ADSORPTION OF POLYMERS ON A FLUCTUATING SURFACE

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Abstract

We study the adsorption of polymer chains on a fluctuating surface. Physical examples are provided by polymer adsorption at the rough interface between two non-miscible liquids, or on a membrane. In a mean-field approach, we find that the self–avoiding chains undergo an adsorption transition, accompanied by a stiffening of the fluctuating surface. In particular, adsorption of polymers on a membrane induces a surface tension and leads to a strong suppression

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of roughness.

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The adsorption of polymers on a surface is of both technological and biological importance. The coating of a rigid wall by polymers has been studied extensively [1]. The adsorption of polymers (e.g. proteins) on a cell membrane is further complicated by the fluctuations of the adsorbing surface. This problem bears some resemblance to the wetting of a substrate [2], which is easier to study due to the absence of self-avoiding constraints for the wetting interface [3]. The latter problem has been studied more recently in the presence of (quenched or annealed) roughness of the adsorbing surface [4, 5].

In this letter, we study the adsorption of a single polymer, or a dilute solution of polymer chains, on a soft (fluctuating) surface. A related case has been studied by de Gennes [7]. Examples of soft surfaces are provided by the boundary of a liquid, or the interface between two non-miscible fluids below their demixing point. Fluctuations of the surface in these examples are controlled by the surface tension. Other examples are fluid (or polymerized) membranes, where fluctuations are governed by the resistance to bending (or anomalous rigidity). An ideal polymer chain is always adsorbed to an attracting surface, hard or soft. Using a variational approach, we show that there is an unbinding transition for self-avoiding polymers. The critical temperature $T_c$, is inversely proportional to the excluded volume parameter $v$, and to the surface concentration of monomers $c$. The adsorption of polymers at temperatures below $T_c$ is accompanied by a stiffening of the surface. This effect is most pronounced for fluid membranes, which acquire an effective surface tension from the adsorbed polymer layer.

Consider a fluctuating $D$ dimensional “surface” embedded in $d = D + 1$ dimensional space. Within the SOS (solid-on-solid) approximation, configurations of the surface are parametrized by its height $z(x)$, where $x$ is a $D$ dimensional vector spanning the $z = 0$ plane. The surface has linear dimension $L$ and an area that scales as $L^D$. We assume that it is in contact with a dilute solution of $N$ chains of $N$ monomers each, such that the total number of monomers $N_m = N N$, also scales as $L^D$. The conformations of the polymers are indicated by $d$ dimensional vectors $\{r_i(s)\}$, where $s$ denotes the curvilinear abscissa of a monomer of Kuhn length $a$. Using a coarse grained Hamiltonian for the long wavelength
fluctuations, the partition function is

\[
Z = \int \mathcal{D}z(x) \prod_{i=1}^{N} \mathcal{D} \vec{r}_i(s) \exp \left[ -\frac{K}{2} \int^L d^Dx (\nabla^n z(x))^2 - \frac{d}{2a^2} \sum_{i=1}^{N} \int_0^N ds \left( \frac{d \vec{r}_i}{ds} \right)^2 \right] \times \exp \left[ -\frac{v}{2} \sum_{i,j=1}^{N} \int_0^N ds \int_0^N ds' \delta(\vec{r}_i(s) - \vec{r}_j(s')) \right] \times \exp \left[ \beta \int^L d^Dx \sum_{i=1}^{N} \int_0^N ds \delta(\vec{\rho}(x) - \vec{r}_i(s)) \right].
\]

(1)

The first two terms in the above expression denote respectively the elastic energy costs of distorting the surface and the polymers. The exponent \(n\) is equal to 1 for interfaces (surface tension dominated), and 2 for fluid membranes (bending energy). The third term represents the repulsion between monomers in a good solvent (\(v > 0\) is the excluded volume parameter). The final term mimics a short range attraction between the monomers and the surface (with \(\beta = 1/T\)). The vector \(\vec{\rho}(x) = (x, z(x))\) represents a generic point on the surface, and we have assumed that a monomer at \(\vec{r}_i(s)\) interacts with the point \(\vec{\rho}(x)\) on the surface via a short range (\(\delta\) function) attraction. (The bound \(L\) on the \(x\) integrals represents the upper cut-off due to finite surface size.)

