linear and nonlinear bending regimes. The free energy per rod of the bent brush in the linear regime is given by equations (3.4) and (3.7). Comparing this value to $k_B T$ gives

$$R_c \approx \frac{15\pi\epsilon b L^2}{8d^2}. \quad (3.8)$$

This radius is very large for strong attraction and long side chains.

To study the large bending regime ($R < R_c$), we start from the concave part of the bent molecule. Since the fluctuations are not important here, we can safely put the temperature $T = 0$. In this case the rods tend to be as close to each other as possible and form the structure shown in Fig. 6. The orientation angle φ_2 for this conformation is determined from geometry

$$\varphi_2 = \arcsin \left(\frac{d}{b} + \frac{L}{R} \right) - \frac{b}{2R}. \quad (3.9)$$

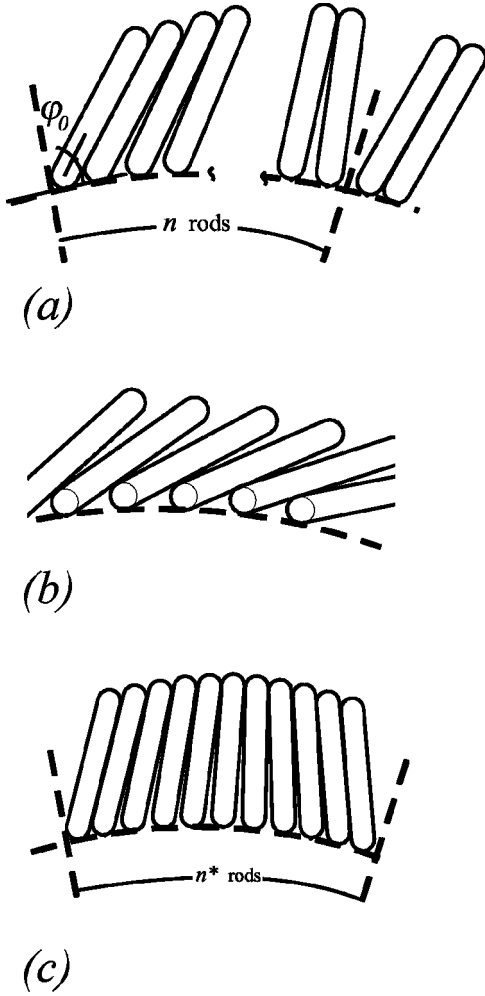


FIG. 7. Domain of n rods on the convex part of the molecule: (a) the general case considered in Eq. (3.13); (b) the ordering corresponding to $n=1$; (c) the “complete” cluster ($n=n^*$).

Proceeding with the calculations one should take into account the approximation $d/b=1-\delta^2/2$, substitute Eq. (3.9) into the general expression (A7) for the attraction energy and expand it into a series of the small parameter L/R . This leads to a correction to the energy of the straight brush given by

$$\Delta E_{concave} = \frac{3\pi\epsilon L}{8} \frac{d}{d} \left[\frac{5L}{2R} - \frac{35L^2}{6R^2} \right]. \quad (3.10)$$

Note that the linear term in the expansion is *positive*.

For the convex part of the molecule the situation is quite different. Due to bending, the available angle space increases. It makes the existence of a continuous structure formed by rods impossible; inevitably some gaps should appear. The space filled by rods between two consecutive gaps will be called domain. Inside such a domain rods form a densely packed system. The “first” rod in the domain [see Fig. 7(a)] will have the smallest angle allowed by steric repulsion

$$\varphi_0 = \arcsin \frac{d}{b} - \frac{b}{2R} \quad (3.11)$$

and the positions of all other rods in the same domain can be calculated from the condition of touching. This leads to the following recursive relation for the orientation angle $y(k)$ of the k th rod

$$y(k+1) = y(k) - \frac{a}{\delta} \left[\cos \left(y(k) \delta - \frac{b}{2R} \right) - \left(1 - \frac{\delta^2}{2} \right) \right] - \frac{b}{R\delta}. \quad (3.12)$$

Knowing that the first rod is oriented according to Eq. (3.11) as

$$y(1) = 1 + \frac{b}{2R\delta}$$

and using the attraction energy between rods in the form (A7) we obtain the change due to bending of the energy per rod for a domain consisting of n rods

$$\Delta E^{(n)} = \frac{3\pi\epsilon d^4 L}{8 b^5} \left[\frac{5}{2} \left(1 + (n-2) \frac{b}{L} \delta \right) \frac{L}{R} - 5n \frac{L^2}{R^2} \right]. \quad (3.13)$$

