These results were obtained under the assumption of full thermodynamic equilibrium, which is not obviously reached experimentally. If an undersaturated copolymer layer exists, the B part of this layer creates a strong potential barrier for new adsorbed chains due to the excluded volume repulsion between monomers. A possible way to form an end-grafted layer at equilibrium would perhaps then be to adsorb first a homopolymer A with a reactive end group and then to polymerize the B block in situ. Theoretically, a natural extension of this work would then be the study of the adsorption kinetics, which would make this approach to equilibrium more quantitative.

The predictions made here could be directly compared to neutron scattering or reflectivity measurements on colloidal systems. An alternative way to probe experimentally the structure of adsorbed copolymer layers is to coat with block copolymers the mica surfaces of a force measurement apparatus. Such experiments have already been made by Tirrell and co-workers,[18] Klein and co-workers,[19] and Hair and co-workers.[20] It seems, however, that in many cases the solvent is neither a highly selective solvent nor a nonselective solvent and that a detailed analysis of the crossover between these two regimes is needed for a quantitative comparison between theory and experiments.

Acknowledgment. We thank P.-G. de Gennes for stimulating discussions.

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Polymer Adsorption and Electron Binding on Rough and Fractal Surfaces

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ABSTRACT: Mean-field theory is used to study the adsorption of polymer chains on a rough surface, both with and without excluded-volume interactions. In particular, the adsorption on a fractal surface generated from a hierarchy of small-amplitude sinusoidal perturbations is investigated. It is found that there is a simple scaling relation between the concentration of adsorbate on a fractal and on a plane boundary. Surface irregularity greatly enhances the adsorption of polymer. The probelm is mathematically equivalent to the binding of quantum mechanical particles by rough interfaces.

I. Gaussian Adsorption

1. Introduction. In the scientific literature it is generally assumed that polymers adsorb on regular smooth surfaces: lines, planes, or spheres, for example.[1,2] Some recent work by Hone et al.[3] has considered adsorption on a sinusoidal interface, but many naturally occurring surfaces are rough over many length scales. In some cases the surface geometry has been characterized as fractal.[4,5]

In this paper we will introduce a model fractal surface, which has already been used to study the scaling structure of viscous fingering[6] and the impedance of a rough electrode–electrolyte contact.[7] We consider the adsorption of polymer within mean-field theory, using a renormalization scheme developed by Ball and Blunt.[7]

First, though, we shall briefly introduce the Edwards[8] mean-field approach to polymer statistics, which we use here to formulate the problem. The reader is referred to de Gennes[9] or Doi and Edwards[10] for a more comprehensive treatment.

A diffusion or Schrödinger-like equation may be written for the Green function of a polymer chain.

$$\left[\frac{\partial}{\partial L} - \frac{l}{6}\nabla^2 + V(\mathbf{r})\right]G(\mathbf{r},\mathbf{r}',L) = \delta(\mathbf{r}-\mathbf{r}')\delta(0) \qquad (1)$$

$G(\mathbf{r},\mathbf{r}',L)$ is the statistical weight for a polymer chain which starts from $\mathbf{r}'$ to land at $\mathbf{r}$ in L steps of length l in a potential V. If L is replaced by imaginary time then this equation becomes equivalent to the Schrödinger equation.

The δ functions impose the boundary conditions that $G(\mathbf{r},\mathbf{r}',0) = \delta(\mathbf{r}-\mathbf{r}')$ and $G(\mathbf{r},\mathbf{r}',L{<}0) = 0$. $V(\mathbf{r})$ is the external potential in units of k_BT; it may include a term to account for self or excluded-volume interactions.

The Green function may be written as an expansion in the eigenfunctions of the differential operator.

$$G(\mathbf{r},\mathbf{r}',L) = \sum_n \psi_n(\mathbf{r})\psi_n(\mathbf{r}')\exp(-E_nL) \qquad (2)$$

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For bound states the energy spectrum is discrete and E is negative. In the limit of very long chains ($L \rightarrow \infty$) the ground state dominates the sum and

$$G \approx \psi_0(\mathbf{r})\psi_0(\mathbf{r}') \exp(-E_0 L) \qquad (3)$$

The probability of finding a polymer at r is proportional to $\psi(\mathbf{r})^2$. We rewrite the differential operator in eq 1 and obtain the following dimensionless equation for ψ. Lengths are measured in units of the Kuhn length, l.

$$\nabla^2\psi = \alpha^2\psi + \beta\psi^3 + V'\psi \qquad (4)$$

where α^2 is $-E_0$ and V' is the external potential, but we have explicitly written down the excluded-volume interaction, $\beta\psi^3$—representing a repulsive potential proportional to the local concentration of polymer. For polymers at the Θ temperature, the attractive and repulsive two-body interactions are equal, and β is zero. Moreover, in polymer melts the excluded-volume interaction also effectively cancels. In these cases we have Gaussian chains, described in mean-field theory by the equation

$$\nabla^2\psi = \alpha^2\psi + V'\psi \qquad (5)$$

This is, of course, identical with the time-independent Schrödinger equation. Real α corresponds to bound states (i.e., negative energies) and, in the polymer problem, has a physical interpretation as the negative free energy of adsorption. This treatment also considers the corresponding quantum mechanical problem of single electron bound states.

In this section we describe the adsorption of Gaussian chains using (5). In section II the calculations are extended to describe the behavior with excluded-volume interactions.

2. Adsorption on a Planar Surface. We now wish to model the interaction between a polymer chain and an attractive surface. We shall introduce a simple description. We assume that away from the surface the polymer feels no external potential and so $V'(r)$ is zero. At the surface single monomers are attracted via very short range forces: for instance screened electrostatic or van der Waals interactions or covalent bonding with the material of the boundary. If these interactions occur on a scale less than the Kuhn length l, we cannot describe them in terms of a continuum potential. The polymer density is zero inside the surface, and on the outside, where the polymer is adsorbed, it will be decreasing away from the boundary.

If we have an impenetrable planar surface lying in the y–z plane such that x is the normal component, then the simplest description, if we cannot use an explicit form for the attractive potential, is to model the adsorption in terms of one parameter, κ, via the radiation boundary condition introduced by de Gennes:[9]

$$\left[\frac{1}{\psi}\frac{\mathrm{d}\psi}{\mathrm{d}x}\right] = -\kappa \qquad (6)$$

evaluated at $x = 0$. The plane at $x = 0$ can therefore be considered as the attractive surface.

The behavior of the polymer molecules is dominated by the relative importance of entropic and enthalpic considerations. The wall presents an attractive surface, and so the chain gains potential energy by adsorbing. However, the polymer is now constrained to lie in a layer close to the wall and the possible configurations of the constituent subunits are restricted—in effect, the chains have collapsed from three to two dimensions. This considerably reduces the entropy of the polymer. Positive κ corresponds to a surface potential sufficiently attractive to overcome the entropy; from (6) the polymer density is greatest near the wall and decreases away from it. We have a positive free energy of adsorption. Similar considerations pertain for quantum mechanical bound states close to an impenetrable wall—the particle pays a kinetic energy penalty in being confined near the boundary which is offset by the potential energy gain.

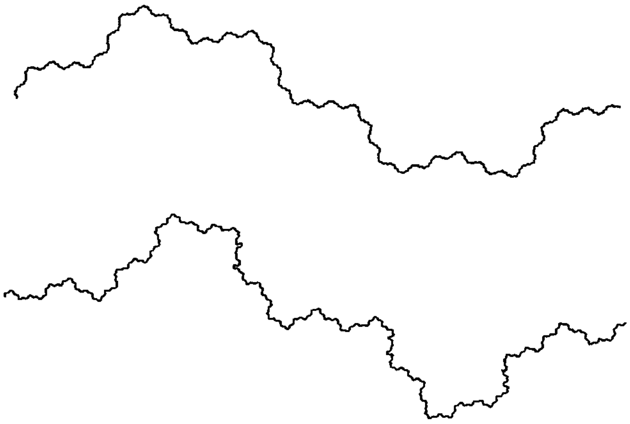

Figure 1. Two fully developed fractal curves. (a, top) $m = 5$, $\epsilon = 0.8$, and the fractal dimension $d_f \approx 1.10$; (b, bottom) $m = 3$, $\epsilon = 0.8$, and $d_f \approx 1.15$. Surfaces are generated by extending the curves perpendicular to the plane of the paper. The corresponding surface fractal dimensions are one larger than those for the curves.