By performing standard Gaussian transforms, the interaction terms in eq.(1) can be rewritten, yielding

\[
Z = \int \mathcal{D}(\vec{\rho}) \int \mathcal{D}(\Psi(\vec{r}), \Psi^\dagger(\vec{r})) \exp \left[ -\int d^d r \left( \frac{1}{2} \Psi^2(\vec{r}) + \Psi^\dagger(\vec{r})\Psi(\vec{r}) \right) \right] \int \mathcal{D}z(x) \exp \left[ -\int^L d^Dx \left( \frac{K}{2} (\nabla^n z(x))^2 - \sqrt{\beta} \Psi(x, z(x)) \right) \right] \int \prod_{i=1}^{N} \mathcal{D} \vec{r}_i(s) \exp \left[ -\sum_{i=1}^{N} \int_0^N ds \left( \frac{d}{2a^2} \left( \frac{d \vec{r}_i}{ds} \right)^2 + i\sqrt{v}\Phi(\vec{r}_i(s)) - \sqrt{\beta}\Psi^\dagger(\vec{r}_i(s)) \right) \right].
\]

(2)

The direct interactions of the polymer coordinates have now been removed and the final integration describes the motion of polymers in an effective potential \(i\sqrt{v}\Phi(\vec{r}) - \sqrt{\beta}\Psi^\dagger(\vec{r})\). The polymeric contribution is thus equivalent to the path integral for the evolution of \(N\) quantum particles moving in this effective potential \([8]\). This analogy indicates that, in the limit of long chains \(N \to \infty\), properties of the path integral are dominated by the ground state of the particle in the potential \([4]\). In a variational treatment of the corresponding Schrödinger equation, the ground state wave-function and energy are obtained from
\[ E_0 = \min \left\{ \int d^d r \left[ \frac{a^2}{2d} (\nabla \varphi(\vec{r}))^2 + \left( i \sqrt{\beta} \Phi(\vec{r}) - \sqrt{\beta} \Psi(\vec{r}) \right) \varphi(\vec{r})^2 - E \varphi(\vec{r})^2 \right] \right\}, \] (3)

where, in the final term, the Lagrange multiplier \( E \) is used to enforce the normalization condition on the wave-function \( \varphi(\vec{r}) \).

After substituting \( \exp \left\{ -N_m E_0 \left[ \Phi, \Psi^\dagger, z \right] \right\} \) for the polymeric integrals in eq.(2), the functional integrals over \( \Phi \), and \( (\Psi, \Psi^\dagger) \) can be performed to yield

\[ Z = \int Dz(x) \exp \left[ -\int d^d x \left( \frac{K}{2} (\nabla^n z(x))^2 + N_m U[z(x)] \right) \right], \] (4)

where \( N_m = N \mathcal{N} \) is the total number of monomers, and

\[ U[z(x)] = \min \left\{ \int d^d r \left[ \frac{a^2}{2d} (\nabla \varphi(\vec{r}))^2 + \frac{N_m v}{2} \varphi^4(\vec{r}) - E \varphi^2(\vec{r}) \right] - \beta \int d^d x \varphi^2(x, z(x)) \right\}. \] (5)

For a uniform surface \( z(x) = z_0 \), translational invariance requires that the ground state wave-function have the form \( \varphi(\vec{x}, z) \sim \phi(z - z_0) \). We make the assumption that in the presence of a small surface distortion \( z(x) \), the minimum of eq.(5) is only weakly modified and is self-affinely distorted to

\[ \varphi(\vec{x}, z) = \frac{1}{L_D^{d/2}} \phi(z - z(x)). \] (6)

With the added scaling factor in eq.(5), the new wave function must be normalized such that \( \int dz \phi(z)^2 = 1 \).

With the above ansatz, the only dependence of \( U[z(x)] \) comes from the \( (\nabla \varphi)^2 \) term in eq.(5), and leads to

\[ Z \propto \int Dz(x) \exp \left[ -\int d^d x \left( \frac{K}{2} (\nabla^n z(x))^2 + \frac{ca^2}{2d} (\nabla^2 z(x))^2 \int dz \left( \frac{\partial \phi}{\partial z} \right)^2 \right) \right]. \] (7)

We can now perform the Gaussian integrals over \( z(x) \) to obtain

\[ \frac{\beta F}{L_D} = \min \left\{ \frac{1}{2} \int \frac{d^d k}{(2\pi)^d} \ln \left( K k^{2n} + \frac{ca^2}{d} k^2 + \frac{ca^2}{2d} \int dz \left( \frac{\partial \phi}{\partial z} \right)^2 \right) - c \beta \int dz \delta(z) \phi^2(z) + \frac{vc^2}{2} \int dz \phi^4(z) + c E \int dz \phi^2(z) \right\}, \] (8)
where \( c = N_m/L^D \) is the monomer concentration per unit area of the interface. The minimization with respect to \( \phi \) yields the differential equation

\[
- \frac{a^2}{2d} \left[ 1 + \int \frac{d^D k}{(2\pi)^D} \frac{k^2}{Kk^{2n} + \frac{ca^2}{d}k^2} \int dz \left( \frac{\partial \phi}{\partial z} \right)^2 \right] \phi''(z) - \beta \delta(z)\phi(z) + vc\phi^3(z) = E\phi(z), \quad (9)
\]

which is similar to the equation describing polymer adsorption to an attractive potential at \( z = 0 \), with a renormalized Kuhn length \([1]\).

