Notes

On the Adsorption of Polymer Solutions on Random Surfaces: The Annealed Case

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Adsorption of single polymer chains and polymer solutions on surfaces has been the focus of numerous studies in recent years.[1,2] In most of those studies the adsorbing surface with whom the polymer has a preferred interaction is assumed to be ideal, i.e., the surface is completely smooth and chemically homogeneous. However, real surfaces are rough and chemically heterogeneous. Those nonideal but important situations have been studied only sporadically in the past.[3-7]

In this paper we investigate the adsorption of a semidilute polymer solution on chemically heterogeneous surfaces. We show that the polymer profile equation in the presence of annealed heterogeneities, i.e., impurities or surfactant molecules in thermal equilibrium, is *identical* with the profile equation of polymers adsorbing on random surfaces proposed by Odijk.[7] The polymer concentration profile and the surface excess are then calculated as a function of surface heterogeneity, yielding results that are quite different from those of ref 7.

Let us consider a polymer solution in the presence of a boundary. This boundary can be either a solid surface or a liquid/air interface. If $h(\vec{r})$ is a variable characterizing the local concentration of surface impurities, the free energy of the combined polymer/impurity system depends on whether $\{h(\vec{r})\}$ is a *quenched* or *annealed* random variable. In the former case, the quenched random variable $h(\vec{r})$ describes a *rough* solid surface or chemical impurities that are randomly and irreversibly attached to the solid surface. Hence, the polymer partition function $Z\{h(\vec{r})\}$ is calculated for each configuration of the random surface variable $h(\vec{r})$, and the free energy $\mathcal{F}_q$ is obtained by averaging $\log Z\{h(\vec{r})\}$

$$\mathcal{F}_q/T = -\langle \log Z\{h(\vec{r})\}\rangle_h \qquad (1)$$

where $\langle ... \rangle_h$ denotes the ensemble average of the random variable $h(\vec{r})$, T is the temperature, and the Boltzmann constant is set to be unity. On the other hand, when $h(\vec{r})$ is an annealed degree of freedom, the average over the h's is done for the partition function itself and the free energy $\mathcal{F}_a$ is given by

$$\mathcal{F}_a/T = -\log \langle Z\{h(\vec{r})\}\rangle_h \qquad (2)$$

For polymer solution in a semidilute regime,[8,9] the polymer order parameter, ψ, is proportional to the square root of the local polymer concentration, $\psi^2(\vec{r}) = c(\vec{r})$. Formally, if one ignores correlations and describes the polymer chain configurations in a mean-field fashion,[10] the free energy of a spatially varying polymer concentration can be obtained from the Hamiltonian

$$\mathcal{H}_0[\psi]/T = \int \left[\frac{a^2}{6}(\nabla\psi)^2 + \frac{1}{2}\beta\psi^4 + \mu_0\psi^2 \right] d\vec{r} \qquad (3)$$

where a is a microscopic length associated with the monomer size, β is the excluded-volume parameter, and μ_0 is the polymer chemical potential. The free energy is calculated from (3) by

$$\mathcal{F}_0/T = -\log \int \mathcal{D}\psi e^{-\mathcal{H}_0[\psi]/T} \qquad (4)$$

In a mean-field approximation, the equation for the profile is given by a steepest descent approximation on (4) yielding

$$\frac{a^2}{6}\nabla^2\psi + \beta\psi^3 + \mu_0\psi = 0 \qquad (5)$$

Taking one boundary condition at $z = 0$ and the other at $z \to \infty$, the concentration ψ depends only on the z coordinate and the bulk concentration $c_0 = \psi^2|_{z\to\infty}$ is thus related to the chemical potential, $\mu_0 = -\beta c_0$. In terms of a dimensionless concentration $\chi^2 = \psi^2/c_0$, the profile equation (5) can be written as

$$\xi_b^2 \frac{d^2\chi}{dz^2} + 2\chi(1 - \chi^2) = 0 \qquad (6)$$

where $\xi_b = (a^2/3\beta c_0)^{1/2}$ is the bulk correlation length.