Consider now adsorption on the plane $x = 0$. The solution to (5) which is bounded at infinity is

$$\psi = \exp(-\alpha x) \qquad (7)$$

The boundary condition (6) sets $\alpha = \kappa$. The condition for bound states is clearly that $\kappa > 0$.

We shall now try to tackle the problem of adsorption on a rough surface. In general this will lead to a very complicated relationship between κ and the eigenvalue α, dependent on the particular geometry. However, what we will do is solve the eigenproblem analytically for a simple family of rough surfaces, which are fractal. That is, they possess statistically similar structure over a range of lengths. The solution will suggest that behavior of more realistic surfaces. We will find the relationship between κ and α and show that for highly crinkled interfaces α may be much larger than the bare value of κ, κ_0.

3. Calculation on a Fractal Surface.

The Fractal Surface. The fractal model used here has already been described in greater detail.[6,7] It is a smooth and statistical adaptation of the Koch curve construction.[4] We take a small-amplitude cosine wave, $x = a_0 \cos(k_{\min} y)$. The wavelength, $\lambda_{\max}$ ($=2\pi/k_{\min}$), is about the size of the system and $a_0 k_{\min} = \epsilon < 1$. Along the length of this we buckle another wave m times smaller. Another is now drawn along the secondary wave and so on, for N stages, down to a small size cutoff. Each wave has a random phase with respect to the previous ones. The values of ϵ and m at each stage are the same. This is not the simple addition of waves, as the next stage is added perpendicular to the existing curve. Two fully developed curves are shown in Figure 1. Notice that we can produce overhangs. The interface is generated from the same structure over a range of lengths and it is therefore fractal. The surface in the y–z plane is formed by sweeping the curve along the z axis. The fractal dimension, d_f, is calculated by considering the change in surface area at each stage of buckling.[4,6]

$$d_f = 2 + \epsilon^2/4 \ln(m) + O(\epsilon^4) \qquad (8)$$

The Problem. We now wish to solve the problem of Gaussian chain adsorption on this fractal surface. Consider a cross section of the fractal surface in the x'–y' plane as shown in Figure 2. The problem tackled here is essentially

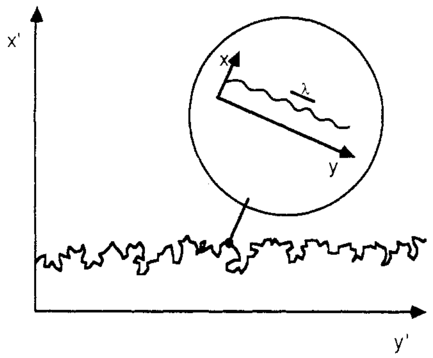

Figure 2. Cross section in the x'-y' plane of the fractal surface. The circle shows the structure of the surface at the smallest length scale $\approx \lambda_{\min}$.

two dimensional; the behavior is constant along the z axis. This does not affect the physical results. We wish to solve

$$\nabla_{x',y'}{}^2\psi(x',y') = \alpha^2\psi(x',y') \qquad (9)$$

If the boundary is no longer flat, then the simplest generalization of the de Gennes boundary condition is

$$\left[\frac{1}{\psi}\frac{\partial\psi}{\partial n}\right]_{\text{surface}} = -\kappa \qquad (10)$$

where n is a coordinate normal to the surface.

This relation assumes that the potential energy gain for a unit length of polymer is constant regardless of the orientation of the surface and its curvature. It can be shown that for polymer chains interacting near a continuum potential (10) would have to contain a curvature term.[11]

The surface is composed of a succession of buckles of widely separated wavelengths. The probelm is solved by successively smoothing out the buckles and renormalizing κ at each stage. In the next section we will derive the renormalization scheme.

The Renormalization Scheme. We shall calculate the bound states on our model by considering each buckle in turn. First, suppose we look at the surface at the scale of the smallest wavelength buckle, $\lambda_{\min}$. For length scales of roughly $\lambda_{\min}$ the surface appears almost planar but with a small-amplitude buckle on it. We therefore assume that for distances far from the surface (but still less than $\lambda_{\min}$) the surface appears flat and that the effect of the buckling is only to renormalize the boundary condition parameter, κ. This is possible since the buckling is treated only as a perturbation.

Let x and y be local Cartesian components. At length scales of the order of $\lambda_{\min}$ (which from now on we shall call λ) the perimeter of the surface, at some point, is given by $\Lambda(y) = a \cos(ky)$. This is shown in Figure 3. The wavenumber, $k = 2\pi/\lambda$, and $ak = \epsilon$, where $\epsilon < 1$.

For a sinusoidal boundary with wave number k, ψ may be expressed as a Fourier decomposition:

$$\psi(x,y) = \sum_{n=0}^{\infty} B_n f_n(x) \cos(nky) \qquad (11)$$

where the B_n are of order ϵ^n.

If ψ is substituted into (9) and harmonics of cos (ky) are equated we find

$$\mathrm{d}^2 f_n(x)/\mathrm{d}x^2 = (n^2k^2 + \alpha^2) f_n(x) \qquad (12)$$

f_0 is the average field. We shall assume that the f_n for $n > 0$ will decay more quickly than f_0 so that far from the surface the sum is dominated by f_0 and hence ψ tends to ψ^{app}, which equals $B_0 f_0$. Here ψ^{app} is the apparent form of ψ if the far-field behavior is extrapolated back to the surface.

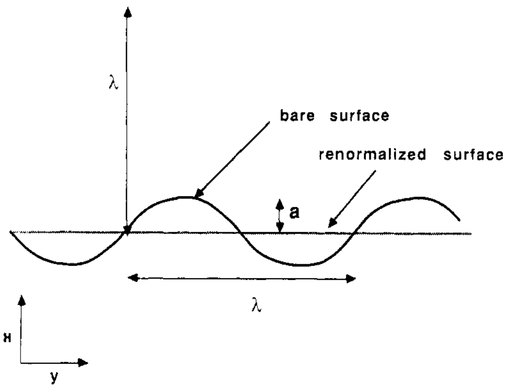

Figure 3. Cross section of the surface at the scale of the smallest wavelength buckle. We replace the crinkled boundary with a smooth one whose effective binding gives the correct far-field behavior. Repeating this for the next largest perturbation, and so on, tells us the binding energy of the multiply buckled surfaces shown in Figure 1.

From (12) we see, by setting $n = 0$, tnat ψ^{app} is a solution for a planar surface with the renormalized boundary condition:

$$\left[\frac{1}{\psi^{\text{app}}}\frac{\mathrm{d}\psi^{\text{app}}}{\mathrm{d}x}\right]_{x=0} = -\kappa^{\text{app}} \qquad (13)$$

κ^{app} is, therefore, the value κ would have if the buckled surface was replaced by a plane surface and the far-field behavior is preserved.

We define $\psi^{\text{app}}(0)$ and $f_{n>0}(0)$ to be unity. A solution to (12) for the zeroth harmonic is

$$\psi^{\text{app}} = \exp(-\alpha x) + \Delta \exp(+\alpha x) \qquad (14)$$

Remember that for adsorption on a plane surface, ψ is bounded at infinity, which means that the boundary condition at $x = 0$ implies that $\alpha = \kappa$. In the renormalization scheme, however, the boundary condition parameter, κ, is renormalized, so the eigenvalue is left undetermined. At the beginning of the renormalization α is chosen arbitrarily. Only at the end of the renormalization, when all the crinkles have been smoothed so that the effective surface is planar, can the condition κ equals α and Δ is equal to zero be sought. This implies from the boundary condition, (13), that

$$\Delta = \frac{\alpha - \kappa^{\text{app}}}{\alpha + \kappa^{\text{app}}} \qquad (15)$$

We can solve for the $f_n(x)$ straight away, because ψ must tend to ψ^{app} far from the surface so that all the $f_n(x) \rightarrow 0$ as $x \rightarrow \infty$. Thus from (12)

$$f_n = \exp(-\alpha^n x) \qquad (16)$$

where $\alpha^n = (n^2\alpha^2 + k^2)^{1/2}$.