The non-linear self-consistent equation (9) is still too complicated to be solved exactly. Instead we use a restricted class of wave functions, namely normalized Gaussians

\[
\phi^2(z) = \frac{1}{\sqrt{2\pi w^2}} \exp \left( -\frac{z^2}{2w^2} \right), \quad (10)
\]

with the width \( w \) as the only variational parameter, to minimize the free energy in eq.(8). (This approximation works quite well in other adsorption problems.) The calculations are now straightforward, and we obtain

\[
\frac{\beta F}{L^D} = \min \left\{ \frac{1}{2} \int \frac{d^D k}{(2\pi)^D} \ln \left( Kk^{2n} + \frac{ca^2}{4dw^2}k^2 \right) + \frac{ca^2}{8dw^2} - \frac{c\beta}{\sqrt{2\pi w}} + \frac{vc^2}{4\sqrt{\pi w}} \right\}_w. \quad (11)
\]

The extremal values of \( w \) satisfy

\[
\frac{a_R^2}{4d} + \frac{cv}{4\sqrt{\pi w^2}} = \frac{\beta}{\sqrt{2\pi w^2}}, \quad (12)
\]

with

\[
a_R^2 = \left( 1 + \int \frac{d^D k}{(2\pi)^D} \frac{k^2}{Kk^{2n} + \frac{ca^2}{4dw^2}k^2} \right) a^2. \quad (13)
\]

Note that, within this approximation, the height-height correlation function of the surface is

\[
\langle |z(k)|^2 \rangle = \frac{1}{Kk^{2n} + \frac{ca^2}{4dw^2}k^2}, \quad (14)
\]

leading to a surface width

\[
\gamma = \int \frac{d^D k}{(2\pi)^D} \frac{1}{Kk^{2n} + \frac{ca^2}{4dw^2}k^2}. \quad (15)
\]
In the following, we shall focus on the surface in three dimensional space \((d = 3)\) and \((D = 2)\). Independent of \(n\), the system undergoes a second order phase transition at

\[
T_c = \frac{2\sqrt{2}}{cv}.
\]  

(16)

At high temperatures, the polymer is not adsorbed and eq.(12) is minimized for

\[
w \to +\infty.
\]  

(17)

The fluctuating surface is rough, with a width which diverges with its size \(L\) as

\[
\gamma = \frac{1}{2\pi K} \ln(\Lambda L) \quad \text{for } n = 1,
\]  

(18)

where \(\Lambda\) is a short distance cut–off, and

\[
\gamma = \frac{1}{4\pi K} L^2 \quad \text{for } n = 2.
\]  

(19)

Below the critical temperature, the polymer is adsorbed on the interface and \(w\) is finite. Note that the critical temperature decreases when the polymer concentration or excluded volume increases. In particular, Brownian chains are always adsorbed to the surface.

The critical behavior is easily obtained from eqs.(12) and (13). Defining the reduced temperature \(t = T_c - T\), we find:

(i) For an elastic interface \((n = 1)\),

\[
w \sim \frac{1}{v^2 c^2} t^{-1} \quad \text{and} \quad \gamma = \frac{1}{2\pi K_R} \ln(\Lambda L),
\]  

(20)

where the stiffness \(K_R\) behaves as

\[
K_R \sim K + c t^2,
\]  

(21)

close to the transition. On the other hand, at low temperatures the width of the polymer layer goes to zero as \(w \sim T\) and \(K_R\) diverges as \(c T^{-2}\).

(ii) For the fluid membrane \((n = 2)\),

\[
w \sim -\frac{1}{v^2 c^2} t^{-1} \ln t \quad \text{and} \quad \gamma \sim \frac{(\ln t)^2}{c^5 v^4 t^2} \ln L.
\]  

(22)
Although there is no surface tension in the free system, the adsorption of polymers produces a stiffness for the membrane. The critical behavior of the width of the adsorbed layer $w$, is larger by a logarithmic factor than for an elastic membrane. The overall fluctuations of the membrane $\gamma$, are strongly reduced due to the induced stiffness.

To summarize, we have studied (in a mean-field like approximation) the adsorption of (self–avoiding) polymer chains on a fluctuating surface. At low temperatures the polymers are adsorbed in a thin layer to the surface, while at high temperatures they desorb and move freely into the solution. The adsorption of polymers stiffens the surface and reduces the extent of transverse fluctuations. Adsorption of polymers thus provides a useful mechanism for controlling the fluctuations of membranes, as well as the degree of swelling in lamellar phases. Presumably more rigid polymers are even more efficient in controlling fluctuations; the extreme limit of polyelectrolytes being quite interesting. Other extensions of this work could be the study of the adsorption of copolymers (block or statistical), or different types of polymers.

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