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Semiflexible Polymers near Attracting Surfaces

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The chain backbone stiffness, one of the basic characteristics of polymer properties, means the existence of orientation "memory" between segments along chain. The semiflexible, wormlike chain is an intermediate case of polymer stiffness between a rigid rod and an ideally flexible chain. The persistence length of a long semiflexible chain is much smaller than the total contour length, so it can be treated as a flexible one, when we are interested in universal polymer properties measured over the whole macromolecular dimension. However, on length scales smaller than the persistence length, the semiflexible structure can be considered as an array of rigid rods and therefore on these scales the polymer properties are essentially different from those of flexible ones. A wide class of synthetic and biological macromolecules (for instance, the DNA double helix) can be described as composed of semiflexible chains. Among the many significant phenomena induced by polymer stiffness we can mention first the nematic liquid-crystalline ordering[1,2] of semiflexible polymer segments in many different situations including polymers near surfaces and interface regions.[3−5]

The liquid-crystalline (LC) ordering must take place near an attracting surface because the segments with stiffness tend to orient along the surface. The desorption−adsorption (D−A) transition and the properties of adsorbed polymers have been theoretically studied intensively for the cases of flexible chains (see, for instance, refs 6−11). Only a few studies, however, have been devoted to stiffness effects on adsorption,[12−19] despite numerous practical situations involving the persistence length longer than the range of surface attraction. Moreover both in analytical studies and in computer simulations the effects have been analyzed mainly for very short-range surface attraction (see, however, ref 18). Although it is doubtful that many of these approaches in principle can be applied to microscopic surface layers, they are capable of yielding certain aspects of chain stiffness, including stronger tendency to adsorption.

In this communication we investigate the effect of chain stiffness on long semiflexible chains near a flat surface, for a wide range of the ratios of chain persistence length and temperature respectively to the range and depth of the surface attraction potential. To this end, we incorporate within our scaling theory the polymer free energy contributions due to the surface attraction and confinement into its range, which have not been considered explicitly in previous scaling approaches. Our new scaling theory gives a overall physical picture of the various phases, i.e., the desorbed phase and adsorbed phases with isotropic and LC chain distributions and the transitions between them. For more detailed description of the phase diagram and polymer behaviors near the surface we resort to the Green's function approach to semiflexible chains. We develop a perturbation scheme (incorporating the Edwards equation[20] in the zeroth order), which is found to give a reliable support to our scaling-theory picture.

We consider homogeneous semiflexible polymers with a persistence length l much smaller than the contour length L in a dilute solution. We will neglect intersegmental interactions (including excluded volume interactions) other than that incorporated in chain connectivity. The attracting field from a flat surface can be characterized by the range b and the depth U, as in the hard square-well potential where the interaction energy *per unit length* is $U(z) = \infty$ for $z \le 0$, $U(z) = -U$ for $0 < z \le$ b, and $U(z) = 0$ for $z > b$. It is natural to consider the chain persistence length l as the length of a polymer segment. Then $N = L/l \gg 1$ is the total number of segments in a chain and $-lU$ is the potential energy for the segment. Moreover we introduce another length ξ, characteristic of the segment-density (n) change in the direction perpendicular to the surface, the so-called polymer thickness.[6]

Scaling Theory. For very long ($N \gg 1$) semiflexible polymers the free energy change per chain induced by adsorption is given by

