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Polymer Adsorption on Rough Surfaces. 1. Ideal Long Chain

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ABSTRACT: We consider the adsorption of an ideal polymer chain on a rough surface, in the limit of chain length sufficiently great to give ground-state dominance in the related effective eigenvalue problem. Detailed results are obtained for the special case of a sinusoidal grating. The confinement thickness of the chain and the monomer distribution on the surface are studied in all regimes of relative values of the three relevant lengths: confinement thickness D, surface roughness amplitude z_0, and grating wavelength λ.

I. Introduction

The problem of the adsorption of long flexible polymer chains at surfaces has been of long-standing interest. Previous effort[1-9] has been devoted to the adsorption onto completely smooth, highly symmetric surfaces—primarily planes, though spheres and cylinders[10] have been treated in recognition of the importance of adsorption onto small colloidal particles for practical catalytic processes. However, we must recognize that surface roughness may play an important role in practice; it will be present on some scale for even the most carefully prepared sample. In this paper we begin the investigation of the consequences of surface roughness on polymer adsorption. Although physical reality suggests a study of random roughness, we take advantage of the major mathematical simplifications in the detailed analysis of a grating geometry (Figure 1) —periodic fluctuation of the surface from a flat plane along a single direction in that plane: $z = z_0 \cos (2\pi y/\lambda)$, where z is the local height of the surface with respect to a reference plane and y is a coordinate axis in the plane (perpendicular to z). We do not anticipate qualitatively essential features to be introduced by this regularity, and we argue that the results describe the adsorption behavior on a more realistic rough surface of mean-square amplitude variation of order z_0^2 and characteristic horizontal scale λ of surface fluctuation.

For this initial investigation we make three major approximations. First, we treat only the very dilute case, where the polymer chains act independently, and it suffices to consider the surface effects for a single chain. Second, we treat the chain as ideal, without interactions between monomers, as appropriate to Θ-point solutions.[11] Finally, we take the limit of arbitrarily long chains, so that we can make use of ground-state dominance in the analysis (see section II). Studies of finite molecular weight and excluded volume effects will appear in future publications.

Let us first review briefly a simple scaling treatment of an ideal chain adsorbed on a flat surface. Following de Gennes,[11] we write the free energy of the adsorbed polymer as

$$F_0/T = (R_0/D^*)^2 - \epsilon N f \tag{I.1}$$

where T is the temperature, N the number of monomers, a an average monomer length, $R_0 \sim aN^{1/2}$ the typical linear dimension of an ideal chain in solution, and D^* the confinement layer thickness. The effective attraction of a monomer to the surface is ϵT, and f is the fraction of bound monomers. The first term in eq I.1 represents the entropy loss of the entire chain associated with the spatial restrictions from confinement; the second term describes the contact interactions with the surface. We obtain a rough estimate of f by assuming the monomers are uniformly distributed in space, giving for a flat surface $f \approx a/D^*$. Then minimization of the free energy with respect to D^* yields $D^* \approx a/\epsilon$. Thus D^* is uniquely determined here by the effective attractive energy per monomer.

Roughness introduces two additional length scales to the problem, namely, z_0 and λ. The coverage of the surface is no longer uniform, and one must in general redefine D; this is especially important in the limit of large roughness. The relative magnitude of the three lengths determines the nature and extent of the effects of roughness on adsorption; these may vary, as we shall see, from minor perturbational modifications to major qualitative changes.

There are two principal physical effects of surface fluctuations on polymer adsorption: (i) the projected area—i.e., the surface area per unit area on the reference plane—increases; (ii) entropy considerations lead to preferential polymer adsorption on regions of low curvature.[10] As we shall see in the detailed calculations of sections II and III, the increased adsorbing surface dominates. This allows us to present an elementary argument which provides a physical picture for the results derived in sections II and III for the free energy, g, per monomer of binding to the surface. For the planar surface discussed above this amounts to $g \approx T(a/D^*)^2$. Thus a spherical blob of radius D^* centered on the surface is bound to the surface by an energy of order T, and consequently D^* plays the role of a correlation length induced by the external potential (i.e., the polymer density is nearly constant over that length scale). For the rough surface we expect the confinement thickness D to be modified relative to the flat surface value D^*. Consider a blob of radius D (and therefore of nearly uniform polymer density) centered on an arbitrary point of the interface. The number of binding sites for a monomer will be proportional to the surface area passing through the blob $\langle A \rangle$, where $\langle A \rangle$ is the area of the interface within the blob averaged over all points on the surface. Then the free energy per chain in eq I.1 becomes

$$F/T = (R_0/D)^2 - \epsilon N(a/D)(\langle A \rangle/D^2) \tag{I.2}$$

where the factor $\langle A \rangle/D^2$ represents the increased binding associated with the increased interface passing through the blob. If the surface is described by $z = \zeta(x,y)$, with the reference plane (x,y) chosen so that the average slope $(\nabla\zeta)$ vanishes, then $\langle A \rangle/D^2$ is given by $\langle [1 + (\nabla\zeta)^2]^{1/2} \rangle$, where the average is over a blob of radius D. Minimization with respect to D yields

$$D^*/D \approx \langle [1 + (\nabla\zeta)^2]^{1/2} \rangle \tag{I.3}$$

For a flat, or locally flat (on the scale of D), surface we immediately have $D \approx D^*$. In particular, this will be the case either for D much smaller than the lengths z_0,λ characterizing the surface or in the long wavelength limit where $\lambda >> z_0,D$; we expect and will find only perturba-

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tional corrections to the flat surface results in these instances. For large confinement thickness (correlation length) $D >> z_0, \lambda$ (excluding $\lambda << z_0$), we will find below that for the cylindrical grating $D^*/D \approx (1 + \rho^2/2)^{1/2}$, where $\rho = 2\pi z_0/\lambda$, a result clearly consistent with eq I.3. This leaves the particularly interesting case of a very rough surface, $\lambda << D, z_0$. The general result here (contained in eq II.38 and II.39 below) for the cylindrical grating is not immediately transparent in the simple terms of eq I.3, but the two limiting cases *are*. When $z_0 << D$, the reference sphere of radius D covers the full amplitude and many oscillations of the surface, and we find $D^*/D \approx 4z_0/\lambda$ for the grating, of the order expected from I.3 (the expected enhancement for general, rather than cylindrical, roughness is of the order $(z_0/\lambda)^2$ in this case). In the opposite regime of this very rough limit, namely, $z_0 >> D$, the reference sphere of radius D intercepts only small pieces of many peaks of the surface. The analysis below of that geometry again shows that the explicit result $D^*/D \approx 2(D^*/\lambda)^{1/2}$ is consistent with eq I.3.