We will want to calculate the renormalized boundary condition to order ϵ^2. To do this it is only necessary to keep the zeroth and first harmonics of the Fourier decomposition, i.e.

$$\psi(x,y) = \exp(-\alpha x) + \left(\frac{\alpha - \kappa^{\text{app}}}{\alpha + \kappa^{\text{app}}}\right)\exp(+\alpha x) + B_1 \exp(-\alpha' x)\cos(ky) + O(\epsilon^2) \qquad (17)$$

It is important to remember that this form of ψ is only valid for x in the range $a \cos(ky) \leq x < \lambda$. At distances greater than approximately λ, the effect of larger length scale buckling becomes important and there will be interference from other parts of the surface. Thus we cannot impose the behavior of ψ as x tends to infinity as this would overspecify the problem.

For the renormalization scheme to be valid the polymer layer thickness, $\approx 1/\alpha$, must be larger than the buckle amplitude, a; in other words, $\alpha a < 1$. This is because only then can one assume that the surface appears planar at distances far (but still less than λ) from the surface. Furthermore the dimensionless amplitude, ϵ (=ak), is less than one so that the buckling is treated as a perturbation; ϵ is a perturbation parameter.

We are left with two unknowns, κ^{app} and B_1, which are determined by the boundary condition (10) on the surface $x = a \cos{(ky)} \Longrightarrow$

$$\left|\frac{1}{\psi}\left\{\frac{1}{1 + (\mathrm{d}x/\mathrm{d}y)^2}\right\}^{1/2}\left(\frac{\partial\psi}{\partial x} - \frac{\mathrm{d}x}{\mathrm{d}y}\frac{\partial\psi}{\partial y}\right)\right|_{x=a\cos(ky)} = -\kappa \qquad (18)$$

We substitute ψ from (17) into the above equation. We work to second order in ϵ and αa. By equating zeroth and first harmonics of cos (ky) the following expressions for κ^{app} and B_1 are found:

$$\kappa^{\text{app}} = \kappa + \frac{\epsilon^2\kappa^{\text{app}}}{4}\left(1 + \frac{2(\alpha^2 - \kappa\alpha')(\alpha^2 - \kappa^{\text{app}}\kappa)}{\kappa^{\text{app}}k^2(\alpha' - \kappa)}\right) \qquad (19)$$

and

$$B_1 = \frac{a(\alpha^2 - \kappa^{\text{app}}\kappa)}{\alpha' - \kappa} \qquad (20)$$

where $\alpha' = (\alpha^2 + k^2)^{1/2}$. If we work strictly to order ϵ^2, κ^{app} on the right-hand side of (19) can be replaced by κ.

This is the renormalization scheme. The information concerning the geometry is contained implicitly within κ^{app}. Having smoothed out the smallest crinkles and renormalized κ we next look at length scales of the order $m\lambda_{\min}$ and likewise renormalize κ. The bare value of κ on the fully crinkled surface shall now be called κ_0 and the effective value after the consideration of i stages is κ_i, which is a function of α, k_i, and κ_{i-1}. α is only the correct eigenvalue if at the final (Nth) stage $\kappa_N(\alpha,k_N,\kappa_{N-1}) = \alpha$. It is thus convenient to scale all inverse lengths by α. At the ith renormalization we have the recursion relation:

$$\tilde{\kappa}_{i+1} = \tilde{\kappa}_i + \frac{\epsilon^2\tilde{\kappa}_i}{4}\left(1 + \frac{2(1 - \tilde{\kappa}_i\tilde{\alpha}'_i)(1 - \tilde{\kappa}_i{}^2)}{\tilde{\kappa}_i\tilde{k}^2{}_i(\tilde{\alpha}'_i - \tilde{\kappa}_i)}\right) \qquad (21)$$

We have used a tilde to indicate scaled variables. Now $\tilde{\alpha}'_i = (1 + \tilde{k}_i{}^2)^{1/2}$ and $\tilde{k}_i = \tilde{k}_{\max}m^{N-i}$, where we now call the wavenumber of the first stage $\tilde{k}_{\max}$.

This generates a renormalization flow for κ, which is shown in Figure 4 for $\epsilon = 0.8$ and $m = 3$. Each stage changes κ by a small amount, but the total deviation from κ_0 may be large. Notice that the flow can be calculated if ϵ and m are not the same at each stage, provided that $\epsilon < 1$ and $m > 1$. Then the curve may no longer be fractal, but it is still rough.

The calculation presented here is only two dimensional. However, each stage of the buckling is treated independently. Hence the renormalization scheme is also applicable to a surface generated from a succession of crisscrossing undulations. At each stage we would consider a local perturbation of the form $x = a \cos{(\mathbf{k}\cdot\mathbf{r})}$, where the vectors $\mathbf{k}$ and $\mathbf{r}$ lie in the y-z plane. The orientations of $\mathbf{k}$ for each buckling can be arbitrary: they are not necessarily all parallel.

One Buckle. If we were considering just one stage of buckling, then we would specify $\kappa^{\text{app}} = \alpha$ in (19) and obtain

$$\alpha = \kappa_0(1 + \epsilon^2/4) \qquad (22)$$

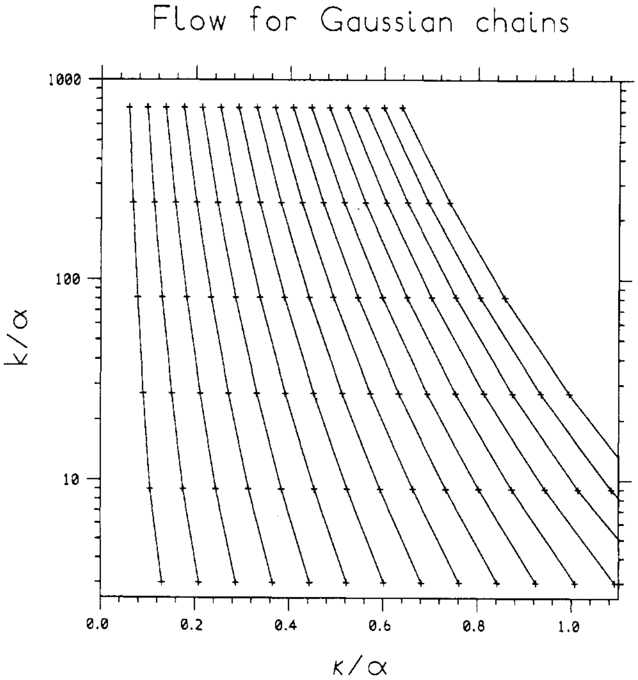

Figure 4. Flow diagram of the effective binding, κ/α, for Gaussian chains and for a surface with $m = 3$ and $\epsilon = 0.8$. This is the curve shown in Figure 1b. The flow lines start at the top of the diagram and show the effective value of κ as progressively larger sizes of buckling, with wavenumber k, are considered. The crosses indicate the values of κ in the discrete renormalization scheme, (21). Different flow lines correspond to different values of κ_0/α, the binding on the fully buckled surface. The solution giving a bound state is the flow line which reaches $\kappa = \alpha$ at the last stage.

The value of α increases in proportion to the change in surface area. Hone et al.[3] have also studied the interaction of long Gaussian chains at an attractive surface within mean-field theory and derived the same result. They also find α when αa and ϵ are large. However, instead of the de Gennes boundary condition (10), they consider the polymer interacting with an attractive δ function potential along the surface. This enables them to use Green function methods to calculate ψ. This means that the boundary is transparent—they have the same concentration profile within the surface as outside it. They are unable to distinguish between adsorption on the peaks and the troughs. The correct boundary condition needs to specify $\psi = 0$ just behind the interace, which leads to the addition of curvature terms in (10).[11] Moreover, we are concerned with roughness of many sizes, which they do not consider.

4. Discussion. The flow diagram (Figure 4) has been derived for a fractal model whose structure consists of a series of small-amplitude perturbations well separated in length. However, we hope that the results give some indication of the behavior of real boundaries with structure of many sizes. We expect our work to be applicable to surfaces with a fractal dimension close to 2.