The domain size n can vary from 1 up to n^* (the value of n^* will be defined below). The equilibrium value of n can be found from minimization of Eq. (3.13). Two different regimes are possible depending on the magnitude of curvature. For very large radius of curvature $R > R^*$ where

$$R^* = \frac{2L^2}{b\delta}, \quad (3.14)$$

the energy (3.13) is a monotonously increasing function of n . This means that the minimal value of the energy will be attained for $n=1$, a situation that is depicted in Fig. 7(b). In this case, the energy per rod is given by

$$\Delta E^{(1)} = \frac{3\pi\epsilon d^4 L}{8 b^5} \left[\frac{5}{2} \left(1 - \frac{b}{L} \delta \right) \frac{L}{R} - 5 \frac{L^2}{R^2} \right]. \quad (3.15)$$

For $R < R^*$, $\Delta E^{(n)}$ decreases with increasing n . In this case the domain will grow until the maximal size n^* allowed by geometry of the bent molecule [see Fig. 7(c)]. This size n^* is to be found from Eq. (3.12) by integration

$$n^* = 2 \int_{y(1)}^0 \frac{dy}{y(k+1) - y(k)}. \quad (3.16)$$

After direct calculation n^* appears to be proportional to the logarithm of the radius of curvature R

$$n^* \simeq \frac{2L}{b\delta} \ln \frac{2\delta^2 R}{L}. \quad (3.17)$$

Finally, the energy per rod in the domain shown in the Fig. 7(c) can be found from Eqs. (3.13) and (3.17)

$$\Delta E^* = \frac{3\pi\epsilon L}{8} \frac{d}{d} \left[5 \frac{L}{R} \ln \frac{2\delta^2 R}{L} + \dots \right]. \quad (3.18)$$

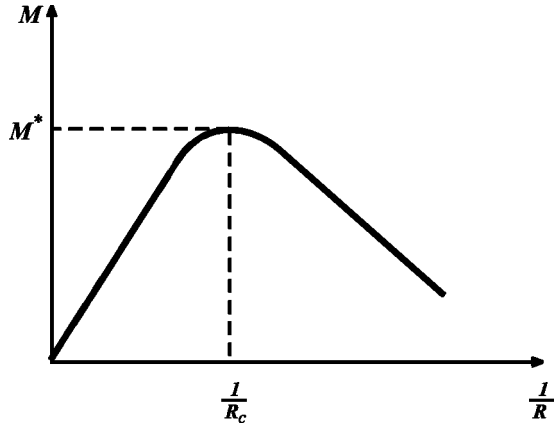


FIG. 8. Schematic representation of dependence of the bending moment on the curvature.

Now the first term in the expansion is proportional to $\ln L/R$ rather than L/R [Eq. (3.15)].

The total energy of the brush is the sum of the concave (3.10) and the convex part, where the convex part is given either by Eq. (3.15) or by Eq. (3.18) depending on the curvature. For radius $R > R^*$ it reads

$$\Delta F = \frac{15\pi\epsilon L}{8} \frac{L}{d} \left[\frac{L}{R} - \frac{13}{6} \frac{L^2}{R^2} \right]. \quad (3.19)$$

As follows from the expansion for the energy of the comb copolymer molecule its stiffness in the strong attraction limit has a nonpersistent character. The presence of a positive linear term implies that the brush will behave like a hard rod: a finite force is needed to start bending. The moment of this force can be defined as the derivative of the free energy with respect to the curvature $M = \partial F / \partial (1/R)$ and equals

$$M \approx \frac{15\pi\epsilon L^2}{8} \frac{L}{d} \left(1 - \frac{13}{3} \frac{L}{R} \right). \quad (3.20)$$

Once the force applied to the straight molecule exceeds the critical value the cylindrical brush will be “broken” and further bending will be much easier. In the linear regime $M \approx \lambda b/R$ increases with increasing curvature $1/R$. The moment of the force as a function of curvature $1/R$ is shown in Fig. 8. It passes through a maximum value $M \sim \epsilon L^2/d$ for $R \sim R_c$.

IV. CONCLUDING REMARKS

In the present paper we described the conformational behavior of comb copolymer molecules with stiff side chains confined to a plane. A mean field approach was used to examine the properties in different regimes. It was shown that attraction between side chains plays a crucial role and that depending on its relative strength different types of behavior are possible.