A number of different, but essentially equivalent, approaches have been developed for the polymer adsorption problem.[1-9] Here (in section II) we adopt the Edwards propagator approach,[12] as it is readily adaptable to the case of a rough surface. We will find it convenient to convert the usual differential equations to integral form, as a natural way to incorporate the irregular boundary surface. We explore the various possible regimes of relative size of the lengths, z_0, λ, and D. Section III is devoted to a discussion of these results, including comparison with smooth surface adsorption. In the Appendix we present a justification of our use of transparent surfaces, rather than the opaque surface of the actual physical situation, in the mathematical analysis.

II. Propagator Description

A. Formulation. A natural approach to describing a polymer chain in an inhomogeneous environment is provided by the propagator method formulated by Edwards[12] and reviewed by de Gennes.[1,11] For variations of physical quantities slow on the spatial scale of the monomer length a, it can be demonstrated that the propagator $G_N(\vec{r},\vec{r}')$, the statistical weight for a polymer to proceed from a point $\vec{r}$ to $\vec{r}'$ in N steps, is given by the solution of a Schrödinger-like partial differential equation:

$$-\frac{\partial G}{\partial N} = -\frac{a^2}{6}\nabla^2 G + \frac{U(\vec{r})}{T}G \equiv \mathcal{H}G \qquad \text{(II.1)}$$

where $U(\vec{r})$ is an external potential describing the attraction of a single monomer to the surface (it may also include internal interactions within a mean-field approximation). We emphasize that the continuum approximation (II.1) breaks down if $U(\vec{r})$ is so strong that the polymer is confined to the surface in a layer whose thickness is on the scale of the monomer size. We explicitly exclude that case in this paper. In particular, this means that $U(\vec{r})/T << 1$ when averaged over the length scales of interest here, as was in fact assumed in writing the equation in the form (II.1). The boundary condition is that in the limit $N \to 0$ the propagator $G_N(\vec{r},\vec{r}') \to \delta^3(\vec{r} - \vec{r}')$. Then $G_N(\vec{r},\vec{r}')$ may be expressed in terms of the eigenfunctions of the Hermitian operator $\mathcal{H}$:

$$G_N(\vec{r},\vec{r}') = a^3\sum_m \phi^*_m(\vec{r}')\phi_m(\vec{r})e^{-N\omega_m} \qquad \text{(II.2)}$$

where the ϕ_m are normalized eigenfunctions of $\mathcal{H}$ with eigenvalues ω_m:

$$\omega_m\phi_m = \mathcal{H}\phi_m; \qquad \int d^3r\, |\phi_m(\vec{r})|^2 = 1 \qquad \text{(II.3)}$$

The local monomer concentration $C(\vec{r})$ can be expressed in terms of the ϕ_m. If the chain occupies a fixed volume, the "ground state" ϕ_0 (with the lowest eigenvalue $\omega_0 < \omega_m$) dominates for sufficiently large N, and $C(\vec{r})$ becomes

$$C(\vec{r}) = N|\phi_0(\vec{r})|^2 \qquad \text{(II.4)}$$

where ϕ_0 is the normalized ground-state eigenfunction.

For simplicity of analysis we consider a polymer adsorbed on a cylindrically rough surface,

$$z = \zeta(y) \qquad \text{(II.5)}$$

where we have introduced the usual Cartesian coordinate system $0xyz$, and the surface height function $\zeta(y)$, assumed differentiable, is independent of x (see Figure 1). We represent surface attraction by a δ-function potential. This "transparent" surface, in contrast to the opaque physical one, leaves both sides accessible to the polymer. The seriousness of this approximation is assessed in the Appendix, where we find it a reasonable price to pay for making the calculations tractable; the important physics is preserved. Then eq II.3 for the ground state takes the form

$$(a^2/6)\nabla^2\phi_0 + \epsilon a[1 + (d\zeta/dy)^2]^{1/2}\delta(z - \zeta(y))\phi_0 = -\omega_0\phi_0 \qquad \text{(II.6)}$$

where the square-root weighting function is required by the choice of the coordinate z rather than the local surface normal in the argument of the δ-function. For a flat surface, $\zeta(y) = 0$, eq II.6 reduces to

$$\nabla^2\phi_0 + \frac{6\epsilon}{a}\delta(z)\phi_0 = -\frac{6\omega_0}{a^2}\phi_0 \qquad \text{(II.7)}$$

with the solution

$$\phi_0 = e^{-\kappa^*|z|} \qquad \omega_0 = -(\kappa^* a)^2/6; \qquad \kappa^* \equiv 3\epsilon/a$$

It is then natural to identify the confinement length D with $1/\kappa^*$.

In general we define

$$\kappa \equiv (-6\omega_0/a^2)^{1/2}$$

and we rewrite eq II.6 as

$$[\nabla^2 - \kappa^2]\phi_0 = -2\kappa^*[1 + (d\zeta/dy)^2]^{1/2}\delta(z - \zeta(y))\phi_0 \qquad \text{(II.8)}$$

By symmetry we expect the ground state ϕ_0 to be independent of x, and eq II.8 can conveniently be recast in integral form by using the Green's function of the two-dimensional Helmholtz equation:

$$\phi_0(y,z) = \frac{\kappa^*}{\pi}\int_{-\infty}^{\infty} dy' \, [1 + (d\zeta/dy')^2]^{1/2} \times K_0[\kappa(y - y')^2 + [z - \zeta(y')]^2]^{1/2}\phi_0(y',\zeta(y')) \qquad \text{(II.9)}$$

where $K_0(x)$ is the modified Bessel function of order zero. The kernel of the integral involves the solution ϕ_0 only on the surface, $z = \zeta(y)$. Thus, determination of ϕ_0 on the surface reduces the full solution to quadratures. We introduce the notation

$$\psi(y) = \phi_0(y,\zeta(y)) \qquad \text{(II.10)}$$

Then the problem reduces to the one-dimensional integral equation (eq II.9 with $z = \zeta(y)$):

$$\psi(y) = \frac{\kappa^*}{\pi}\int_{-\infty}^{\infty} dy' \, [1 + (d\zeta/dy')^2]^{1/2}K_0[\kappa((y - y')^2 + [\zeta(y) - \zeta(y')]^2)^{1/2}]\psi(y') \qquad \text{(II.11)}$$