If $k \gg \alpha$, then the first term in (21) dominates and, as for a single buckle, κ simply increases in proportion to the change in surface area of the boundary. For a fractal surface this leads to a scaling relation. If we have N stages of crinkling between $k_{\min}$ and $k_{\max}$ then $m^{N-1} = k_{\max}/k_{\min}$. The final value of κ, κ_N, in terms of the bare κ is given by, for large N

$$\kappa_N = \kappa_0(1 + \epsilon^2/4)^{N-1} \qquad (23a)$$

$$\kappa_N \approx \kappa_0(k_{\max}/k_{\min})^{\epsilon^2/4\log(m)} \qquad (23b)$$

$$\kappa_N \approx \kappa_0(k_{\max}/k_{\min})^{d_f-2} \qquad (23c)$$

This is a scaling relation giving the proportional change in κ in terms of the range of lengths over which the boundary is rough and the fractal dimension. When $\epsilon < k/\alpha < 1$ there are departures from simple scaling and

$$\kappa_{i+1} = \kappa_i\left(1 + \frac{\epsilon^2}{4}\right) + \frac{\epsilon^2\alpha(\alpha^2 - \kappa_i^2)}{2k_i^2} \qquad (24)$$

Binding is enhanced on a rough surface. The polymer is able to sample a greater area of boundary than on a corresponding smooth interface. Thus the balance of entropy and potential energy becomes more strongly tilted in favor of adsorption. When the width of the layer of polymer is much greater than the amplitude of the roughness, then the effective binding strength, κ, increases in proportion to the fractional increase in apparent surface area, giving the scaling relation of (23). When the layer is more confined we have calculated the corrections to scaling.

In the flow diagram, Figure 4, the flow which reaches $\kappa = \alpha$ at the final stage of buckling represents a bound state. Lines which do not reach this point are unbounded at infinity and do not represent solutions. However, the relation $\kappa_N = \alpha$ is only true for binding on a surface which is macroscopically flat (i.e., on the scale of the width of the polymer layer)—the precise relation will depend on the geometry of the system. Hence values of κ_N in the flow diagram which lie close to α may yield bound solutions, depending on the particular large-scale geometry.

Although our final value of α may be much larger than κ_0, we do not see bound states for κ_0 less than zero. It can be proved that the condition for bound states is still $\kappa_0 > 0$.[12] It is shown in ref 11 that consideration of adsorption in a continuum potential leads to corrections in the expression for κ in eq 10 due to the curvature of the boundary. Then some bound states are possible for negative κ_0.

5. Conclusions. We have calculated the behavior of an adsorbed polymer or electron on a fractal surface, where the confinement thickness is greater than the amplitude of the roughness and the surface fractal dimension is near to 2. This means that our work is applicable to polymers interacting with a surface which is rough over sizes between the Kuhn length, l, and the mean chain radius. For electrons, we are considering very low energy binding where the wavefunction is delocalized over several atomic diameters. We found a scaling relation, involving the fractal dimension, which related the effective binding on the fractal surface to that on an equivalent smooth surface.

In all cases interfacial roughness enhances adsorption. For the analogous problem of single electron surface states, studies by Rahman and Maradrudin on image potentials also showed that the effect of surface irregularities is to increase the attractive force on the electron.[13] Moreover, Garcia et al. calculated image potential surface states on silver (100) surfaces and showed that roughness can provide up to two-thirds of the binding energy, in good agreement with experiment.[14]

Because a Gaussian chain does not interact with itself, there is no limit to the density of polymer that can be supported at an adsorbing wall. Excluded-volume interactions need to be considered to determine the surface density of polymer allowed on a boundary which is saturated, i.e., no more polymer can adsorb. This problem is tackled in the next section.

We have included this calculation before discussing the case of excluded-volume adsorption for three reasons. First, the work is valid in its own right for Θ-point solutions and polymer melts. Second, the quantum mechanical analogy helps to emphasise that interfacial roughness can considerably enhance single electron surface state binding energies. Third, the calculation for excluded volume is more involved and this section serves as a useful introduction to the more sophisticated renormalization scheme to be presented. Although the physical interpretation of κ will be different, the recursion relation which we shall derive will give similar results to the Gaussian calculation, but we are able to calculate the corrections due to the excluded-volume interaction.

II. Adsorption with Excluded Volume

1. Adsorption on a Planar Surface. First we will briefly review equilibrium mean-field polymer adsorption on plane surfaces. The first mean-field treatment was given by Jones and Richmond[1] although the treatment here follows de Gennes.[9]

We start from (4) with the external potential set to zero.

$$\nabla^2\psi = (-\mu + \beta\psi^2)\psi \qquad (25)$$

where we have replaced α^2 with $-\mu$ which is proportional to the chemical potential. If the concentration (ψ^2) at infinity is c, then we have that $\mu = \beta c$. The calculation with Gaussian chains ignored the term $\beta\psi^2$ in (25) and was equivalent to solving the time-independent Schrödinger equation. When $\beta\psi^2$ is included, the problem still has a quantum mechanical analogy. Equation 25 is now the nonlinear Schrödinger equation for an interacting Bose gas in free space using the Hartree approximation:[15] $\beta\psi^2$ is the Hartree potential. Thus, although throughout this section we will talk only about the adsorption of polymer, we are also considering the binding of an interacting gas of bosons.

The boundary conditions on ψ are

$$\psi \rightarrow c^{1/2} \quad \text{as} \quad x \rightarrow \infty \qquad (26)$$

and the de Gennes condition at the interacting surface (6). The effect of excluded volume is to make κ a function of surface density; the mutual repulsion of the chains will tend to screen out the bare attraction of the surface.

The solution of (25) which satisfies eq 26 is

$$\psi = c^{1/2}h(x) \qquad \text{where} \quad h(x) = \coth\left(\frac{x + x_0}{(2/\beta c)^{1/2}}\right) \qquad (27)$$

When $\psi = 0$ at infinity, we find

$$\psi = \frac{(2/\beta)^{1/2}}{x + x_0} \qquad (28)$$

and $\mu = 0$. From the boundary condition at $x = 0$, we derive

$$\kappa = \left(\frac{\beta c}{2}\right)^{1/2}\frac{h(0)^2 - 1}{h(0)} \qquad (29)$$

When $\psi(\infty) = 0$, this condition is simply $x_0 = 1/\kappa$.

It is convenient to define $\beta\psi^2(0)$ as σ, the "surface density" (actually it is the surface density scaled by the excluded-volume parameter). Then for $\psi(\infty) = 0$, (29) can be rewritten as

$$\kappa = (\sigma/2)^{1/2} \qquad (30)$$

We are now going to study adsorption on a rough surface where the layer of excess polymer is thicker than the amplitude of the roughness. In such a case, at large distances, we expect ψ to have the same form as in (27) or (28). The solution will be equivalent to a flat boundary at $x = 0$ with an effective surface concentration, σ, and binding strength, κ_N, where the relationship between σ and κ_N is given by

(29). κ_N is a measure of the quantity of polymer adsorbed at the surface. Finding the relationship between κ and κ_N for a boundary with roughness of many sizes is, in general, an extremely difficult problem even numerically; using mean-field theory, we have to solve a nonlinear partial differential equation, (25).

2. The Renormalization Scheme. The renormalization scheme for a polymer with excluded-volume interactions has some subtleties not present in the Gaussian case, because κ is now a function of the surface density, which is itself a function of position on the surface.

We now wish to solve the problem on the fractal surface introduced in the previous section. We will first outline the approach and then, in more detail, show how to obtain a way of renormalizing the function, $\kappa(\sigma)$.

The excluded-volume interaction screens the attractive potential at the surface. Hence κ in (10) is reduced from the constant value, κ_0, it would have for Gaussian adsorption. We can derive[16] that

$$\kappa(\sigma) = \kappa_0 - \gamma\sigma \qquad (31)$$

γ is the effective width of the surface potential and is, for our model, smaller than a Kuhn length. This is the simplest linear relation between κ and σ. σ varies along the surface.

As before we shall find a solution for ψ near a single buckle in terms of local tangential and normal coordinates, as in Figure 2. At distances of about a wavelength from the surface, the effect of the perturbations will be small and so ψ will depend only on x. Hence the far-field behavior will resemble a solution, ψ^{app}, for adsorption on a plane surface at $x = 0$ with an effective boundary condition as in (13). However, κ will now be a function $\kappa^{\text{app}}(\sigma^{\text{app}})$ where σ^{app} is the apparent surface density at $x = 0$. It is constant over the size of the smallest crinkles, but it will vary on larger scales.