In the weak attraction limit these comb copolymer molecules resemble persistent chains, although the corrections to the backbone’s persistence length λ_0 are not necessarily small and scale as the second power of the molecular weight

of the side chains $\lambda \approx L^2/b$. In the preferable conformation all rods are uniformly distributed along the backbone and stay perpendicular to the backbone position. This result coincides with that predicted for comb copolymer molecules in three dimensions [14].

For relatively strong attraction the system switches to the tilting conformation and the molecule is characterized by a different scaling law for the persistence length, first $\lambda \approx \epsilon^2 L^4 b/d^4$ and beyond a critical curvature $R_c \approx \epsilon L^2 b/d^2$, a nonlinear bending regime appears with a nonpersistent mechanism of stiffness and decreasing bending moment of force as function of the curvature.

In this regime the side rods arranged in the convex part of the chain undergo the transition, when radius of curvature $R = R^* \sim 2L^2/b\delta$, from uniform ordering to nonuniform ordering with formation of domains consisting of $n^* \approx 2L \ln(2\delta^2 R/L)/b\delta$ rods. This transition is connected with the fact that the minimum of the free energy is attained for the domain structure rather than for uniform orientation, which is characterized by more free space. We also expect (if for some values of parameters $R^* > R_c$ is satisfied) that the domain structure will be formed beyond the transition point.

In experiments the transition from the weak to the strong attraction limit, which may be induced by lowering the temperature, should show itself as an effective stiffening of comb copolymer molecules strongly adsorbed on a surface. In practice the transition from the second power law (3.5) to the fourth power law (3.7) may be accompanied by an isotropic-nematic transition due to drastic stiffening of the molecule. This is of considerable interest as a possible way to adjust the molecular ordering. For very strong attraction (or equivalently for low temperatures), where nonlinear behavior is important, bending requires a critical value for the moment of force (3.20) after which it becomes “softer.”

In the previous sections we were primarily interested in the dependence of the conformational characteristics of the molecule on the energy parameter ϵ and the length of side chains L . We considered a completely symmetric and regular comb structure. In principle it is possible to imagine a system where flipping of side rods over the backbone from one side to the other is possible. This can be realized, for instance, by thermal fluctuations for a comb copolymer molecule confined to the interface between two immiscible fluids. In this case the average value of b is a free parameter and can be varied by flips of side chains. For the weak attraction limit the free energy expression (2.13) shows that this will lead to an increase of the free energy. Thus even if flipping is possible, the rods will stay on different sides of the main chain to optimize the average distance between two neighbors. For strong attraction the state with the smallest value of b is preferable. This implies the possible formation of domains of side chains all flipped to the same side of the backbone with wall defects between two consecutive domains. The characteristic length of such domains will be determined by interplay between energy and entropy of defects (see Ref. [28]). As a result inside one domain the molecule becomes asymmetric. Molecules with different grafting densities at both sides of the main chain were considered in some recent articles [20,22,23]. There the authors assumed a frozen asym-

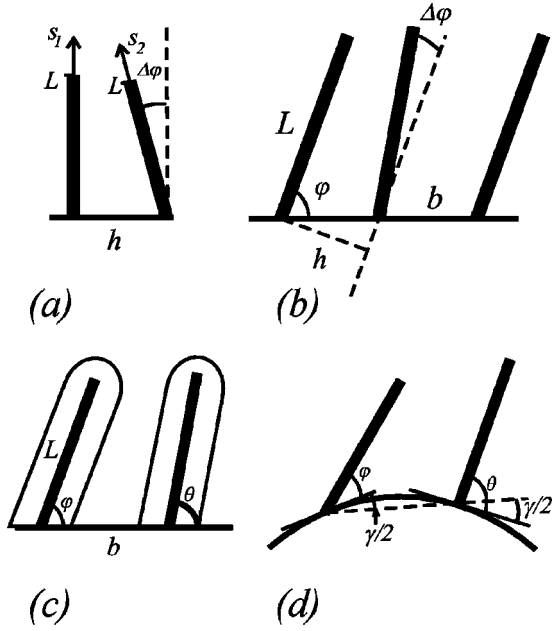


FIG. 9. Illustration for the calculation of the attraction between two rods: (a) two rods of length L at a distance h from each other ($h \ll L$); (b) the test rod between its nearest neighbors fixed in their average position on the straight backbone; (c) two arbitrary oriented neighboring rods on the straight brush; (d) two arbitrary oriented neighboring rods on the bent brush.

metry, whereas in our case it occurs spontaneously as a result of the attractive interaction.