We now introduce randomness in the adsorbing surface. The surface is taken to be perfectly flat. The z coordinate describes the distance from the surface located at $z = 0$. The local field $h(\vec{r})$ represents the local positive (or negative) interaction of the surface with the polymer links and thus is coupled linearly to the local polymer density, resulting in an added term $h(\vec{r}) \psi^2(\vec{r})$ in the Hamiltonian (3). For simplicity, we assume that the local field has a zero average $\langle h \rangle = 0$ and the following spatial correlation[7]

$$\langle h(\vec{r}) h(\vec{r}')\rangle_h = V(z,z') \xi_s^2 \delta(x-x') \delta(y-y') \qquad (7)$$

The correlation in (7) is chosen to be short range within the surface plane $z = 0$, with a surface correlation length ξ_s much shorter than the bulk one ξ_b. The correlation in the z direction is also of a finite range: $V(z,z') = 0$ if z or z' are larger than a distance d from the surface. The limit $d \to 0$ is simply obtained by $V(z,z') = Vd^2\delta(z-z')\delta(z)$ where V is a constant. As was discussed above, the random field $h(\vec{r})$ can be viewed as a quenched (stochastic) random degree of freedom or as an annealed surface variable in thermal equilibrium. Note that the polymer concentration itself is an annealed degree of freedom.

If the remainder of the paper we will treat $h(\vec{r})$ as an annealed degree of freedom. From the partition function (2) we get

$$e^{-\mathcal{F}_a/T} = \int \mathcal{D}\psi \int \mathcal{D}h\, P(h) e^{\mathcal{H}_0[\psi]/T - \int h(\vec{r})\psi^2(\vec{r})d\vec{r}} \qquad (8)$$

where $P(h)$ is the probability distribution of the h variable. For small fields, $\{h(\vec{r})\}$, a cumulant expansion of (8) yields

$$\int \mathcal{D}h \, P(h) \, e^{-\int h(\vec{r}) \psi^2(\vec{r}) d\vec{r}} \simeq e^{(1/2) \int\int \langle h(\vec{r}) h(\vec{r}') \rangle \psi^2(\vec{r}) \psi^2(\vec{r}') d\vec{r} d\vec{r}'} \quad (9)$$

Equation 9 is exact for Gaussian-distributed $h(\vec{r})$. Using the correlations of $h(\vec{r})$, we get from (7)–(9)

$$e^{-\mathcal{I}_a/T} = \int \mathcal{D}\psi e^{-(\mathcal{H}_0 + \mathcal{H}_{int})/T} \quad (10)$$

where the effective interaction part of the Hamiltonian, $\mathcal{H}_{int}$, is

$$\mathcal{H}_{int}/T = -\frac{1}{2}\xi_s^2 \int V(z,z') \, \psi^2(z) \, \psi^2(z') \, dx \, dy \, dz \, dz' \quad (11)$$

The equation for the profile $\psi(z)$ is then obtained by a steepest descent approximation on (10). Since there is no in-plane correlation, ψ depends only on the coordinate z.

$$\frac{\delta}{\delta\psi(z)}[\mathcal{H}_0 + \mathcal{H}_{int}] = 0 \quad (12)$$

yielding the profile equation

$$-\frac{a^2}{6}\frac{d^2\psi(z)}{dz^2} + \mu_0\psi(z) + \beta\psi^3(z) -$$
$$\xi_s^2\psi(z)\int_0^d V(z,z') \, \psi^2(z') \, dz' = 0 \quad (13)$$

or for the dimensionless profile variable $\chi^2(z) = \psi^2(z)/c_0$

$$-\frac{a^2}{6}\frac{d^2\chi(z)}{dz^2} + \mu_0\chi(z) + \beta c_0\chi^3(z) -$$
$$c_0\xi_s^2\chi(z)\int_0^d V(z,z') \, \chi^2(z') \, dz' = 0 \quad (14)$$

Equation 14 is identical with the profile equation that has been derived by Odijk[7] as an approximation to a quenched surface randomness using the Furutsu–Novikov identity[12] for Gaussian stochastic fields. The last term in (14) is the sole effect of the randomness. When $V(z,z') = 0$, eq 14 reduces to the ideal surface problem (6). We note that using results for annealed randomness as approximations for quenched randomness can lead in some cases to incorrect interpretations of random fields.[11] We have verified that a second-order cumulant expansion of the polymer free energy gives different results for the profile equation and surface excess in the quenched and annealed cases.