This is a Fredholm integral equation of the second kind, which determines both the eigenvalue κ and the eigenfunction on the surface $\psi(y)$. Consider, e.g., the trivial case of the surface $\zeta(y) = cy$ (c = constant)—i.e., the flat surface

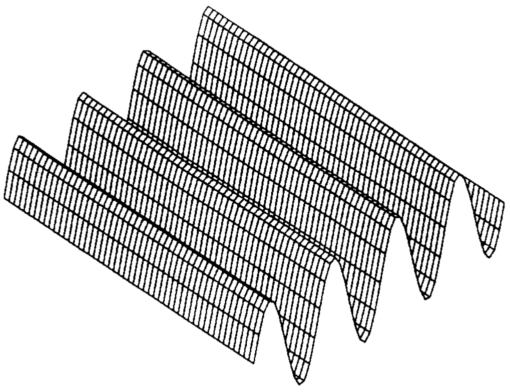

Figure 1. Sinusoidal cylindrical grating used in this paper as a model rough surface.

with a perverse choice of coordinates. By symmetry $\psi(y)$ must be constant. Then eq II.11 gives immediately an equation for the eigenvalue κ:

$$1 = \frac{\kappa^*}{\pi}\int_{-\infty}^{\infty}\mathrm{d}y'\,(1+c^2)^{1/2}K_0[\kappa(1+c^2)^{1/2}|y'-y|] \qquad \text{(II.12)}$$

with the solution $\kappa = \kappa^*$, independent of c, as it must be. The eigenfunction, of course, is exponential in the coordinate normal to the surface. For a sinusoidal surface, $\zeta(y) = z_0 \cos qy$, we have

$$\psi(y) = \frac{\kappa^*}{\pi}\int_{-\infty}^{\infty}\mathrm{d}y'\,(1+\rho^2\sin^2 qy')^{1/2}K_0[\kappa[(y-y')^2 + z_0^2(\cos qy - \cos qy')^2]^{1/2}]\psi(y') \qquad \text{(II.13)}$$

where $\rho = qz_0$. In the following discussion we shall solve eq II.13 for $\psi(y)$ and κ corresponding to the ground state. For the infinite chain problem, in which ground-state dominance is exact, the square of the absolute value of $\psi(y)$ describes the monomer distribution on the surface, and the value of κ^{-1} sets the thickness of the chain confinement region (because of the exponential decay of the modified Bessel function K_0 with its argument).

B. Solution. There are three lengths characterizing the problem (the fourth—the monomer length a—is necessarily much smaller than the others if the above continuum description and resultant fundamental equation are to be used at all): (i) the amplitude of the roughness, here represented by the sinusoidal amplitude z_0; (ii) the horizontal scale over which the surface height changes appreciably—e.g., the inverse logarithmic derivative of the height function—here given by the wavelength $\lambda = 2\pi/q$; (iii) the thickness D of the confinement layer, here set by $1/\kappa$. It is convenient to consider the various possible regimes of relative sizes of these lengths and to use suitable approximate methods to examine the solutions for each.

(1) $D \gg z_0,\lambda$ (Excluding $\lambda \ll z_0$). Here the surface variations take place on length scales much smaller than the confinement thickness D. In the integral of eq II.13, since the Bessel function $K_0(\kappa x)$ goes to zero asymptotically as $e^{-\kappa x}/x^{1/2}$, there are important contributions to the integral out to $x \sim 1/\kappa = D$. Over most of this range the square root in the argument of K_0 is dominated by the first term, $(y - y')^2$, since the second is less than $(2z_0)^2$ for all values of y and y'. Its relative contribution is negligibly small even though $K_0(\kappa x)$ diverges logarithmically in the small κx region where this oscillatory term is comparable to $(y - y')^2$ (namely, when $|y - y'| \lesssim z_0$):

$$\frac{\int_0^{z_0}\mathrm{d}x\,K_0(\kappa x)}{\int_0^{\infty}\mathrm{d}x\,K_0(\kappa x)} \approx \kappa z_0 \ln \kappa z_0 \ll 1 \qquad \text{(II.14)}$$

Then the fundamental equation (II.13) reduces to a convolution integral form:

$$\psi(y) = (\kappa^*/\pi)\int \mathrm{d}y'\,\psi(y')(1+\rho^2\sin^2 qy')^{1/2}K_0(\kappa|y-y'|) \qquad \text{(II.15)}$$

This is not yet totally trivial because of the square root weighting factor. However, this factor can be written as

$$\left(1+\frac{\rho^2}{2}\right)^{1/2}\left(1-\frac{\rho^2}{\rho^2+2}\cos 2qy'\right)^{1/2} = \left(1+\frac{\rho^2}{2}\right)^{1/2}\sum_n A_n e^{2inqy'} \qquad \text{(II.16)}$$

a series which converges quite rapidly, even for $\rho \sim 1$ (the largest value of ρ permitted, since we have explicitly excluded the case for $\lambda \ll z_0$, for which limit see section (4) below). Then, Fourier transformation of eq II.15 gives

$$\tilde{\psi}(k) = \kappa^*\left(1+\frac{\rho^2}{2}\right)^{1/2}\sum_n \frac{A_n}{[\kappa^2+(k+2nq)^2]^{1/2}}\tilde{\psi}(k+2nq) \qquad \text{(II.17)}$$

where $\tilde{\psi}(k)$ is the Fourier transform of $\psi(y)$. Since the A_n decrease with n, and $k \ll q$, so that the denominator increases nearly linearly with n, we can to a good approximation keep only the first few terms $-n = 0, \pm 1$, say—and eq II.17 becomes a small set of linear homogeneous equations for each value of k. As the Bloch–Floquet theorem demands,[3] the solutions for $\psi(y)$ are periodic functions (with period λ), multiplied by the plane wave e^{iky}. The ground state corresponds to $k = 0$ (as for the flat surface, which can be regarded here as simply the special case $qz_0 \equiv \rho = 0$). The secular equation for $k = 0$ then gives