$$F = E - T(S_{\mathrm{tr}} + S_{\mathrm{or}}) \tag{1}$$

The free energy of a desorbed chain as a whole does not appear in eq 1, since it is independent of N due to chain connectivity; eq 1 includes only the free energy of adsorption, which is proportional to N. The first term in eq 1 describes the attraction energy acquired by the polymer segments placed inside the potential well, $E = -l\,UN_{\mathrm{in}}$, where $N_{\mathrm{in}} \sim (b/\xi)\,N$ is the number of segments inside the well. S_{tr} and S_{or} are the entropy reductions due to what we call translational and orientational confinements, respectively. If $\xi \gg l$ and $\xi \gg b$ (near the desorption-adsorption transition) we can consider the semiflexible polymer as a flexible one on the scales of ξ and apply the ideal chain scaling arguments[6] for S_{tr}: since $S_{\mathrm{tr}} \propto \mathrm{N}$ and is governed by two lengths, $R \sim \mathrm{N}^{1/2}l$, the unperturbed polymer radius, and ξ, it is given in dimensionless units ($k_{\mathrm{B}} = 1$) by $S_{\mathrm{tr}} \sim -(R/\xi)^2 \sim -N(l/\xi)^2$. The orientational entropy loss or, equivalently, the entropy loss for segments placed inside the well arises from an ordering of polymer segments near the surface. This ordering has to exist, though it is small, even for flexible polymers, because all chains must bend (align) along the surface to "return" to the region with nonzero concentration. If $b \gg l$, we should have an isotropic-type structure of flexible polymers inside the potential well. Since S_{or} for this case is proportional to $N_{\mathrm{in}} \gg 1$ and is governed by b instead of ξ we can retain the scaling argument for S_{tr}, with ξ and N replaced by b and N_{in}, respectively: $S_{\mathrm{or}} \sim -N_{\mathrm{in}}(l/b)^2$. To acquire enough potential energy for adsorption, the polymer segments should keep as many segments as possible inside the well. If the persistence length is larger than the range of attraction, segments will tend to orient along the surface without having much chance to form loops reaching into the bulk. Above a certain value of

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l/b there exists on the surface "pancakelike" LC ordering for polymer segments. The $S_{\rm or}$ then has to be proportional to the number $N_{\rm in}$ of segments inside the potential well as before. Because the polymer segments are oriented along the surface, the persistence length l has an influence on the polymer dimensions in directions along the surface mainly, and therefore the l is absent in the leading term in $S_{\rm or}$ at least for the freely jointed chain model: $S_{\rm or} \sim -N_{\rm in}$. Different estimations for a similar confinement energy for wormlike chains are discussed in refs 18 and 21. However they do not change any qualitative conclusions of the present scaling theory. Summing up, we write eq 1 for the free energy change as

$$\frac{F}{TN} \sim \left[-\frac{lU}{T} + \begin{Bmatrix} \left(\frac{l}{b}\right)^2, & \text{(IA)} \\ 1, & \text{(NA)} \end{Bmatrix} \right] \left(\frac{b}{l}\right)\left(\frac{l}{\xi}\right) + \left(\frac{l}{\xi}\right)^2 \tag{2}$$

where the notations (IA) and (NA) refer respectively to isotropic and LC adsorbed states. When the square bracketed material in eq 2 is a positive value, the free energy change is a minimum, $F = 0$, at $n \sim 1/\xi = 0$ ($\xi \to \infty$), corresponding to the desorbed (D) phase. If the bracketed term is negative, then the free energy change has a negative minimum value at a finite value of the equilibrium length ξ, corresponding to an adsorbed (A) phase for each case of isotropic and LC distribution. The intermediate case, where the bracketed term is zero, corresponds to the conditions for desorption−adsorption (D−A) transitions, specifically, between desorbed−isotropic adsorbed phases (D−IA) and desorbed−LC adsorbed phases (D−LCA):

$$\frac{T_{\rm D-A}}{lU} \sim \begin{cases} (l/b)^{-2} & \text{for D−IA} \\ 1 & \text{for D−LCA} \end{cases} \quad \text{or} \quad \frac{T}{bU} \sim \begin{cases} (l/b)_{\rm D-A}^{-1} & \text{for D−IA} \\ (l/b)_{\rm D-A} & \text{for D−LCA} \end{cases} \tag{3}$$

