

ADSORPTION OF POLYMER SOLUTIONS ON HETEROGENEOUS SURFACES

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Abstract : We discuss the adsorption of polymer solutions on chemically heterogeneous surfaces. Two types of heterogeneities are considered, annealed and quenched. In both cases, the disorder increases the adsorption. For a same adsorption strength, the adsorbed amount of polymer is higher on an annealed surface than on a quenched surface. The adsorption on an annealed surface can induce a two-dimensional phase transition on the surface.

INTRODUCTION

Polymer adsorption from solution plays an essential role in many applications ranging from colloid stabilisation to adhesion or lubrication. When the monomers forming the polymer are attracted by an interface, due to the cooperativity between monomers of the same chain the polymer chains adsorb strongly and a thick adsorption layer forms. Detailed theoretical models of these adsorption layers in good agreement with experimental results now exist based either on a self-consistent mean field theory for not too long chains (Ref.1) or on a scaling theory in the limit of infinitely long chains (Ref.2). These theories however deal only with ideal non heterogeneous surfaces (neither rough nor chemically heterogeneous). Many real surfaces are heterogeneous but the non ideal situations have received very little theoretical attention (Refs.3-5). In a recent work (Refs.6,7), we have studied the effect of random chemical heterogeneities on the properties of adsorbed polymer layers, we give here a short review of some of our important results.

The parameter that governs the adsorption of polymer chains on surfaces is the free energy gained by a single monomer upon adsorption $\epsilon(\rho)$. On an ideal surface this free energy is a constant independent of the position ρ on the surface where the monomer adsorbs. On a chemically heterogeneous surface, the adsorption free energy ϵ fluctuates with position, its fluctuation characterizes the local concentration of surface impurities. We consider here only the case where ϵ is a random variable with a zero average. On average, the interface is thus neither attractive nor repulsive for the polymer molecules and if the surface were homogeneous, the monomer concentration in the solution close to the interface would remain constant and equal to the bulk value. The effective attraction or depletion of monomers at the interface is only due to the heterogeneities.

As in many problems where impurities play an important role, the properties of the adsorbed layer depend strongly on whether $\epsilon(\rho)$ is a quenched or an annealed variable. The field $\epsilon(\rho)$ is a quenched variable when the impurities are fixed on the adsorbing surface ; this is often the case for adsorption on a solid surface. In this situation, one must first calculate the physical properties of the adsorbed layer and then average them with respect to the randomness. The heterogeneity is annealed if the impurities are free to move on the interface and are at thermodynamic equilibrium. As our example of annealed heterogeneity we will consider in the following polymer adsorption on an air water interface covered by a surfactant monolayer. The heterogeneity $\epsilon(\rho)$ is then in a first approximation proportional to the surfactant concentration fluctuation and will be referred to as the surfactant concentration below.

We now briefly discuss the adsorption of a single polymer chain and then the adsorption of semi-dilute solutions on annealed and then on quenched heterogeneous surfaces.

SINGLE CHAIN ADSORPTION

Although this is a rather academic problem, we first discuss the adsorption on a heterogeneous surface of a single polymer chain ; this problem can be treated in a very simple manner and gives some physical insight.

Consider first the annealed case. On average, the polymer chain is not attracted to the interface and would not adsorb if the surface remained homogeneous. However, locally the concentration of impurities can be larger than on average. Such a region becomes attractive to the monomers and the polymer chain adsorbs. The adsorbed state is stable only if its total free energy is lower than that of a free chain and a homogeneous surface. The total free energy change upon adsorption includes three terms, a confinement free energy of the polymer in its adsorbed configuration, an attraction between the polymer and the heterogeneities and the free energy of the heterogeneity.

$$F/kT = 1/2(R^2/D^2) - N\epsilon(a/D) + R^2 \{ \epsilon^2/2\Delta^2 + u\epsilon^4/4 \} \quad (1)$$

The polymer contains N monomers and is considered to be Gaussian, its radius is $R=N^{1/2}a$ where a is the monomer size. The first term in equation (1) is the confinement energy of the polymer in the adsorption layer of thickness D (Ref.8). The second term is the local attraction of the interface ; as is usually done in the mean field theory (Ref.9), we have assumed that the concentration in the adsorbed layer is a constant and that the fraction of monomers in contact with the surface is a/D . The last term is the increase of the surfactant (impurity) free energy due to the increase of surface concentration in the area where the polymer adsorbs. We have written this free energy as a Landau expansion of a free energy density integrated over the area R^2 ; Δ^2 is proportional to the two-dimensional osmotic compressibility of the monolayer that can in general be adjusted by varying temperature and u is a positive constant.