We discuss now the solution of (14) in the case where the annealed impurities lie only on the $z = 0$ plane (insoluble surfactant molecules), and $V(z,z') = Vd^2\delta(z)\delta(z-z')$.

$$-\frac{a^2}{6}\frac{d^2\chi(z)}{dz^2} + \beta c_0\chi(z) \, (\chi^2(z) - 1) = c_0 V\xi_s^2 d^2\delta(z) \, \chi^3(z) \quad (15)$$

It is convenient to introduce the reduced coordinate $u = z/\xi_b$ and a dimensionless parameter $\Delta = \xi_s^2 d^2 V/\beta\xi_b$. The latter is proportional to the surface random field V and to the square root of the bulk polymer concentration, $(c_0)^{1/2}$. The profile equation (15) is then reduced to

$$-\frac{d^2\chi}{du^2} + 2\chi(\chi^2 - 1) = 2\Delta\delta(u) \, \chi^3 \quad (16)$$

The polymer profile $\chi(u)$ from (16) is the same as that in the nonrandom case

$$\chi(u) = \coth(u + b) \quad (17)$$

while the sole effect of the randomness is on the boundary

condition at $u = 0$

$$\frac{1}{\chi_s^3}\frac{d\chi_s}{du} = -2\Delta = \frac{1 - \chi_s^2}{\chi_s^3} \quad (18)$$

where $\chi_s = \chi(u=0)$ is the surface concentration.

A quantity of experimental interest is the total excess of polymer concentration above its bulk value. This surface excess is defined as:

$$\Gamma = \int_0^\infty [c(z) - c_0] \, dz = c_0\xi_b\int_0^\infty (\chi^2 - 1) \, du \quad (19)$$

Since the randomness affects only the boundary condition, (18), Γ can be calculated by integrating the profile equation (16) and is simply related to the surface concentration χ_s:

$$\Gamma = c_0\xi_b(\chi_s - 1) \quad (20)$$

The profile $\chi(u)$, the surface value χ_s, and the surface excess Γ can now be obtained from (16)–(20) as functions of the surface randomness strength Δ. For weak random field, $\Delta \ll 1$

$$\Gamma = c_0\xi_b\Delta\left(1 + \frac{5}{2}\Delta\right) + \dots = \frac{c_0\xi_s^2 d^2 V}{\beta}\left[1 + \frac{5}{2}\frac{\xi_s^2 d^2 V}{\beta\xi_b}\right] + \dots \quad (21)$$

This is an interesting result since it shows that for annealed randomness the surface excess is positive, i.e., bigger than $\Gamma = 0$, corresponding to an ideal surface ($\Delta = 0$). For the pure case the wall is neutral since the average of $h(\vec{r})$ is chosen to be zero. Hence, although randomness has no average positive interaction with the polymer, $\langle h \rangle = 0$, the collective behavior of the surface with the polymer solution is attractive and the surface excess is positive. In addition, it can be seen from (21) that Γ is an increasing function of the surface randomness Δ.

Furthermore, from (18) it is also apparent that a solution for the polymer profile exists only for $0 < \Delta < \Delta_{max} = 1/(3\sqrt{3})$. For $\Delta > \Delta_{max}$, no value of χ_s satisfies the boundary condition. The homogeneous surface concentration of impurities (surfactant molecules) becomes unstable for $\Delta > \Delta_{max}$ and indicates a tendency to phase separate. A complete investigation of this transition involves higher order terms in a Landau expansion of the impurity free energy and will be published elsewhere.[13] The maximum surface excess is found to be

$$\Gamma_{max} = c_0\xi_b(\sqrt{3} - 1) \quad \text{for} \quad V_{max} = \frac{\beta\xi_b}{3\sqrt{3}\xi_s^2 d^2} \quad (22)$$

and Γ has a square root singularity close to Γ_{max}.

The results above, (18), (21) and (22), do not agree with previous results of ref 7, treating the same profile equation (14) but for different boundary conditions for the surface randomness. In the limit of strong randomness with finite correlations in the z-direction [as in our (7)], the surface excess Γ was found[7] to scale like $(\beta V)^{-1/2}$. This is in qualitative disagreement with our results (21) and (22) since we find that Γ increases with the randomness strength V up to a maximum value above which no solution exists, whereas in ref 7, Γ is found to be a decreasing function of V.

The results presented here are of relevance to mixed polymer/surfactant systems where both the surfactant and polymer are in thermal equilibrium. The surfactant can either lie on a liquid/air interface or on a solid surface assuming that the adsorption process is reversible. On a liquid/air interface, the surfactant concentration can be conveniently adjusted either directly or by changing the

surface pressure. The annealed randomness treated here in very different from the quenched one[13] where the surfactant molecules or impurities are irreversibly attached to a solid surface in contact with a polymer solution.

References and Notes

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