$$\kappa \approx \kappa^*(1-\gamma^2)\left(1+\frac{\rho^2}{2}\right)^{1/2}\left[1+\frac{\kappa^*}{q}\gamma^2\left(1+\frac{\rho^2}{2}\right)^{1/2}\right] \qquad \text{(II.18)}$$

where

$$\gamma \equiv \frac{\rho^2}{4(\rho^2+2)} < \frac{1}{4}$$

and we have kept only first-order corrections in $\kappa^*/q \sim \lambda/D$. We note that the result gives $\kappa > \kappa^*$, so that the confinement thickness has decreased from that of the flat surface. The dominant physical effect is an increase in the effective surface area per unit length of y, as discussed more fully in section III. Similarly, the ground state surface amplitude $\psi(y)$ has a small correction relative to the constant value appropriate to the flat surface:

$$\psi(y) \approx 1 - \frac{\kappa^*}{q}\gamma\left(1+\frac{\rho^2}{2}\right)^{1/2}\cos 2qy \qquad \text{(II.19)}$$

(2) $\lambda \gg z_0,D$. This is the limit of long-wavelength (slow) fluctuations of the surface, $|\mathrm{d}\zeta/\mathrm{d}y| \ll 1$. Here we would expect the polymer approximately to follow the surface smoothly, adapting to the local orientation, and a perturbative approach should converge rapidly. We rewrite the integral equation (II.13) as

$$\mathcal{L}(y,y')\psi(y') = (\pi/\kappa^*)\psi(y) \qquad \text{(II.20)}$$

where $\mathcal{L}(y,y')$ is a linear integral operator. If we separate $\mathcal{L}$ into the operator $\mathcal{L}_0$ appropriate to the flat surface plus a "small" correction $\mathcal{L}_1$, then we can use directly the full formal machinery of quantum mechanical perturbation theory. By definition

$$\mathcal{L}(y,y')\psi(y') \equiv \int \mathrm{d}y'\, K_0(\kappa|y-y'|)\psi(y') \qquad \text{(II.21)}$$

where we have chosen for simplicity to use κ, rather than κ^*, in the argument of K_0 (they are nearly the same, of course, in this perturbation regime). The unperturbed eigenfunctions $\phi_k(y)$ and eigenvalues α_k are defined by

$$\mathcal{L}_0(y,y')\phi_k(y') = \alpha_k\phi_k(y) \qquad \text{(II.22)}$$

where

$$\phi_k(y) = e^{iky}/(2\pi)^{1/2}; \qquad \alpha_k = \pi/(\kappa^2 + k^2)^{1/2} \qquad \text{(II.23)}$$

Now, as in the previous limit (1), the periodic perturbation connects ϕ_k only to ϕ_{k+2nq}, with integer n, so we have a discrete spectrum in each k-manifold and can use bound state perturbation theory:

$$\pi/\kappa^* \approx \alpha_k + \int \mathrm{d}y\; \phi_k(y)\mathcal{L}_1(y,y')\phi_k(y') \qquad \text{(II.24)}$$

$$\psi_k(y) \approx \phi_k(y) + \sum_n a_n\phi_{k+2nq}(y) \qquad \text{(II.25)}$$

$$a_n \approx \int \mathrm{d}y\; \frac{\phi_{k+2nq}(y)\mathcal{L}_1(y,y')\phi_k(y)}{\alpha_k - \alpha_{k+2nq}} \qquad \text{(II.26)}$$

where $|a_n| << 1$ if the perturbation expansion is to converge. We are interested here primarily in the ground state, $k = 0$.

We can carry out the calculation analytically, if approximately, by expansion of the kernel in the small length ratios appropriate to this regime. First, since $\lambda >> z_0$, or $\rho << 1$, we can expand both the square-root weighting factor and the Bessel function K_0 in power series in ρ; we will keep terms only up to second order. Moreover, the rapid decay of K_0 with its argument as before gives significant contributions only for $|y - y'| \lesssim 1/\kappa \sim D << \lambda$, so $\cos qy'$ can be usefully expanded about $y' = y$. Then

$$\mathcal{L}_1(y,y')\psi(y') \approx (\rho^2/2)\int_{-\infty}^{\infty} \mathrm{d}y'\,\psi(y')\Bigg[[\sin^2 qy + q(y'-y)\sin 2qy + q^2(y'-y)^2\cos 2qy]K_0(\kappa|y'-y|) + \kappa|y'-y|\left[\sin qy + \frac{q(y'-y)}{2}\cos qy - \frac{q^2(y'-y)^2}{6}\sin qy\right]^2 K_1(\kappa|y'-y|)\Bigg] \qquad \text{(II.27)}$$

To this order we then find from eq II.24 that

$$\kappa \approx \kappa^*\left[1 + \left(\frac{q^2 z_0}{4\kappa^*}\right)^2\right] \qquad \text{(II.28)}$$

again an increase over the flat surface value. The corresponding eigenfunction, from eq II.26, is

$$\psi_0(y) \approx 1 - (3/8)\rho^2\cos 2qy \qquad \text{(II.29)}$$

with, as before, only small corrections from constant polymer density along the surface.

(3) $z_0 >> \lambda >> D$. Here the surface oscillates rapidly: $\rho \equiv qz_0 >> 1$. Nevertheless, the confinement thickness D is small compared to either length characterizing the surface, so the polymer can still follow the surface closely, and the perturbational approach of the preceding subsection (2) can be used again. The restriction of important values of y' to $|y - y'| \lesssim 1/\kappa \sim D << \lambda$ again makes it useful to expand $\sin qy'$ and $\cos qy'$ around $y = y'$. However, since $\rho >> 1$, a power series expansion of the weighting factor $(1 + \rho^2\sin^2 qy)^{1/2}$ is no longer useful; the "unperturbed" reference state can no longer be taken as a single flat surface. Instead, at each point y we take as a reference the plane *locally* tangent to the surface:

$$\mathcal{L}_0(y,y')\psi(y') = (1 + \rho^2\sin^2 qy)^{1/2}\int_{-\infty}^{\infty}\mathrm{d}y'\,\psi(y')K_0[\kappa(1 + \rho^2\sin^2 qy)^{1/2}|y-y'|] \qquad \text{(II.30)}$$

which has the obvious ground-state solution $\psi_0(y)$ = constant, corresponding to $\kappa = \kappa^*$. The excited states are more complicated, in that they are not plane waves:

$$\mathcal{L}_0(y,y')e^{iky'} \approx \frac{\pi}{\kappa}\left[\left(1 - \frac{k^2}{2\kappa^2\rho}\right) - \frac{k^2}{2\kappa^2\rho}\sum_n \cos 2nqy + \mathcal{O}(1/\rho^2)\right]e^{iky} \qquad \text{(II.31)}$$

but the necessary corrections to give the correct Bloch states are clearly small (of order $1/\rho << 1$). With similar approximations we also find

$$\frac{\kappa^*}{\kappa} \approx 1 - \frac{7(2^{1/2})}{8(\kappa^* z_0)^2} \qquad \text{(II.32)}$$