If Δ is smaller than a , the minimum of the free energy is obtained for $\epsilon=0$ and the polymer does not adsorb. If Δ is larger than a , the surfactant monolayer is more compressible and the minimum of the free energy is reached for a positive value of ϵ ; the surfactant concentration increases locally and the polymer adsorbs. The transition towards adsorption when $\Delta=a$ is here second order and above the threshold, the thickness of the adsorbed polymer layer decreases as

$$D = u^{-1/2} (1 - a^2 \Delta^{-2})^{-1/2} \quad (2)$$

A better description of the impurity free energy is obtained if one takes into account the spatial variation of ϵ and includes in the Landau expansion a term proportional to $(\nabla\epsilon)^2$. This term is equivalent to a line tension at the edge of the surface where the polymer adsorbs. The line tension term is however a small correction to equation (1) that does not change qualitatively the adsorption behavior. A similar behavior is also expected when excluded volume interactions are taken into account although the values of the adsorption threshold and of the thickness of the adsorbed layer are slightly modified.

If the impurity is quenched on the surface, the value of ϵ is frozen and the surfactant concentration cannot increase locally. It was shown however (Ref.10) that due to the finite size of the chain, the polymer can wander along the interface until it finds a place where there is a large enough fluctuation of ϵ to allow for adsorption. For a single chain the quenched and the annealed problems are then expected to lead to the same behavior. This is somehow an artefact due to the finite size of the chain in the quenched problem.

ADSORPTION OF A SEMI-DILUTE SOLUTION ON AN ANNEALED HETEROGENEOUS SURFACE

We now consider the more realistic case of a semi-dilute polymer solution of bulk concentration c_b adsorbing on a surfactant monolayer (an interface with annealed impurities). As for the adsorption of a single chain, if the osmotic compressibility of the monolayer is large enough, regions can form in the monolayer where the surfactant concentration is higher and where the polymer can adsorb. The total amount of surfactant in the monolayer being constant we expect for large enough values of Δ a two-dimensional phase separation between a dense surfactant region where the polymer adsorbs and a dilute surfactant region from which the polymer is depleted (Ref.12).

In order to study more quantitatively this transition, we write the total free energy of the solution as a sum of three terms, the free energy of the polymer solution, the free energy of the surfactant monolayer and a coupling between polymer and surfactant. The last two terms have the same structure as for a single chain above. Within a mean field approach, the free energy of a semi-dilute polymer solution can be written as a functional of the so-called order parameter ψ related to the local concentration c by $c = \psi^2$ (Ref.8).

$$F_{po}/kT = \int dr \{ a^2/6 (\nabla\psi)^2 + 1/2 v(\psi^2 - \psi_b^2)^2 \} \quad (3)$$

The first term represents the elasticity of the polymer chains and the second term the excluded volume interactions, v ($\sim a^3$) being the excluded volume. The value of the order parameter in the bulk is $\psi_b = c_b^{1/2}$.

The total free energy can thus be written as

$$F/kT = \int dr \{ a^2/6 (\nabla\psi)^2 + 1/2 v(\psi^2 - \psi_b^2)^2 + \delta(z) [-a\epsilon\psi^2 + \epsilon^2/2\Delta^2 + u\epsilon^4/4] \} \quad (4)$$

The Dirac δ function indicates that both the surfactant contribution and the coupling term are two-dimensional free energies in the plane of the monolayer. The free energy functional must be minimized with respect to both the polymer order parameter ψ and the surfactant concentration that is also an annealed variable.

The minimization with respect to the order parameter gives the concentration profile of the polymer along the z direction perpendicular to the monolayer

$$c(z) = c_b \coth^2 [(z+b)/\xi] \quad (5)$$

where the bulk correlation length ξ is defined by $\xi^2 = a^2/3vc_b$. The integration constant b is related to the monomer concentration at the interface $c_s = \coth^2 b = \psi_s^2$. The minimization with respect to the surface order parameter ψ_s then yields a relation between ψ_s and the local surfactant concentration ϵ

$$(\psi_s/\psi_b)^2 - 1 = (6\xi\psi_s\epsilon) / (a\psi_b) \quad (6)$$

Substituting these two equations into the free energy (4), one obtains the free energy per unit area of the solution as a function of the sole variable ϵ . For small values of the compressibility Δ^2 , the second derivative of this free energy at $\epsilon = 0$ is positive and the monolayer is stable. The second derivative of the free energy vanishes for $\Delta^2 = v\xi/(2a^2)$ indicating a spinodal instability of the monolayer and thus a phase transition. The transition is first order and occurs for a value of the compressibility $\Delta^2 = uv^2/(32a^2)$ smaller than the spinodal value. The density in the dense phase is then $\epsilon = 8a/uv$ and the polymer concentration at the interface $c_s = 12\epsilon^2/v$.

The relevant experimental quantity for polymer adsorption is the surface excess

$$\Gamma = \int_0^{\infty} dz [c(z) - c_b].$$

At low values of the compressibility, the interface is on average neutral for the solution. However, the surface excess does not vanish because of the coupling of the polymer order parameter to the thermal fluctuations of ϵ . It has a positive value $\Gamma = a^2\Delta^2c_b/v$. At the transition, in the dense surfactant phase of the monolayer the polymer adsorbs and Γ

jumps discontinuously to a larger value $\Gamma = 16a^2/uv^2$. This surface excess is typically of order a^{-2} and corresponds thus to a strong adsorption of the polymer by the monolayer.