When we look at even larger distances, the effect of the next buckling becomes apparent. Again we renormalize the perturbation, replacing it with an effective binding and surface concentration. We rename $\kappa^{\text{app}}(\sigma^{\text{app}})$ as $\kappa_1(\sigma_1)$, where σ_1 varies over the second and larger bucklings and we replace $\kappa(\sigma)$ with $\kappa_1(\sigma_1)$, our effective binding, in the boundary condition, (10). We repeat this process to obtain a recursion relation for the $\kappa(\sigma)$ as we smooth out successive buckles. At the final stage of the scheme, we can impose the condition that $\psi \to c^{1/2}$ as $x \to \infty$ and hence the correct far-field behavior is given by (27) or (28). This is the essence of the scheme. We will now show how to renormalize the function $\kappa(\sigma)$.

Imagine that we are now looking at the ith stage of buckling. That is, we have already derived $\kappa_{i-1}(\sigma_{i-1})$ and we want to obtain $\kappa_i(\sigma_i) = \kappa^{\text{app}}(\sigma^{\text{app}})$. We write ψ_i as

$$\psi_i(x,y) = \eta(\psi_i^{\text{app}}(x) + \psi_i^{\text{p}}(x) + Bf_i(x)\cos(k_iy)) \qquad (32)$$

where, to calculate the change in κ to order $O(\epsilon^2)$, we can ignore higher order harmonics. We define $\psi_i^{\text{app}}(0) = 1$.

ψ_i^{app} is the apparent field due to the renormalized, plane boundary, with an apparent surface density, σ^{app}, equal to $\beta\eta^2$. By definition ψ_i^{app} obeys

$$\mathrm{d}^2\psi_i^{\text{app}}/\mathrm{d}x^2 = \sigma^{\text{app}}(\psi_i^{\text{app}})^3 - \mu\psi_i^{\text{app}} \qquad (33)$$

ψ_i^{p} is an x-dependent perturbative term.

Let ψ_i^{surface} denote $\psi_i(32)$ evaluated at the surface. Then the average surface density over the buckle $x = a_i \cos(k_iy)$ is given by

$$\bar{\sigma}_i = \int_0^{\lambda_i} \beta[\psi_i^{\text{surface}}(s)]^2\,\mathrm{d}s \Big/ \int_0^{\lambda_i} \mathrm{d}s \qquad (34)$$

s is the arc length along the curve representing the surface, $\mathrm{d}s = (\mathrm{d}x^2 + \mathrm{d}y^2)^{1/2}$. $\bar{\sigma}_i$ does not equal the surface density on the renormalized surface, σ^{app}. $\kappa_{i-1}(\sigma_{i-1}(x,y))$ is a function of position on the ith buckle and is defined by the boundary condition (10).

The renormalized boundary condition, $\kappa^{\text{app}}(\sigma^{\text{app}}) = \kappa_i(\sigma_i)$, is not a function of position on the ith buckle. Although at the first stage the function $\kappa(\sigma)$ is given simply by (31), in general, when we consider the other buckles, the relationship is more complicated. However, because we have a small-amplitude perturbation, the surface concentration, σ, is always close to $\bar{\sigma}$. Hence we can write

$$\kappa_i(\sigma_i) = \kappa_i(\bar{\sigma}_i) + (\sigma_i - \bar{\sigma}_i)|\partial\kappa_i/\partial\sigma_i|_{\bar{\sigma}_i} + \ldots \qquad (35)$$

and substitute this expression into (10).

We thus have a scheme by which we can express $\kappa^{\text{app}}(\sigma^{\text{app}})$ as a function of $\kappa_{i-1}(\sigma_{i-1})$, $\kappa'_i(\sigma_{i-1})$, σ_{i-1}, and k_i, where the prime denotes a derivative with respect to the argument. However, this is not quite as we want it, as in the renormalization scheme we would like to express $\kappa^{\text{app}}(\sigma^{\text{app}})$ as a function of $\kappa_{i-1}(\sigma^{\text{app}})$ so that σ^{app} becomes a dummy variable, σ, say. Then $\kappa(\sigma) = F(\kappa_i(\sigma), \cdots)$ so that F renormalizes κ for an arbitrary argument. So we substitute

$$\kappa_i(\sigma_i^{\text{app}}) = \kappa_i(\bar{\sigma}_i) - (\bar{\sigma}_i - \sigma_i^{\text{app}})|\partial\kappa_i/\partial\sigma_i|_{\bar{\sigma}_i} + \ldots \qquad (36)$$

and

$$\kappa'_i(\sigma_i^{\text{app}}) = \kappa'_i(\bar{\sigma}_i) + \ldots \qquad (37)$$

into (10). $(\bar{\sigma}_i - \sigma^{\text{app}})$ is second order in ϵ and κ' appears as a second-order term, so we need only keep the terms shown.

Finally we obtain $\kappa^{\text{app}}(\sigma^{\text{app}}) = F(\kappa_{i-1}(\sigma^{\text{app}}), \kappa_{i-1}'(\sigma^{\text{app}}), \sigma^{\text{app}}, k_i)$. σ^{app} is a constant over the ith buckle.

When the last buckle has been smoothed ($i = N$), σ^{app} is to be regarded as the apparent surface density on the renormalized plane surface. We therefore choose the argument so that at the last stage of the renormalization, κ_N is the same as in eq 29. Reexpressing $h^2(0)$ in terms of σ, we obtain

$$\kappa_N(\sigma) = \frac{\sigma - \mu}{(2\sigma)^{1/2}} \qquad (38)$$

The correct value of the argument, σ, will satisfy this relation. $\sigma - \mu$ is a measure of the difference between the apparent surface concentration on the renormalized boundary and the bulk concentration. If $\sigma - \mu$ is small, so too is κ_N and the surface is only weakly attractive. When $\mu = 0$, in contrast, we have bound states with all the polymer confined near the boundary.

3. Power Series Approach. The renormalization scheme is now the same as the Gaussian calculation except that we now use the power series approach. (From now on we will drop the i subscripts.) Since we are only interested in the near-field behavior, we may expand ψ^{app} and f as a power series in x.

$$\psi^{\text{app}} = 1 + Ax + Cx^2 + Dx^3 + \ldots \qquad (39a)$$

$$f = 1 - Ex + \ldots \qquad (39b)$$

substitution of ψ^{app} into eq 33 gives $2C = \sigma^{\text{app}} - \mu$, and $2D = A(\sigma^{\text{app}} - \mu/3)$: $\sigma^{\text{app}} = \beta\psi^2$. Equation 13 implies that $A = -\kappa^{\text{app}}$. For the power series to converge $1/a > (\sigma^{\text{app}}/2)^{1/2}$ and $1/a > \mu^{1/2}$. We are insisting that the height of the boundary, a, is smaller than the width of the adsorbed layer of polymer.

We substitute ψ (eq 32) into the defining differential equation (25) and equate harmonics of cos (ky). To see where the perturbative part, ψ^{p}, comes from consider ψ_{L}

$= \psi^{\mathrm{app}} + \psi^{\mathrm{p}}$. ψ_{L} is the wavefunction that is left when the y dependence, included in the term $Bf(x)\cos(ky)$, eq 32, is removed. ψ is substituted into (25) and the first and zeroth harmonics of $\cos(ky)$ are equated. We derive

$$\mathrm{d}^2\psi_{\mathrm{L}}/\mathrm{d}x^2 = \sigma^{\mathrm{app}}(\psi_{\mathrm{L}}^3 + \tfrac{3}{2}\psi_{\mathrm{L}}B^2f^2) - \mu\psi_{\mathrm{L}} \tag{40}$$

and

$$\mathrm{d}^2f/\mathrm{d}x^2 = (k^2 - \mu + 3\sigma^{\mathrm{app}}\psi_{\mathrm{L}}^2)f \tag{41}$$