The ground-state eigenfunctions will have a small (order $1/\rho$) sinusoidal admixture, of period $\lambda/2$.

(4) $\lambda << D,z_0$. There remains fundamentally the most interesting case, where the wavelength λ is the smallest of the three lengths, and the solution is intrinsically nonperturbational. This includes the extension of case 1 to the region where λ is much less than z_0, while both remain small compared to D, as well as the totally new case, $z_0 >> D >> \lambda$. In both instances we start with explicit recognition of the structure of the eigenfunctions—in particular, the ground state $\psi(y)$ is periodic,

$$\psi(y) = f(y \bmod \lambda) \qquad \text{(II.33)}$$

where $f(x)$ is defined in the interval $-\lambda/2 \le x \le \lambda/2$. The basic integral equation (II.13) then becomes

$$f(y) = (\kappa^*/\pi)\int \mathrm{d}x\, f(x)(1 + \rho^2\sin^2 qx)^{1/2}\sum_{n=-\infty}^{\infty} K_0[\kappa[(x - y + n\lambda)^2 + z_0{}^2(\cos qx - \cos qy)^2]^{1/2}] \qquad \text{(II.34)}$$

The central feature of this regime is that K_0 decays with x only over distances much greater than λ, so that many terms in the sum over n (around $n = 0$) contribute importantly. Thus we can replace the sum to a good approximation by an *integral* over n. This integral, after trivial change of variable, can be found in standard integral tables; the result is

$$f(y) = \frac{\kappa^* q}{\pi\kappa}\int_{-\lambda/2}^{\lambda/2}\mathrm{d}x\, f(x)(1 + \rho^2\sin^2 qx)^{1/2}e^{-\kappa z_0|\cos x - \cos y|/2} \qquad \text{(II.35)}$$

The square root can be replaced by $\rho|\sin qx|$ except in the narrow region $|qx| \le 1/\rho$. That region is negligible unless $f(x)$ is highly peaked there; it is not difficult to show by techniques essentially identical with those below that no such solution exists. We further recognize that $f(x)$, as an even function, must in fact be a function only of $\cos qx$:

$$f(x) \equiv g(\cos qx) \qquad \text{(II.36)}$$

and we then rewrite the integrat equation as

$$\frac{\pi\kappa}{2\kappa^*\rho}g(u) \approx \int_{-1}^{u}\mathrm{d}w\; g(w)e^{\kappa z_0(w-u)/2} + \int_{u}^{1}\mathrm{d}w\; g(w)e^{-\kappa z_0(w-u)/2} \qquad \text{(II.37)}$$

We can find the general solution to this most readily by converting it to a differential equation. In fact, simply by differentiating eq II.37 twice, we find

$$g''(u) = -\mu^2 g(u); \qquad \mu^2 = (2/\pi)\kappa^* z_0 \rho - (\kappa z_0/2)^2 \tag{II.38}$$

with general solutions $g(u) = a \cos \mu u + b \sin \mu u$ (and we recall $u \equiv \cos qy$). The boundary conditions are effectively contained in the original integral equation. Substitution of the general solution back into eq II.37 then shows that the solutions (which exist only for $\mu^2 > 0$) are

$$f(y) = \cos (\mu \cos qy) \quad \text{with} \quad \mu \tan \mu = \kappa z_0/2$$

$$f(y) = \sin (\mu \cos qy) \quad \text{with} \quad \mu \cot \mu = \kappa z_0/2 \tag{II.39}$$

Here the conditions on the right-hand side, since μ is defined by eq II.38, simply set the value of κ. There are, of course, multiple solutions to these transcendental equations (corresponding, in the language of solid-state physics, to different energy bands, but all at the zone center, since the solutions are purely periodic). For the ground state we seek the largest value of κ or the smallest value of μ (other than $\mu = 0$, which corresponds to the eigenfunction $f(y) \equiv 0$; see eq II.39). It is easy to see graphically that this always corresponds to the cos ($\mu \cos qy$) solution, and $\mu \tan \mu = \kappa z_0/2$. For limiting cases we can readily obtain analytic approximations: for $\kappa z_0 << 1$ we also have $\mu << 1$, $\tan \mu \approx \mu$, and $\mu^2 \approx \kappa z_0/2$. Then

$$\kappa z_0 \approx 2\kappa^* z_0 \rho/\pi \quad \text{when} \quad \kappa z_0 << 1 \tag{II.40}$$

This is possible, of course, only for a small right-hand side compared to unity and thus only for the ordering $D >> z_0 >> \lambda$ (so that $\kappa^* z_0 \sim z_0/D$ can be sufficiently small, though $\rho >> 1$). In the opposite limit, $\kappa z_0 >> 1$, we have $\mu \approx \pi/2$, which by definition of μ immediately gives

$$\kappa z_0 \approx (2\kappa^* z_0 \rho/\pi)^{1/2} \quad \text{when} \quad \kappa z_0 >> 1 \tag{II.41}$$

We note that this can be rewritten as

$$\kappa\lambda \approx 2(\kappa^*\lambda)^{1/2} \tag{II.42}$$

which explicitly demonstrates the independence of κ on z_0, as expected in this limit.