Finally, note that the attraction can also result in spiraling of the comb copolymer molecule (as a part of coil-globule transition) if the contour length is large enough.

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APPENDIX: ENERGY OF ATTRACTION OF TWO LONG RODS

Let us consider two rods of length L grafted as shown in Fig. 9(a) on a distance $h \ll L$ from each other, interacting with a van der Waals potential. The total energy of attraction can be obtained by an integration of Eq. (2.1) along both rods

$$E = -\epsilon d^4 \int_0^L \int_0^L \frac{ds_1 ds_2}{[(h - s_2 \sin \Delta\varphi)^2 + (s_1 - s_2 \cos \Delta\varphi)^2]^{3/2}}, \quad (\text{A1})$$

Introducing new variables

$$y = \frac{s_2}{L},$$

$$\omega = \frac{s_1 - s_2 \cos \Delta\varphi}{h - s_2 \sin \Delta\varphi} \quad (\text{A2})$$

and performing the integration in Eq. (A1) using the strong inequality $L \gg h$, one obtains for the energy

$$E = -\frac{3\pi\epsilon d^4 L}{8} \frac{1}{h^5} \frac{1}{4x} \left(\frac{1}{(1-x)^4} - 1 \right), \quad (\text{A3})$$

where

$$x = \frac{L \sin \Delta\varphi}{h}. \quad (\text{A4})$$

It is easy to apply expression (A3) to the case depicted in Fig. 9(b) in order to get an expression for the energy of attraction between the test rod and its nearest neighbors

$$E = -\frac{3\pi\epsilon d^4 L}{8} \frac{1}{(b \sin \varphi)^5} \frac{1}{8x} \left(\frac{1}{(1-x)^4} - \frac{1}{(1+x)^4} \right). \quad (\text{A5})$$

Here $h = b \sin \varphi$.

In the limit $d/b = 1 - \delta^2/2$ with $\delta \ll 1$ considered in this paper, it is easier to expand the general expression (A1) for the attraction energy into a series of the small parameter δ and then solve the integrals. If y_θ and y_φ are orientation parameters associated with the angles θ and φ [see Fig. 9(c)] according to

$$y = \frac{1}{\delta} \left(\frac{\pi}{2} - \varphi \right)$$

the potential energy can be written in the form

$$U_0(y_\varphi, y_\theta) = -\frac{3\pi\epsilon d^4 L}{8} \frac{1}{b^5} \left[1 - \frac{5}{2} \frac{L\delta}{b} (y_\theta - y_\varphi) + \frac{5L^2\delta^2}{b^2} (y_\theta - y_\varphi)^2 + \frac{5\delta^2}{4} (y_\theta^2 + y_\varphi^2) \right]. \quad (\text{A6})$$

To generalize Eq. (A6) for the case of the bent molecule one should take into account that the angles φ and θ in Fig. 9(c) for the straight molecule correspond to the angles $\varphi + \gamma/2$ and $\theta - \gamma/2$ in Fig. 9(d) when the brush is bent ($\gamma = b/R$). Rewriting these conditions in terms of y_θ and y_φ we arrive at the expression

$$U(y_\varphi, y_\theta) = -\frac{3\pi\epsilon d^4 L}{8} \frac{1}{b^5} \left[1 - \frac{5}{2} \left(y_\theta - y_\varphi + \frac{\gamma}{\delta} \right) \frac{L\delta}{b} + 5 \left(y_\theta - y_\varphi + \frac{\gamma}{\delta} \right)^2 \frac{L^2\delta^2}{b^2} + \frac{5}{4} \delta^2 \left(\left(y_\theta + \frac{\gamma}{2\delta} \right)^2 + \left(y_\varphi - \frac{\gamma}{2\delta} \right)^2 \right) \right]. \quad (\text{A7})$$

Note that in Eq. (A7) θ and φ are the angles between the rod and the tangent to the backbone in the grafting point. Similar expression should be written for the concave part.

Finally, the energy of attraction of the test rod oriented with an angle θ with respect to its two neighbors (both are oriented with φ to the tangent) can be derived from Eq. (A6) and reads

$$U_{neigh}(y_\varphi, y_\theta) = \frac{1}{2} \left[U_0 \left(y_\varphi - \frac{\gamma}{2\delta}, y_\theta + \frac{\gamma}{2\delta} \right) + U_0 \left(y_\theta - \frac{\gamma}{2\delta}, y_\varphi + \frac{\gamma}{2\delta} \right) \right]. \quad (\text{A8})$$

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