Notice from eq 40 that ψ_{L} does not obey an equation of the form eq 33, thus it is not the apparent field extrapolated from infinity to the renormalized plane surface. It is as a consequence of solving a nonlinear differential equation that ψ^{p} is nonzero: we did not have to consider such a term in the Gaussian calculation. Defining ψ^{app} by eq 33 we are able to use (40) to derive an expression for ψ^{p}:

$$\mathrm{d}^2\psi^{\mathrm{p}}/\mathrm{d}x^2 = 3\sigma^{\mathrm{app}}\left((\psi^{\mathrm{app}})^2\psi^{\mathrm{p}} + \frac{B^2}{2}\psi^{\mathrm{app}}f^2\right) - \mu\psi^{\mathrm{p}} \tag{42}$$

Far from the surface the effect of the buckling is not explicitly observed, so ψ tends to $\eta\psi^{\mathrm{app}}$ as x tends to infinity, which implies that f tends to zero. This means that far from the surface ψ_{L} obeys an equation similar to (33) and ψ_{L} tends to ψ^{app} smoothly as f^2 tends to zero. Hence ψ^{p} is "driven" by f^2 in eq 42 and the complementary part is zero for all x. It is solved approximately in Appendix I and is valid provided that $(3\sigma^{\mathrm{app}} - \mu + k^2)^{1/2} > \kappa^{\mathrm{app}}$.

$$\psi^{\mathrm{p}} = \frac{3\sigma^{\mathrm{app}}B^2\exp(-2Ex)}{2(4E^2 - 3\sigma^{\mathrm{app}} + \mu)} \times \left(\frac{4EA + 4E^2 - 3\sigma^{\mathrm{app}} + \mu}{4E^2 - 3\sigma^{\mathrm{app}} + \mu} + Ax + ...\right) \tag{43}$$

Equation 41 can be approximately solved for f. First, we anticipate from the Gaussian calculation that f will appear as a second-order correction to κ. Therefore, as ψ^{p} is proportional to B^2 and B is of order ϵ, we deduce that ψ_{L} in (41) can be replaced by ψ^{app}. The boundary conditions on f are that $f(0) = 1$ and $f(\infty) = 0$. Let $\delta^2 = 3\sigma^{\mathrm{app}}(\psi^{\mathrm{app}})^2 - \mu + k^2$, which by assumption varies more slowly than f. Hence we suppose a WKBJ method to be valid:

$$f(x) = \frac{(3\sigma^{\mathrm{app}} - \mu + k^2)^{1/4}}{(\delta(x))^{1/2}}\exp\left(-\int_0^x \delta(x)\,\mathrm{d}x\right) \tag{44}$$

This is strictly true only if $k/(3\sigma^{\mathrm{app}} - \mu)^{1/2} > 1$. By using this expression and substituting ψ^{app} and f for small x, we are able to determine an expression for E, eq 39b:

$$E = (3\sigma^{\mathrm{app}} - \mu + k^2)^{1/2} + \frac{3A\sigma^{\mathrm{app}}}{2(3\sigma^{\mathrm{app}} - \mu + k^2)} + ... \tag{45}$$

A more rigorous approximation is shown in Appendix II. $\bar{\sigma}$ is found by using eq 34; it differs from σ^{app} by an order ϵ^2.

$$\bar{\sigma} = \sigma^{\mathrm{app}}\left(1 + 2\psi^{\mathrm{p}}(0) + \frac{\epsilon}{k}B(A - E) + \frac{\epsilon^2}{2k^2}(A^2 + \sigma^{\mathrm{app}}) + \frac{B^2}{2}\right) \tag{46}$$

We are left with two unknowns, κ^{app} and B which are determined by the boundary condition on the surface $x = a\cos(ky)$ (see eq 18).

$\kappa(\sigma(x,y))$ is replaced by $\kappa(\sigma^{\mathrm{app}})$ and κ' from eq 36 and 37. Equating zeroth and first harmonics of $\cos(ky)$ and expanding to order ϵ^2, we find

$$\kappa^{\mathrm{app}} = \kappa + \frac{\kappa\epsilon^2}{4}\left[1 - \frac{2\sigma^{\mathrm{app}}}{k^2} + \frac{2B_0}{\kappa k^2}(3\sigma^{\mathrm{app}} - \mu - E\kappa) + \frac{4\psi^{\mathrm{p}}(0)}{\epsilon^2} + \frac{4\psi^{\mathrm{p}\prime}(0)}{\kappa\epsilon^2} + \frac{2\sigma^{\mathrm{app}}\kappa'}{\kappa k^2}(3(B_0 - \kappa)^2 - 2B_0E + \sigma^{\mathrm{app}} - \mu) + \frac{2\sigma^{\mathrm{app}}\psi^{\mathrm{p}}(0)\kappa'}{\kappa\epsilon^2}\right] \tag{47}$$

where

$$\psi^{\mathrm{p}}(0) = \frac{3\sigma^{\mathrm{app}}B_0^{\,2}\epsilon^2(4E^2 - 4E\kappa - 3\sigma^{\mathrm{app}} + \mu)}{2k^2(4E^2 - 3\sigma^{\mathrm{app}} + \mu)^2} \tag{48}$$

$$\psi^{\mathrm{p}\prime}(0) = -\frac{3\sigma^{\mathrm{app}}B_0^{\,2}\epsilon^2}{2(4E^2 - 3\sigma^{\mathrm{app}} + \mu)k^2} \times \left[\frac{2E(4E^2 - 4E\kappa - 3\sigma^{\mathrm{app}} + \mu)}{4E^2 - 3\sigma^{\mathrm{app}} + \mu} + \kappa\right] \tag{49}$$

and

$$B_0 = \frac{B}{a} = \frac{\kappa^2 - \sigma^{\mathrm{app}} + 2\sigma^{\mathrm{app}}\kappa\kappa' + \mu}{\kappa - E + 2\sigma^{\mathrm{app}}\kappa'} \tag{50}$$

Beginning the Renormalization. The renormalization begins by taking a surface, composed of a succession of buckles, and smoothing out the smallest buckle first. Consider the bare fractal surface, where the value of κ is given by eq 31. Hence, at the first stage, $\kappa'_1 = -\gamma$ and $\kappa^{\mathrm{app}} = \kappa_1 + O(\epsilon^2)$ so $\kappa'^{\mathrm{app}} = \kappa'_1 + O(\epsilon^2)$. But since κ' appears as $O(\epsilon^2)$ in eq 47, we deduce that $\kappa'_1 = -\gamma$ for all i.

4. A Recursion Relation. Remember that the surface density on a planar surface, if $\psi = 0$ at infinity, is determined by the relation in eq 30. Also, at any stage of the iteration the argument of κ is arbitrary. We can therefore set it to σ, so that if κ_N is the last iterate, we have a bound state, with $\psi = 0$ in the bulk, if $\kappa_N/\kappa_{\mathrm{plane}} = 1$, where κ_{plane} is defined, from eq 30, to be $(\sigma/2)^{1/2}$. It is thus convenient to scale all inverse lengths by κ_{plane}. This leaves us with a set of dimensionelss scaled variables: $\tilde{k}$ $(=k/\kappa_{\mathrm{plane}})$, $\tilde{\gamma}$ $(=\gamma\kappa_{\mathrm{plane}})$, $\tilde{\kappa}$ $(=\kappa/\kappa_{\mathrm{plane}})$, and $\tilde{\mu}$ $(=\mu/(\kappa_{\mathrm{plane}})^2)$. As we are dealing with adsorption where the amplitude of the roughness is smaller than the adsorbed layer of polymer, or any other length in the system, the equations below are only accurate when $\tilde{k} > \epsilon$, $\tilde{k} > \tilde{\gamma}$, $\tilde{k} > \tilde{\kappa}$, and $\tilde{k} > \tilde{\mu}$. If we consider equilibrium with a bulk concentration, solutions are obtained when, from eq 38, $\tilde{\kappa}_N = 1 - \tilde{\mu}/2$. We can find solutions where $\tilde{\kappa}_N$ is small if $\tilde{\mu}/2$ is close to 1.