III. Discussion

From the explicit solutions of the surface problem in section IIB we have the ground-state eigenfunction

$$\psi(y) \equiv \phi_0(y,\zeta(y)) \tag{III.1}$$

and the eigenvalue κ, in various regimes of relative roughness. From eq II.4 the former gives immediately the polymer (volume) density at the surface, proportional to $|\psi(y)|^2$, which is proportional to the *areal* density of polymer bound to the surface. The eigenvalue κ sets the spatial dependence of the polymer distribution through its parametric appearance in the kernel of the integral equation (II.9), which for the sinusoidal surfaces we have considered becomes explicitly

$$\phi_0(y,z) = \frac{\kappa^*}{\pi}\int_{-\infty}^{\infty} \mathrm{d}y'\,(1 + \rho^2 \sin^2 qy')^{1/2} K_0[\kappa[(y - y')^2 + (z - z_0 \cos qy')^2]^{1/2}]\psi(y') \tag{III.2}$$

In the first three of the four regimes considered above, (1) $D >> \lambda, z_0$; (2) $\lambda >> z_0, D$; and (3) $z_0 >> \lambda >> D$, the surface variations are sufficiently small (amplitude $z_0 << D$) and/or slow (wavelength $\lambda >> D$) that perturbative corrections to the simple problem of a flat (or, at least, locally flat) surface are small. In particular, in each of these instances the eigenvalue κ is approximately the planar surface value κ^* (see eq II.18, II.28, II.32 for more precise results).

In case 1, where the surface oscillations take place on length scales much smaller than the confinement thickness (in particular, $z_0 << D \sim 1/\kappa^*$) we can readily find the asymptotic behavior of $\phi_0(y,z)$ from eq III.2. For $z >> z_0$ we can replace $(z - z_0 \cos qy')^2$ by z^2 in the argument of K_0. Using the result (II.19) for $\psi(y)$, we find

$$\phi_0(y,z) \approx e^{-\kappa|z|} \quad \text{for} \quad |z| >> z_0; \qquad D >> \lambda, z_0 \tag{III.3}$$

(but λ *not* $<< z_0$, for which case see below), with corrections which die off as $\exp[-[\kappa^2 + (2nq)^2|z|]^{1/2}]$ and which have, in general, some periodic modulation in y). As we pointed out in section II, $\kappa > \kappa^*$, so the polymer is more closely bound to the undulating than to the flat surface, for the same attractive potential. This is primarily the effect of more net surface area per unit length in y, by the ratio

$$\frac{1}{\lambda}\int_0^{\lambda} \mathrm{d}y\,(1 + \rho^2 \sin^2 qy)^{1/2} \approx (1 - \gamma^2)(1 + \rho^2/2)^{1/2} \approx \kappa/\kappa^*$$

The meaning of $\psi(y) \approx 1$ is, after all, that the polymer density remains approximately constant on the rough, as on the flat, surface, and is therefore more tightly bound per unit distance in y.

In the long-wavelength limit of regime 2, $\lambda >> z_0, D$, the result is similar, in that $\psi(y)$ is nearly constant (eq II.29; note that $\rho^2 \equiv (qz_0)^2 << 1$ in this limit), and the surface area per unit length in y has again increased over the plane surface value. The slow spatial variation of the surface suggests an exponential decay characterized by κ^* along the local surface normal. Since the slope is everywhere small, we can obtain an analytic expression by expanding in the small quantity ρ^2; to order ρ^2 we find

$$\phi_0(y,z) \approx [1 + (\rho^2/8)(2 - 5 \cos 2qy)]e^{-\kappa(z - z_0 \cos qy)}; \qquad \lambda >> z_0, D \tag{III.4}$$

The net effect at fixed position (x,y) along the surface is a decay set by κ along z measured from the local position of the surface, $z = z_0 \cos qy$. The change in κ from κ^* (see eq II.28) is extremely small—of order ρ^4. The increased area at x,y is essentially compensated by the canting of the normal to the surface there, along which the local decay of ϕ_0 occurs, away from the z direction.

The short-wavelength regime (4) involves two quite different limits, though both were amenable to the same mathematical analysis in section II. The first is $\lambda << z_0 << D$, with $D \sim 1/\kappa$ (in this case quite different from $1/\kappa^*$), where the polymer extends over distances very large compared to the surface oscillations. As in earlier cases $\psi(y)$ is nearly constant; from eq II.39, II.40

$$\psi(y) \approx \cos [(\kappa z_0/2)^{1/2} \cos qy] \approx 1 - (\kappa^* z_0 \rho/\pi) \cos^2 qy \tag{III.5}$$

where we have explicitly used $\kappa z_0 << 1$ and the relation (II.40), which can be written

$$\kappa/\kappa^* \approx 2\rho/\pi >> 1 \tag{III.6}$$

(we reemphasize that this result requires $(\kappa^* z_0)\rho << 1$, which is not automatically assured by the underlying ordering $\lambda << z_0 << D$; if the surface oscillates *too* rapidly, the more general solution, eq II.39, with μ not necessarily small, applies.) The extra binding (in this case very substantial) relative to the planar surface comes again from the additional surface area:

$$\frac{1}{\lambda}\int_0^{\lambda} \mathrm{d}y\,(1 + \rho^2 \sin^2 qy)^{1/2} \approx \frac{\rho}{\lambda}\int \mathrm{d}y\,|\sin qy| = \frac{2}{\pi}\rho$$

Perhaps the most interesting limit is $\lambda << D << z_0$, where

$$\psi(y) \approx \cos\,[(\pi/2)\cos qy]$$

which vanishes at the peaks of the grating and is a maximum at the inflection points of the surface (where $\cos qy = 0$). This is an effect suggested by the earlier results[1,2] for a cylindrical or spherical surface—namely, that increased curvature mitigates against binding of the polymer to the surface. (Indeed, we even see the effect in the perturbational regimes, where $\psi(y) \approx 1 - |\alpha| \cos 2qy$ (see, e.g., eq II.19, II.29) though it is very small there: $|\alpha| << 1$, and it is evident for *all* values of μ in eq II.39, the general result for small λ.) Although $\psi(y)$ vanishes at the surface peaks $\zeta(y) = \pm z_0$, it does extend essentially over the range $-z_0 < z < z_0$ (and little beyond, since $D << z_0$). The full dependence of $\phi_0(y,z)$ on both coordinates is complicated, but the *average* (over y) dependence on z is simple and readily obtained analytically from eq III.2 by doing the averaging integral first:

$$\frac{1}{\lambda}\int_0^{\lambda} \mathrm{d}y\, \phi_0(y,z) \approx \begin{cases} \cos\left(\dfrac{\pi z}{2z_0}\right) + \dfrac{\pi}{2\kappa z_0} e^{-\kappa(z_0 - z)}, & \text{for } 0 \le z \le z_0 \\[2ex] \dfrac{\pi}{2\kappa z_0} e^{-\kappa(z - z_0)}, & \text{for } z \ge z_0 \end{cases} \qquad \text{(III.7)}$$