It is worth noting that the incorporation of $S_{\rm or}$ is essential to make our scaling-theory approach more complete than other scaling approaches (see, for instance, ref 6), without which the desorption transitions can be described only implicitly and thus the transition conditions cannot be evaluated. Within the descriptions of the standard flexible-chain Edwards equation (eq 4) and semiflexible-chain one (eq 6) $S_{\rm or}$ turns out to be the entropy loss due to the confinement of the segments inside the well, while the $S_{\rm tr}$ in previous scaling theories[6] corresponds to outside-well confinement only. The D−A transition temperature $T_{\rm D-A}$ for flexible chains (isotropic case) above is also consistent with that obtained from the Edwards equation.[8,9,22]

Near the D−A transitions the minimum free energy change of the adsorbed phase is found to go like $F_{\rm A}/(TN) \propto -\tau_T{}^2$ or $F_A/(TN) \propto -\tau_{(l/b)}{}^2$, where $\tau_T \equiv (T - T_{\rm D-A})/T_{\rm D-A}$ and $T_{(l/b)} \equiv [(l/b) - (l/b)_{\rm D-A}]/(l/b)_{\rm D-A}$, are the relative distances of the phase from the transition points in terms of the temperature or the ratio l/b, respectively. In any case, we obtain proportionality to the second power of τ as $\tau \to 0$. Thus we can conclude that the desorption-to-weak-adsorption transition is a second-order phase transition, whether the near-surface adsorbed phase is isotropic or LC. For long flexible chains, for which the isotropic structure is the only possibility, this is a well-known result (see, for instance, ref 1).

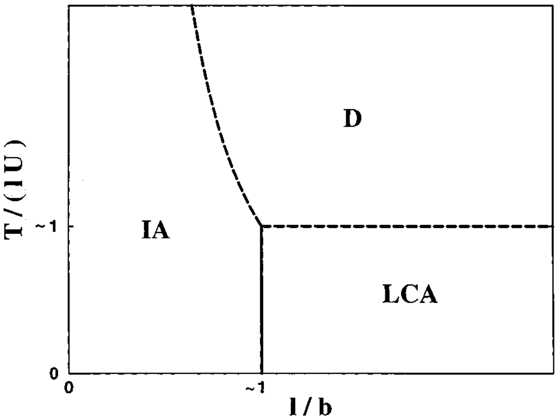

Figure 1. Phase diagram of polymer near an attracting flat surface as predicted by our scaling theory. The region (D) corresponds to the desorbed phase, the regions (IA) and (LCA) are the isotropic and "pancakelike" LC adsorbed phases. The solid and dashed lines correspond to the first and second-order phase transitions, respectively.

As follows from the minima F_{IA} and F_{LCA} of eq 2, for the two adsorbed states with the isotropic and LC structures, the IA-LCA phase transition takes place at $(l/b)_{\rm IA-LCA} \sim 1$. Since $(F_{\rm LCA} - F_{\rm IA})/(TN) \propto -\tau_{(l/b)}$, where $\tau_{(l/b)} \equiv [(l/b) - (l/b)_{\rm IA-LCA}]/(l/b)_{\rm IA-LCA}$, we can conclude that IA-LCA transition is first order as are the isotropic−nematic transitions of other three-dimensional (3D) systems.[1,2]

Using our scaling theory given above, we derive the phase diagram shown in Figure 1. One of the main results, which follows from this diagram, is that as the persistence length l increases the desorption-adsorption transition temperature $T_{\rm D-A}$ decreases (or the transition depth of the potential $U_{\rm D-A}$ increases) for values of l smaller than $\sim b$ and it increases (decreases) for larger values of l. These results are in a qualitative agreement with the fact known from the literature[13−18] that semiflexible chains adsorb more easily than flexible ones. The $T_{\rm D-A}$ does not depend very much on b for small values of b.