At the ith stage of the renormalization the following recursion relation holds:

$$\tilde{\kappa}_{i+1} = \tilde{\kappa}_i + \frac{\tilde{\kappa}_i\epsilon^2}{4}\left[1 - \frac{4}{\tilde{k}_i^{\,2}} + \frac{2B_0}{\tilde{\kappa}_i\tilde{k}_i^{\,2}}(6 - E\tilde{\kappa}_i - \tilde{\mu}) + \frac{4\psi^{\mathrm{p}}(0)}{\epsilon^2} + \frac{4\psi^{\mathrm{p}\prime}(0)}{\tilde{\kappa}_i\epsilon^2} - \frac{4\tilde{\gamma}}{\tilde{\kappa}_i\tilde{k}_i^{\,2}}(3(B_0 - \tilde{\kappa}_i)^2 - 2B_0E + 2 - \tilde{\mu}) - \frac{4\psi^{\mathrm{p}}(0)\tilde{\gamma}}{\tilde{\kappa}_i\epsilon^2}\right] \tag{51}$$

where

$$\psi^{\mathrm{p}}(0) = \frac{3B_0^{\,2}\epsilon^2(2E^2 - 2E\tilde{\kappa}_i - 6 + \tilde{\mu})}{2\tilde{k}_i^{\,2}(2E^2 - 6 + \tilde{\mu})^2} \tag{52}$$

$$\psi^{\mathrm{p}\prime}(0) = -\frac{3B_0^{\,2}\epsilon^2}{(4E^2 - 6 + \tilde{\mu})\tilde{k}_i^{\,2}}\left[\frac{2E(2E^2 - 2E\tilde{\kappa}_i - 6 + \tilde{\mu})}{2E^2 - 6 + \tilde{\mu}} + \tilde{\kappa}_i\right] \tag{53}$$

$$B_0 = \frac{\tilde{\kappa}_i^2 - 2 - 4\tilde{\kappa}_i\tilde{\gamma} + \tilde{\mu}}{\tilde{\kappa}_i - E - 4\tilde{\gamma}} \quad (54)$$

and

$$E = +(6 - \tilde{\mu} + \tilde{k}_i^2)^{1/2} - \frac{3\tilde{\kappa}_i}{6 - \tilde{\mu} + \tilde{k}_i^2} \quad (55)$$

These equations are equivalent to eq 47–50 where $\kappa^{\rm app} = \kappa_{i+1}$, $\kappa = \kappa_i$, $\kappa' = -\gamma$, and $\sigma^{\rm app}$ is replaced by σ ($=2\kappa_{\rm plane}^2$).

These are the complete equations which describe the equilibrium statistical properties of polymers adsorbed on fractal surfaces.

The Weak Coupling Regime. The introduction of the excluded-volume interaction on the surface, via eq 31, introduces a new dimensionless parameter, $\tilde{\gamma} = \kappa_{\rm plane}\gamma$. In principle one has a four-dimensional flow diagram—the axes being $\tilde{k}$, $\tilde{\kappa}$, $\tilde{\mu}$, and $\tilde{\gamma}$.

In the weak coupling regime, however, in which we suppose that equilibrium adsorption occurs, $\tilde{\gamma} \ll 1$. In this regime the surface density always remains small. Hence $\tilde{\gamma}$ is smaller than any other parameter of interest and it can be neglected in eq 51. This means that the variation of κ along the surface due to the variation of the surface density is a small effect.

In the strong coupling regime γ would have to be retained. Under these circumstances, however, it is likely that we have nonequilbrium adsorption,[16,17] which is not dealt with in this paper.

5. Discussion. As in section I, we can trivially extend the analysis to a surface generated from a succession of crisscrossing undulations.

A flow diagram showing how the renormalized κ varies as successively more buckles are smoothed is shown in Figure 5. In general, the flow equations would have to be solved iteratively. A guess would be made for the starting values of the parameters and the renormalization scheme carried out for a surface of known geometry. Solutions are obtained, if, at the last stage, $\tilde{\kappa}_N = 1 - \tilde{\mu}/2$. This appears to be a somewhat involved procedure, although easily tackled numerically. However, rather than list a large number of solutions, we shall show that a few simple analytic results can be derived.

When the wavenumber of the perturbations, $\tilde{k}$, is very much larger than $\tilde{\kappa}$, $\tilde{\mu}$, or $\tilde{\gamma}$, the first term in eq 51 dominates and the recrusion relation is similar to that for Gaussian chains in the limit $k \gg \alpha$: κ simply increases in proportion to the change in surface area of the boundary and we obtain the same scaling relation as in eq 23. Therefore, for weak binding the total amount of adsorbate at saturation increases as the square of the increase in surface area on roughening ($\sigma = 2\kappa^2$), when measured on scales less than the mean chain radius. This result should be taken into account in the scaling relations proposed by Avnir et al.[5] and Brochard,[18] who made a theoretical study of the behavior of single polymer molecules near fractal surfaces.

When the layer of excess polymer is more confined, the largest corrections to scaling give

$$\tilde{\kappa}_{i+1} = \tilde{\kappa}_i\left(1 + \frac{\epsilon^2}{4} - \frac{\epsilon^2}{\tilde{k}_i^2}\right) + \frac{\epsilon^2(2 - \tilde{\mu})(6 - \tilde{\mu})}{2\tilde{k}_i^2 E} \quad (56)$$

The third term in the first bracket is negative and is the contribution of the excluded volume, which on its own tends to decrease κ as the surface concentration rises.

6. Conclusions. In this paper we have formulated a renormalization scheme for the adsorption of a polymer chain on a fractal surface. We have shown that there exists a simple scaling relation between the adsorbate concentration on a fractal surface and a plane surface given by eq 23.

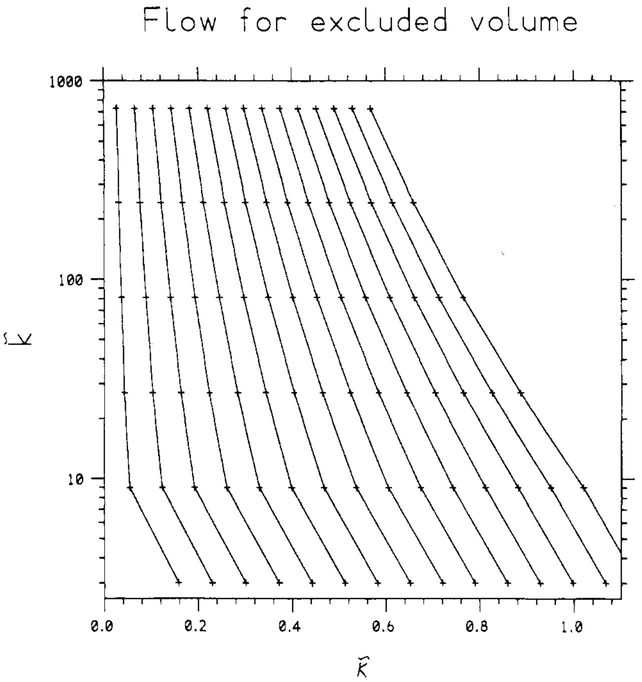

Figure 5. Flow diagram of the effective binding, $\tilde{\kappa}$, for polymer with excluded-volume interactions and for the curve shown in Figure 1b. The flow lines start at the top of the diagram and show the effective value of $\tilde{\kappa}$ as progressively larger sizes of buckling, with wavenumber $\tilde{k}$, are considered. The crosses indicate the values of κ in the discrete renormalization scheme, eq 51. Different flow lines correspond to different values of the binding on the fully buckled surface. $\gamma = 0$ and $\mu = 0$. The solution giving a bound state is the flow line which reaches $\tilde{\kappa} = 1$ at the last stage. Notice that for very large $\tilde{k}$, the diagram is similar to that for Gaussian chains shown in Figure 4.

The qualitative predictions are similar to that of the Gaussian calculation, namely, that the effective κ always increases. The surface enhances its attraction for polymer when rough. The dominant effect comes from the increase in surface area which allows the polymer to explore more configurations on the boundary and hence favors stronger binding. We have also calculated how excluded volume, which causes a mutual repulsion between chains, screens this effect. For weakly bound systems, where the adsorbed layer is wider than the amplitude of the surface roughness, this is a relatively small correction.

Adsorption where the chains interact with a continuum potential, leading to curvature terms in the de Gennes boundary condition, can also be calculated.[11]

A more accurate theoretical resolution of adsorption on a rough surface, where the roughness and the width of the polymer layer are of about the same size, can probably only be tackled numerically. New effects such as the entropic trapping of polymer in crevices may be seen. However, the scaling relation that was derived could be tested on surfaces whose dimension can be measured independently.