ADSORPTION OF A SEMI-DILUTE SOLUTION ON A QUENCHED HETEROGENEOUS SURFACE

In this section we consider the adsorption on a solid surface with quenched impurities. We first consider a periodic impurity on the solid surface and then give general results for surfaces with random impurities.

The free energy of the polymer solution is obtained from equation (4) but in the quenched case, only the polymer free energy and the coupling to the surface must be considered.

$$F/kT = \int dr \{ a^2/6 (\nabla\psi)^2 + 1/2 v(\psi^2 - \psi_b^2)^2 - \delta(z)a\epsilon(\rho)\psi^2 \} \quad (7)$$

We study a heterogeneity $\epsilon(\rho)$ periodic along one direction of the surface $\epsilon = \gamma \cos qx$ and calculate the surface excess in the limit of small heterogeneity. This can be done by minimizing the free energy with respect to the order parameter ψ and then expanding $\psi(x,z)$ in powers of the surface attraction γ up to second order.

The order parameter profile is periodic in the x direction and can thus be expanded in a Fourier series

$$\psi(x,z) = \psi_b + \psi_1(z) \cos qx + \{ \psi_2^0(z) + \psi_2^2(z) \cos 2qx \} \quad (8)$$

The determination of the surface excess requires only the calculation of $\psi_1(z)$ and $\psi_2^0(z)$. We find

$$\begin{aligned} \psi_1(z) &= \psi_b(\eta/\omega_1) \exp -(\omega_1 z/\xi) \\ \psi_2^0(z) &= \psi_b \{ \eta^2/[2\omega_1(3+q^2\xi^2)] \} \{ (q\xi)^2/\omega_0 \exp -(\omega_0 z/\xi) + 3/2\omega_1 \exp -(2\omega_1 z/\xi) \} \end{aligned} \quad (9)$$

where we have defined $\eta = 6\gamma\xi/a$ and $\omega_n = 4 + (nq\xi)^2$ n being an integer.

The surface excess is then

$$\Gamma = 9\gamma^2\xi/v [(2+q^2\xi^2)/\omega_1^3] \quad (10)$$

The important result is that even though the average attraction by the surface vanishes there is a positive surface excess due to the oscillations of the interaction.

In the case where the heterogeneity is random we have not calculated in details the surface excess but equation (10) strongly suggests (by a decomposition in Fourier modes) that a quenched random heterogeneity with a zero average also leads to a positive surface excess and thus to an effective adsorption of the polymer.

The effective adsorption can be understood for very strong heterogeneities from the following argument. If the heterogeneity has fluctuations of large amplitude $kT\gamma$ and if it is correlated over a very small distance of order a , the surface can be viewed as a checkerboard with sites of size a where half of the sites are attractive and half of the sites are repulsive. When one monomer adsorbs on an attractive site, it gains an energy $kT\gamma$ much larger than kT . The repulsive sites are strongly repelling the monomers that do not adsorb. However in order to adsorb on the attractive sites, the chains must form loops to avoid the repulsive sites and this reduces their entropy, the corresponding loss in free energy is of the order of kT and is thus much smaller than the gain due to adsorption. In the limit where the amplitude of the fluctuations become very large we thus expect half of the sites on the surface to be covered by adsorbed monomers. This corresponds to a large surface excess of order $\Gamma \sim a^{-2}$.

In order to check this result and to compare annealed and quenched disorder, we have made cumulant expansions on the mean field free energy of the polymer solution. This shows that for the same adsorption strength, the surface excess for quenched heterogeneities is always positive and that the surface excess for quenched disorder is always smaller than the surface excess for annealed disorder.

CONCLUSION

The main conclusion of our work is that both in the case of quenched disorder and in the case of annealed disorder, heterogeneities of the interface always enhance adsorption. This has been shown here when the average adsorption strength vanishes but we have checked within the framework of the same mean field theory that it remains true when the polymer feels a finite average adsorption from the surface.

The correlations between monomers due to the excluded volume are not taken properly into account by the mean field theory. This is particularly true for adsorption problems where the concentration profile becomes singular in the vicinity of a solid adsorbing wall ; this effect is known as the proximal effect. We have investigated the relevance of a quenched heterogeneity on the proximal effects using a so-called Harris criterion ; however the criterion amounts for this problem to comparing the swelling exponent ν of the chains in a good solvent and the crossover exponent ϕ of the special transition that governs the proximal effects. The known values of these exponents are equal in three dimensions within the accuracies of the best numerical estimates (Ref.11), and the Harris criterion is thus not conclusive. Further theoretical work is needed in order to understand the role of heterogeneities for polymer adsorption from a good solvent.

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