Green's Function Perturbation Theory for Semiflexible Chains. On the other hand, an analytical approach to the problem is the Green function $G_N(\boldsymbol{q}_0,\boldsymbol{q}_N)$ of a polymer chain, indicative of the probability of finding one end segment at $\boldsymbol{q}_N$ given the initial segment at $\boldsymbol{q}_0$. While, for flexible chains, the generalized coordinate $\boldsymbol{q}$ includes the 3D position $\boldsymbol{x}$ only, for a semiflexible chain it includes in addition the 2D orientation $\hat{\boldsymbol{u}}$ of the segment. The recurrence equation[1] $G_{N+1} = \hat{Q}G_N$, where $\hat{Q}$ is the transfer operator, for a long chain ($N \gg 1$) can be rewritten as $-\partial G_N/\partial N = (1 - \hat{Q})G_N$. Since the integral of $G_N(\boldsymbol{q}_0,\boldsymbol{q}_N)$ over $\boldsymbol{q}_0$ and $\boldsymbol{q}_N$ yields the partition function, on the basis of ground state dominance approximation for large N an adsorbed polymer has the equilibrium free energy per segment $F/(NT) = -\ln \Lambda \equiv \epsilon$ and the end segment distribution given by $\psi(\boldsymbol{q})$. Here Λ and ψ are respectively the ground-state eigenvalue and eigenfunction of $\hat{Q}$: $\hat{Q}\psi = \Lambda\psi$.

For flexible chains, the last equation is reduced to the Edwards equation of the Schrödinger type[20]

$$(l_{\rm k}{}^2/6)\ \nabla_{\rm x}{}^2\psi(\mathbf{x}) = [\beta l_{\rm k} U(\mathbf{x}) - \epsilon]\psi(\mathbf{x}) \tag{4}$$

where l_k is the Kuhn length and $\beta = 1/T$. A wormlike chain can be viewed as a continuum limit of an interconnected array of rigid-rods with a fixed length $\tilde{l}$

($l \gg \tilde{l}$) and at fixed bond angle $\tilde{\theta}$. For this discrete model the eigenvalue equation leads to[23]

$$\left[-\tilde{l}\,(\mathbf{u}\cdot\nabla_{\mathrm{x}}) + \frac{\tilde{\theta}^2}{4}\nabla_{\mathrm{u}}{}^2\right]\psi(\mathbf{x},\mathbf{u}) = [\beta\tilde{l}U(\mathbf{x},\mathbf{u}) - \epsilon]\,\psi(\mathbf{x},\mathbf{u}) \tag{5}$$

involving the potential U per length that can depend on orientation as well as position, and $\nabla_{\mathrm{u}}{}^2$, the Laplacian operator in the 2D orientational space (on a unit sphere, $|\mathbf{u}| = 1$). Taking the standard continuum limit $\tilde{l} \to 0$ and $\tilde{\theta} \to 0$ with a finite persistent length defined by $l \equiv 2\tilde{l}/\tilde{\theta}^2$ eq 5 is transformed to

$$[-2l\,(\mathbf{u}\cdot\nabla_{\mathrm{x}}) + \nabla_{\mathrm{u}}{}^2]\,\psi(\mathbf{x},\mathbf{u}) = [\beta 2lU(\mathbf{x},\mathbf{u}) - \epsilon]\psi(\mathbf{x},\mathbf{u}) \tag{6}$$

Equation 6 is the main equation for the description of semiflexible polymer properties. The function ψ determines the density distribution of polymer segments:[1] $n(\mathbf{x},\mathbf{u}) = \psi(\mathbf{x},\mathbf{u})\psi(\mathbf{x},-\mathbf{u})$, where $\int n(\mathbf{x},\mathbf{u})\,\mathrm{d}^3x\,\mathrm{d}^2u = N$. We remark here that, although eq 5 is valid for $\beta\tilde{l}U \ll 1$ only, the value $\beta 2lU = (4/\tilde{\theta}^2)\,\beta\tilde{l}U$ in eq 6 can go far beyond this restriction because of the continuum limit $\tilde{\theta} \to 0$.

Within a universality class, the macroscopic properties of polymers do not depend on details of the microscopic chain structure. Indeed on macromolecular scales and for small values of the external field ($\beta 2lU \ll 1$) eq 6 for the wormlike polymer is reduced to the standard Edwards equation, eq 4. On smaller length scales or for larger values of the external field $2lU$ the corrections arising from the polymer stiffness should be taken into account. In ref 3 these corrections were described for a homopolymer globule without external fields. Here we will not assume a priori the smallness of external fields, but consider the correction given by the small length scale description.