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Appendix I. A Calculation of the Perturbation Term $\psi^{\rm p}$

We wish to solve

$$\nabla_x^2\psi^{\rm p} - 3\sigma^{\rm app}(\psi^{\rm app})^2\psi^{\rm p} + \mu\psi^{\rm p} = 3/2\sigma^{\rm app}B^2\psi^{\rm app}f^2 \quad ({\rm AI.1})$$

where we know that the complementary part must be zero for all x and by definition $f(0) = 1$ and $f(\infty) = 0$. Equation AI.1 can be written

$$(D + (3\sigma^{\mathrm{app}}(\psi^{\mathrm{app}})^2 - \mu)^{1/2}) \times (D - (3\sigma^{\mathrm{app}}(\psi^{\mathrm{app}})^2 - \mu)^{1/2})\psi^{\mathrm{p}} = g(x) \quad \text{(AI.2)}$$

where $D = \mathrm{d}/\mathrm{d}x$ and $g(x) = 3/2\sigma^{\mathrm{app}}B^2\psi^{\mathrm{app}}f^2$. Then we can write

$$(D + (3\sigma^{\mathrm{app}}(\psi^{\mathrm{app}})^2 - \mu)^{1/2})t(x) = g(x) \quad \text{(AI.3)}$$

where now ψ^{p} is the solution to

$$(D - (3\sigma^{\mathrm{app}}(\psi^{\mathrm{app}})^2 - \mu)^{1/2})\psi^{\mathrm{p}} = t(x) \quad \text{(AI.4)}$$

We make the assumption that f varies much more rapidly than ψ^{app} so that we expand ψ^{app} in a power series in x and approximate $f(x)$ as $\exp(-Ex)$.

First, let us evaluate (AI.3). Multiply both sides by the integrating factor and integrate over x

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[t(x)\exp\left(\int_0^x (3\sigma^{\mathrm{app}}(\psi^{\mathrm{app}})^2 - \mu)^{1/2}\,\mathrm{d}x'\right)\right] = 3/2\sigma^{\mathrm{app}}B^2\psi^{\mathrm{app}}\exp\left(-2Ex + \int_0^x (3\sigma^{\mathrm{app}}(\psi^{\mathrm{app}})^2 - \mu)^{1/2}\,\mathrm{d}x'\right) \quad \text{(AI.5)}$$

We evaluate the integrals and then expand ψ^{app} on the right-hand side to $O(x)$

$$t(x)\exp((3\sigma^{\mathrm{app}} - \mu)^{1/2}x) = 3/2\sigma^{\mathrm{app}}B^2\int(1 + Ax + \ldots)\exp(-2Ex + (3\sigma^{\mathrm{app}} - \mu)^{1/2}\,\mathrm{d}x) \quad \text{(AI.6)}$$

and also integrating the right-hand side

$$t(x) = 3/2\sigma^{\mathrm{app}}B^2\frac{\exp(-2Ex)}{(3\sigma^{\mathrm{app}} - \mu)^{1/2} - 2E}\left[1 + Ax - \frac{A}{(3\sigma^{\mathrm{app}} - \mu)^{1/2} - 2E}\right] + C \quad \text{(AI.7)}$$

where C is zero because the complementary part must be zero.

Similarly, the same procedure for (AI.4) gives

$$\psi^{\mathrm{p}} = \frac{3\sigma^{\mathrm{app}}B^2\exp(-2Ex)}{2(4E^2 - 3\sigma^{\mathrm{app}} + \mu)}\left(\frac{4EA + 4E^2 - 3\sigma^{\mathrm{app}} + \mu}{4E^2 - 3\sigma^{\mathrm{app}} + \mu} + Ax + \ldots\right) \quad \text{(AI.8)}$$

The assumption that f varies much more rapidly than ψ^{app} means that we are assuming that $|E| > |A|$ or approximately $(3\sigma^{\mathrm{app}} - \mu + k^2)^{12} > \kappa$. We will see later that it is convenient to scale k and κ by $(\sigma^{\mathrm{app}}/2)^{1/2}$ (denoted by a tilde), thus our condition is $(6 - \tilde{\mu} + \tilde{k}^2)^{1/2} > \tilde{\kappa}$. $\tilde{\kappa}$ does not exceed one for bound solutions.

Appendix II. A Better Approximation for *f*

A WKBJ approximation has been used to derive an expression for $f(x)$. In this Appendix we will look more closely at the validity of this expression.

The defining differential equation for f is

$$\mathrm{d}^2f/\mathrm{d}x^2 = (k^2 - \mu + 3\sigma^{\mathrm{app}}(\psi^{\mathrm{app}})^2)f = \delta(x)^2 f \quad \text{(AII.1)}$$

$\sigma^{\mathrm{app}} = \beta(\psi^{\mathrm{app}})^2$ is the surface density and ψ^{app} has replaced ψ_{L} for the reasons explained in the text. We multiply (AII.1) by $\mathrm{d}f/\mathrm{d}x$ and integrate over x

$$\frac{1}{2}\left(\frac{\mathrm{d}f}{\mathrm{d}x}\right)^2 = \int_0^x \delta^2(x')f\frac{\mathrm{d}f}{\mathrm{d}x'}\,\mathrm{d}x' + C \quad \text{(AII.2)}$$

at $x = \infty$ $\mathrm{d}f/\mathrm{d}x = 0$, therefore

$$C = -\int_0^\infty \delta^2(x')f\frac{\mathrm{d}f}{\mathrm{d}x'}\,\mathrm{d}x' \quad \text{(AII.3)}$$

and at $x = 0$ $\mathrm{d}f/\mathrm{d}x = -E$, therefore $E^2/2 = C$.

If $\delta(x)^2$ is a constant, that is, there is none of the x dependence which arises from the excluded volume, then

$$f(x) = \exp(-\delta(0)x) \quad \text{(AII.4)}$$

where $\delta(0)^2 = 3\sigma^{\mathrm{app}} - \mu + k^2$ and thus $E = \delta(0)$.

Now, suppose we iterate on f, using (AII.4) as a starting approximation, to get a better approximation. We expand $\delta(x)^2$ as a power series in x. Then, from (AII.3)

$$E^2/2 = \delta(0)\int_0^\infty (k^2 - \mu + 3\sigma^{\mathrm{app}}(1 + Ax + Cx^2 + Dx^3 + \ldots)^2)\exp(-2\delta(0)x)\,\mathrm{d}x \quad \text{(AII.5)}$$

Provided that ψ^{app} decays more slowly than f we may expand the quadratic bracket and keep low orders of x. Then, performing the integral, we find

$$E^2 = \delta(0)^2 + 3\sigma^{\mathrm{app}}\left(\frac{A}{\delta(0)} + \frac{2C + A^2}{2\delta(0)^2} + \frac{3(D + AC)}{2\delta(0)^3} + \ldots\right) \quad \text{(AII.6)}$$

where $A = -\kappa$, $2C = \sigma^{\mathrm{app}} - \mu$, and $6D = -3\kappa\sigma^{\mathrm{app}} - \mu$. Dividing throughout by $\sigma^{\mathrm{app}}/2$ and denoting scaled variables by a tilde, we obtain

$$E^2 = \delta(0)^2 + 6\left(-\frac{\tilde{\kappa}}{\delta(0)} + \frac{2 - \tilde{\mu} + \tilde{\kappa}^2}{2\delta(0)^2} - \frac{6\tilde{\kappa} - \tilde{\mu} + 3\tilde{\mu}\tilde{\kappa}}{2\delta(0)^3} + \ldots\right) \quad \text{(AII.7)}$$

with $\delta(0)^2 = (6 - \tilde{\mu} + \tilde{k}^2)$. $\tilde{\kappa}$ never exceeds one for bound solutions, therefore we see that this series converges easily for $\tilde{\kappa} > 1$ and only the first few terms are required, but for $\tilde{k} < 1$ the convergence is rather poor and many more terms in the series would be required to guarantee a good approximation for E.

The WKBJ approximation gives

$$E = \delta(0) - \frac{3\tilde{\kappa}}{\delta(0)^2} \quad \text{(AII.8)}$$

which agrees with eq AII.7 in the limit that $\tilde{k} \gg 1$.

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