Although the above detailed analysis could be carried through only for the specified sinusoidal gratings, we can use some of the methods and most of the qualitative results to understand a more general rough surface, described by the function $\zeta(x,y)$. If this is a randomly rough surface, for example, we can make the connection with the sinusoidal grating parameters above through the correlation function (taken to be Gaussian):

$$\langle \zeta(x,y)\zeta(x',y') \rangle \approx {z_0}^2 e^{-|\vec{r}-\vec{r}'|^2/\lambda^2} \qquad \text{(III.8)}$$

Instead of eq II.11 or II.13, the surface integral equation in general takes the form:

$$\psi(x,y) = \frac{\kappa^*}{2\pi}\int \mathrm{d}x'\,\mathrm{d}y'\,(1 + |\nabla'\zeta(x',y')|^2)^{1/2}\,\frac{e^{-\kappa|\vec{R}-\vec{R}'|}}{|\vec{R}-\vec{R}'|}\psi(x',y') \qquad \text{(III.9)}$$

where

$$|\vec{R}-\vec{R}'|^2 \equiv (x - x')^2 + (y - y')^2 + [\zeta(x,y) - \zeta(x',y')]^2 \qquad \text{(III.10)}$$

and ∇' is the gradient with respect to variables x',y'. Note that Green's function is now a Yukawa (screened Coulomb) potential, rather than the Bessel function K_0.

If we concentrate on the most physically interesting quantity, the eigenvalue κ, which sets both the binding free energy and the decay rate of polymer density away from the surface, we can immediately write down a simple and general result. We first recognize that $\psi(x,y)$, the polymer density amplitude at one point on the surface, is influenced directly only by that part of the surface which lies within a distance of order $1/\kappa$ of that point. Mathematically, Green's function (either the Yukawa form in eq III.19 or the Bessel function of eq II.13), which expresses the communication between surface points, dies off in a distance of that order. But the fundamental differential equation (II.8) tells us that it is costly for the eigenfunction $\phi(\vec{r})$, or $\psi(\vec{r})$, to vary on that same length scale (the dimensionless curvature term is $\kappa^{-2}\nabla^2\phi$), so the ground state ϕ_0 will be nearly constant over lengths of order $1/\kappa$. Indeed, we have found that result explicitly in all cases of the sinusoidal grating above. Then to lowest approximation we can replace $\psi(x',y')$ by $\psi(x,y)$ in the integral equation (III.9), the eigenfunction disappears from the equation, and we have reduced the determination of κ (to this approximation) to quadratures. Moreover, Green's function is smooth and monotonic with distance $|\vec{R}-\vec{R}'|$, its principal effect being to restrict the range of integration to a region of area $\sim\kappa^{-2}$ around x,y in the x',y' plane (and within that region to those values such that $\zeta(x',y')$ is within $\sim\kappa^{-1}$ of $\zeta(x,y)$). Then eq III.9 reduces to

$$\kappa/\kappa^* \approx \langle (1 + |\nabla\zeta|^2)^{1/2} \rangle \qquad \text{(III.11)}$$

whose right-hand side has the simple geometrical interpretation of the ratio of two areas: that of the physical surface contained within a sphere of radius $1/\kappa$ about the point $(x,y,\zeta(x,y))$, to κ^{-2}, the projected area of that sphere on the x,y plane. It is true, in general, that this will depend on the point (x,y) chosen, but the dependence is in all cases weak, and unessential to discovering the behavior of κ as a function of the nature of the surface (i.e., of z_0 and λ). For a flat, or locally flat (on the length scale $1/\kappa$), surface we immediately have $\kappa \approx \kappa^*$. Such is the case most trivially for the generalization of limit 3 above, where $D \sim 1/\kappa$ is much smaller than either length z_0,λ characterizing the surface, and the specific grating result of eq II.32 indeed shows little change of κ from the plane surface value κ^*. Similarly, in the generalization of the long-wavelength limit (2), $\lambda >> z_0,D$, the surface gradient $|\nabla\zeta|$ is by definition everywhere small, and again $\kappa \approx \kappa^*$, as in eq II.28. In limit (1), $D >> z_0,\lambda$ (excluding $\lambda << z_0$), we expect an increase of κ over κ^* reflecting the increased surface area, and the only factor on the right-hand side of the grating result (II.18) which can differ substantially from unity is $(1 + \rho^2/2)^{1/2}$, which is about what we would expect from eq III.11.

Finally, we turn to the particularly interesting limit (4) of a very rough surface, $\lambda << D,z_0$. Within this limit, if $z_0 << D$, the reference sphere of radius $D \sim 1/\kappa$ covers the full amplitude and many oscillations of the surface; the expected enhancement factor is then of order $(z_0/\lambda)^2$. For the special case of the cylindrical grating, which is rough in only one of the two directions in the xy plane, the factor should be of order z_0/λ; indeed, eq II.40 gives $\kappa/\kappa^* \approx 4z_0/\lambda$. In the opposite regime of this very rough surface limit, namely, $z_0 >> D$, the reference sphere of radius D intercepts only small pieces of many peaks of the surface (those parts lying on contours of $\zeta(x',y')$ within D of $\zeta(x,y)$), which pass through nearly vertically (because $z_0 >> \lambda$). There are of order D^2/λ^2 such peaks (their characteristic separation being of order λ), and the surface area of each intercepted by the sphere is of order $D\lambda$ (the linear dimensions of the peak in the xy plane are of order λ, and the vertical dimension intercepted is set by the sphere radius of D). Then the total intercepted area is of order $D^3/\lambda \approx (\lambda\kappa^3)^{-1}$, and the right-hand side of eq III.11 is the ratio of this to the projected area $D^2 \approx 1/\kappa^2$:

$$\kappa/\kappa^* \approx 1/\lambda\kappa \quad \text{or} \quad \kappa \approx (\kappa^*/\lambda)^{1/2} \qquad \text{(III.12)}$$

A similar argument in the grating case gives D/λ peaks of intercepted area D^2 each, to yield the same ultimate result as in (III.12), and this is substantiated by the specific result (II.41) above.