The wormlike chain under a hard square-well potential $U(z)$, can be described in terms of two independent variables z, and θ, the angle of segment orientation with respect to the z -axis perpendicular to the surface. Thus $\psi(\mathbf{x},\mathbf{u}) = \psi(z,\theta)$. Let us introduce the dimensionless coordinate $Z \equiv z/(2l)$ and variable $\psi \equiv (\beta 2lU(z) - \epsilon)$. Now expanding ψ in a series of the Legendre polynomials, $\psi(Z,\theta), = \sum_{i=0}^{\infty} \psi_i(Z)P_i(\cos\theta)$, can transform eq 6 to a recurrence relation

$$\psi_i[i(i+1) + \phi] = -\frac{i}{2i-1}\frac{\mathrm{d}\psi_{i-1}}{\mathrm{d}Z} - \frac{i+1}{2i+3}\frac{\mathrm{d}\psi_{i+1}}{\mathrm{d}Z} \tag{7}$$

where $i \geq 0$. In the perturbation scheme, in which the relative curvature $|(4l^2/\psi_0)(\mathrm{d}^2\psi_0/\mathrm{d}z^2)| \ll 1$, eq 6 leads to the Edwards equation, eq 4, with $l_{\mathrm{k}} = 2l$ in the zeroth order, and, with $\psi = \psi_0 + \psi_1 P_1(\cos\theta)$, to the first-order perturbation equation

$$3\phi(2+\phi)\psi_0 = \frac{\mathrm{d}^2\psi_0}{\mathrm{d}Z^2} + \frac{4}{15(2+\phi)(6+\phi)}\frac{\mathrm{d}^4\psi_0}{\mathrm{d}Z^4} \tag{8}$$

where ψ_1 is replaced by ψ_0 using the recurrence relation. For the adsorbed state the physical solutions of this equation should satisfy two natural boundary conditions, (i) $\psi_0 \to 0$ at $Z \to 0$ and $Z \to \infty$, (ii) two conditions of continuity for ψ_0 and $\mathrm{d}\psi_0/\mathrm{d}Z$ at the boundary of the potential well (at $z = b$; i.e., $Z = b/(2l)$), and (iii) a normalization condition.

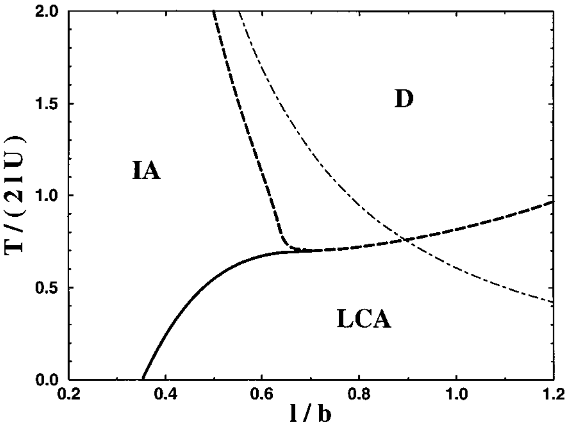

Figure 2. Phase diagram obtained by the Green's function first-order perturbation theory. The notations and description are same as in Figure 1. The dot−dashed line describes the desorption−adsorption boundary in the zeroth order perturbation theory, i.e., the Edwards equation for flexible polymers.