We could pursue this approach further, by Taylor-series expanding $\psi(x',y')$ about $\psi(x,y)$ in eq III.9 to learn more about the ground-state eigenfunctions themselves in the general case. However, given the substantial approximations of the present model (notably, neglect of excluded volume and finite polymer length effects) this does not seem warranted, especially since the detailed study of the gratings above gives a full qualitative and semiquantitative picture of the expected results. Our central result for the general rough surface remains eq III.11.

The extension of these results to chains of finite length involves consideration of the "excited" eigenstates of $\mathcal{H}$. This and the removal of other restrictions to the ideal long chain—notably, the consideration of excluded volume effects—will be treated in future papers.

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Appendix: Transparent vs. Opaque Walls

To obtain some feeling for the effect of the nonphysical, but mathematically convenient, construction of binding surfaces transparent to the polymer, as used above, let us look at a simple soluble example where the results can be compared with those for the corresponding opaque surfaces. Consider a periodic array of plane-parallel walls separated by a length l. First consider the transparent case, as above, where each wall introduces a δ-function attractive potential (as in eq II.6-8):

$$(\nabla^2 - \kappa^2)\phi(z) = -2\kappa^*{}_{\mathrm{t}}\sum_n \delta(z - nl)\phi(0) = -2\kappa^*{}_{\mathrm{t}}\phi(0)\sum_n \delta(z - nl) \quad \text{(A.1)}$$

where n is summed over all integers, negative as well as positive, and the subscript t denotes "transparent".

The solution is

$$\phi(z) = \frac{\kappa^*{}_{\mathrm{t}}}{\kappa}\phi(0)\sum_n e^{-\kappa|z-nl|} \quad \text{(A.2)}$$

which gives immediately, upon setting $z = 0$, the eigenvalue equation

$$\kappa \tanh (\kappa l/2) = \kappa^*{}_{\mathrm{t}} \quad \text{(A.3)}$$

In the corresponding opaque wall case, open rectangular slabs of thickness l are surrounded on both sides by regions inaccessible to the polymer (also, incidentally, rectangular slabs of thickness l). The open slabs are disconnected. In the typical one, $0 \leq z \leq l$, the solution to the fundamental differential equation (A.1) is

$$\phi(z) \sim e^{-\kappa z} + e^{-\kappa(l-z)} \quad \text{(A.4)}$$

The boundary condition sets the eigenvalue κ. Following de Gennes, we take as the boundary condition

$$\left.\frac{\phi'(z)}{\phi(z)}\right|_{z=0,l} = -\kappa^*{}_{\mathrm{o}} \quad \text{(A.5)}$$

which gives

$$\kappa \tanh (\kappa l/2) = \kappa^*{}_{\mathrm{o}} \quad \text{(A.6)}$$

This has the same form as before. In each case $\kappa^*{}_{\mathrm{o}}$ or $\kappa^*{}_{\mathrm{t}}$ characterizes the attraction, but is not known from first principles. It is the variation of κ with parameters (here, the length l) which is of critical interest and, at least in this (admittedly somewhat special) case of planar surfaces, the transparency does not affect that behavior.

Although this is geometrically the simplest case to study, it lacks the intrinsic asymmetry of the opposite sides of any curved surface (opposite signs of curvature). Intuitively, one might expect this to distinguish between transparent and opaque walls, so we also examine here a soluble case involving curved boundaries. We choose for simplicity a regular crystalline array of identical spherical holes of radius R_0. For opaque walls the separate spheres do not communicate; we have for the solution in the interior of a single one

$$\kappa^*{}_{\mathrm{o}}/\kappa = \coth \kappa R_0 - 1/\kappa R_0 \quad \text{(A.7)}$$

For transparent walls we adopt the Wigner–Seitz approximation from solid-state physics. We need solve the problem only within a single unit cell (which is periodically repeated to form the crystal), surrounding one of the spheres. That cell, which reflects the point symmetry of the lattice, is replaced by a sphere (radius R_1) of the same volume. Then the problem regains spherical symmetry, with eigenfunctions $\phi(r)$ which are linear combinations of $e^{\pm\kappa r}/r$. Boundary conditions at $r = 0$, R_0, and R_1 determine the coefficients and κ. There should be only one length scale characterizing the roughness: $R_1 \approx R_0$ (lattice constant and spherical hole radius approximately equal). For simplicity we choose equality: $R_0 = R_1$. Then some algebra yields

$$\frac{\kappa^*{}_{\mathrm{t}}}{\kappa} = \frac{a}{1 - e^{-x}} \quad \text{(A.8)}$$

where

$$x = 2\kappa R_0; \qquad a = \frac{(x + 1)e^{-x} + (x - 1)e^{x}}{(x + 1) + (x - 1)e^{-x}} \quad \text{(A.9)}$$

We compare this with the opaque wall result (A.7) by looking at limiting behavior. For transparent walls,

$$\begin{aligned} \kappa &= (3\kappa^*{}_{\mathrm{t}}/4R_0)^{1/2}, \quad \text{for } \kappa R_0 << 1 \\ &= 1 - \mathcal{O}(e^{-2\kappa R_0}), \quad \text{for } \kappa R_0 >> 1 \end{aligned} \quad \text{(A.10)}$$

whereas for the opaque walls eq A.7 gives

$$\begin{aligned} \kappa &= (3\kappa^*{}_{\mathrm{o}}/R_0)^{1/2}, \quad \text{for } \kappa R_0 << 1 \\ &= 1 - 1/\kappa R_0, \quad \text{for } \kappa R_0 >> 1 \end{aligned} \quad \text{(A.11)}$$

These exhibit the same general behavior, though in detail they are admittedly different.

These examples give us confidence in using transparent walls in the theoretical model so as to make calculations tractable. We might further point out that the transparency also acts to remove an artificial feature of the cylindrical grating—the isolation of individual valleys in the limit of large roughness. The physical surface with similar scale of roughness allows communication on or near fixed surface height contours between widely separated peaks, as is mimicked by transmission across transparent walls separating the various cylindrical valleys in the model.

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