Considering only the first order of perturbation, the solution of eq 8 subject to the boundary conditions can be written as

$$\psi_0 = C_1\sin(\sqrt{m_-}Z) + C_2\sin(\sqrt{m_+}Z) + C_3\,[\cos(\sqrt{\mathrm{m}_-}Z) - \cos(\sqrt{m_+}Z)]$$

inside the potential well ($\phi_{\mathrm{in}} = -\beta 2lU - \epsilon < 0$) and as $\psi_0 = C_0\exp(-\sqrt{k}Z)$ outside it ($\phi_{\mathrm{out}} = -\epsilon > 0$), where $k = (15/8)(2-\epsilon)(6-\epsilon)\{-1 + [1 - (48/15)\,\epsilon/(6-\epsilon)]^{1/2}\}$ and

$$m_{\mp} = \frac{15}{8}(2+\phi_{\mathrm{in}})(6+\phi_{\mathrm{in}})\left[1 \mp \left(1 + \frac{48}{15}\frac{\phi_{\mathrm{in}}}{6+\phi_{\mathrm{in}}}\right)^{1/2}\right]$$

It is clear that using two continuity conditions and the normalization we can determine the equilibrium free energy ϵ and constants C_0 and one of C_1, C_2, and C_3. The two free constants are to be chosen such that a minimum value of the equilibrium free energy ϵ is obtained. As can be seen, the minimal free energy corresponds to one of two following states: (i) $C_1 > 0$ and $C_2 = C_3 = 0$ (identified as an isotropic state with $m_I \equiv m_- < m_+$) and (ii) $C_2 > 0$ and $C_1 = C_3 = 0$ (identified as a LC state with $m_N \equiv m_+$).

As the continuity conditions lead to $\sqrt{m}\cot[(\sqrt{m})b/(2l)] = -\sqrt{k}$, then the condition of the D−A transition, i.e., the condition of forming a bound state with $\epsilon = 0$, can be written as $(\sqrt{m_{\mp}})_{\epsilon=0}\,b/(2l) = \pi/2$, where negative and positive signs refer to isotropic and LC phases. The standard orientation order parameter defined locally by $\eta(Z) = \langle P_2(\cos\theta)\rangle_z$ is found to be of the order $(l/b)^2$ inside the well ($\eta < 0$ near the surface). As the stiffness (persistence length) increases, $|\eta|$ increases, giving rise to an isotropic-to-LC transition in adsorbed states. This transition can occur at $\epsilon_I = \epsilon_N$, hence at $m_I = m_N$. From the expressions of $m_{\mp}$ this condition is met at $\phi_{\mathrm{in}} = -(\beta 2lU + \epsilon) = -10/7$ below the temperature $T/(2lU) = 0.7$ of the bicritical point, and together with the continuity conditions, it determines the boundary between isotropic and nematic phases.

The Figure 2 is the phase diagram that results from this perturbation theory. For flexible chains with very small l/b the D−A transition behaviors approach to those given by the Edwards equation. On the other hand, the figure shows that the semiflexible chain with l larger than b adsorbs more easily (desorption temperature is higher) than is given by the Edwards equation. This fact by itself was mentioned before[13−18] and it takes place due to emergence of the "pancakelike" LC order induced by chain stiffness. The adsorbed state has been discussed as a "squashed regime" in ref 18, where some properties of the unbinding transitions of semiflexible polymers were analyzed. Also this state is very similar to the "pancakelike" orientational wetting layer of semiflexible polymers near a hard wall.[19]

It is shown in our calculations that, in the above desorption-to-weak-adsorption, isotropic-LC transitions are respectively second and first order. The phase diagram (Figure 2) is qualitatively in accord with our scaling theory prediction (Figure 1). The first-order perturbation theory is limited by the condition of small relative curvature, $(4l^2/\psi_0)|d^2\psi_0/d_z^{\,2}|$, however. In the cases of strong adsorption within a short range of attraction, where the curvature can be larger, one has to go beyond the low order perturbation theory. In forthcoming papers,[24] we present an interpolative scheme based upon many order perturbation, which describes the weak-to-strong adsorption transitions, as well as the effect of chain stiffness in more details for $(l/b) > 1$ but nevertheless turns out to retain much of our basic scaling and perturbation theory results given here. To conclude, we predict for semiflexible polymers on surfaces adsorbed phases with both isotropic and "pancakelike" LC chain distributions and we have analyzed the transition between them and their desorption transitions. The transitions are an outcome of the interplay between surface attraction, thermal fluctuation, and chain stiffness.

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