

## Block Copolymer Adsorption in a Nonselective Solvent

C. M. Marques\* and J. F. Joanny

*E.N.S.L., 46 Allée d'Italie, 69364 Lyon, Cedex 07, France. Received April 29, 1988; Revised Manuscript Received July 29, 1988*

**ABSTRACT:** We study the adsorption of an A-B diblock copolymer from a dilute solution onto a solid surface that attracts the A block and repels the B block in a nonselective solvent, good for both blocks. The structure of the adsorbed layer is governed by the asymmetry of the copolymer. When the asymmetry is small, the adsorbing block forms a fluffy layer swollen by the solvent and the nonadsorbing block forms a polymer brush pointing toward the bulk solution. When the nonadsorbing block is much larger than the adsorbing one, the fluffy A layer breaks into individual chains, which form flat pancakes on the wall; this quasi-two-dimensional solution may be either dilute or semidilute. The B chains still form a grafted layer.

## I. Introduction

Colloid stabilization with polymers<sup>1,2</sup> requires the formation of a thick polymer layer around each particle in order to create a repulsive steric force that overcomes the van der Waals attraction. This is usually done by adsorbing on the colloidal particle a polymer solution in a good solvent, which builds up on the surface a fluffy layer with a thickness of the order of the radius of gyration of isolated polymer chains (in general of the order of a few hundred angstroms). It was realized, however,<sup>3-6</sup> that a more efficient way to stabilize colloidal suspensions is to graft polymers by one end in the so called *brush configuration*.<sup>7</sup> One forms then a much thicker layer where all chains are stretched perpendicular to the surface, thus increasing the range of the repulsive steric force. End-grafted polymer layers are obtained in two ways, either by chemical grafting or by diblock copolymer adsorption. In this case one block A, which from now we call the anchor, adsorbs strongly onto the surface; the other block, the buoy B, repelled by the surface, forms the brush around the colloidal particles.

In this spirit, in a recent work<sup>8</sup> we have studied block copolymer adsorption in a highly selective solvent where the anchor is in a poor solvent and the buoy is in a good solvent. On a solid surface, the anchor block forms a molten layer where neither the B block nor the solvent penetrates. At thermodynamic equilibrium, the chain density  $\sigma$  (or equivalently the area per chain  $\Sigma \sim 1/\sigma$ ) and the thickness of the polymer layer are governed by the chemical potential of the solution in equilibrium with the adsorbed layer. In a highly selective solvent, block copolymers have a tendency to self-aggregate and form mesophases in the bulk, even in a dilute solution;<sup>9-11</sup> this self-association plays thus a major role in the study of the adsorbed layer.

We study here the reverse limit of a nonselective solvent where both blocks are still incompatible but where the solvent is equally good for both blocks.<sup>12,13</sup> The solvent penetrates then into the adsorbed anchor layer, which is a fluffy layer very similar to what is obtained in homopolymer adsorption. In particular, this anchor layer is quite dilute, and the direct van der Waals interaction between the polymer and the wall, which plays an important role in a highly selective solvent, is of no importance in a nonselective solvent.<sup>14</sup> Another important difference is the role of the mesophases in the bulk copolymer solution: in a nonselective solvent we expect mesophase formation only in semidilute solutions. We will restrict this work to dilute solutions and assume thus that these solutions are isotropic and homogeneous.

The paper is organized as follows. In the next section we present a mean-field theory of the adsorption, discussing the geometrical characteristics of the adsorbed

layer: the anchor thickness  $d$ , the buoy thickness  $L$ , and the chain surface density  $\sigma$ . We then extend in section III these results to take into account correctly the role of concentration correlations in a good solvent. We follow there closely the theory introduced by de Gennes for homopolymer adsorption.<sup>14</sup> When the block copolymers are very asymmetric, the anchor layer is not continuous: it breaks into small islands on the surface. This regime and the crossover toward a continuous layer are analyzed in section IV. Section V presents a discussion of our results.

## II. Mean-Field Theory

We study the adsorption of diblock copolymers on a flat, idealized solid surface. Both blocks are in a good solvent; we call  $\nu_A$  and  $\nu_B$  the corresponding Edwards dimensionless excluded volume parameters ( $\nu_A \geq 0$ ,  $\nu_B \geq 0$ ). The anchor block A is strongly attracted by the surface, and the buoy block B is strongly repelled by the surface. Polymers A and B will be supposed incompatible; i.e., the Flory interaction parameter  $\chi_{AB}$  is positive and large. In a mean-field theory, the natural radius of gyration of the two blocks is  $R_A = N_A^{1/2}a$  and  $R_B = N_B^{1/2}a$ ,  $N_A$  and  $N_B$  being the degrees of the polymerization of the blocks and  $a$  a monomer size, which we choose equal for both blocks. We measure the asymmetry of the copolymer by the radius ratio

$$\beta = \frac{R_B}{R_A} = \left( \frac{N_B}{N_A} \right)^{1/2} \quad (1)$$

In the following we always assume that  $\beta \gg 1$ .

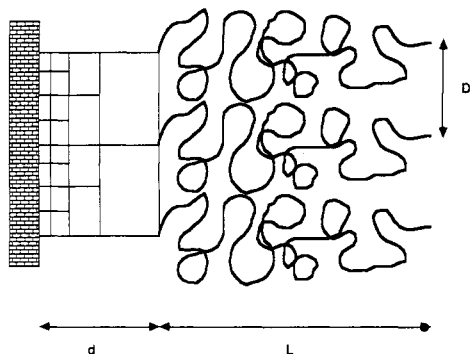
The external solution in equilibrium with the adsorbed layer, where the total monomer concentration is  $\phi_b$ , is dilute and imposes a chain chemical potential  $\mu_{ex}$  and an osmotic pressure  $\Pi_{ex}$ . Throughout this paper, we choose temperature units such that the Boltzmann constant  $k_B$  is equal to unity.

$$\begin{aligned} \mu_{ex} &= T \ln \phi_b \\ \frac{\Pi_{ex}}{T} &= \frac{\phi_b}{N_A + N_B} \end{aligned} \quad (2)$$

The structure of the adsorbed copolymer layer is shown in Figure 1. The A block forms a layer swollen by the solvent, and the B block forms a polymer brush. The characteristics of the layer are obtained by minimization of the grand canonical free energy

$$\Omega = F_A + F_B - \mu_{ex}\sigma\alpha^{-2} + \Pi_{ex}(L + d) \quad (3)$$

$F_A$  and  $F_B$  are the free energies of the A and B layers, respectively;  $\sigma$  is the chain surface density  $\sigma = (a/D)^2$ ,  $D$  being the mean distance between A-B junction points



**Figure 1.** Structure of the adsorbed diblock copolymer layer. The A block is attracted by the wall and builds up a self-similar layer. The B blocks point toward the solvent in a brush configuration.

parallel to the surface;  $L$  is the thickness of the B layer; and  $d$  is the thickness of the A layer.

The free energy of the anchor layer  $F_B$  is that of a so-called grafted polymer brush with a given chain density  $\sigma$ . In a mean-field theory this problem has been studied by Alexander<sup>7</sup> and de Gennes<sup>15</sup> and more recently by Milner et al.<sup>16</sup> Although the simpler theory of Alexander does not give the correct concentration profile inside the brush, it is sufficient for our purpose, giving the correct scaling behavior. When the surface density  $\sigma$  is high enough ( $\sigma N_B \gg 1$ ), the free energy  $F_B$  is written as

$$\frac{F_B \alpha^2}{T} = \frac{3}{2} \sigma \frac{L^2}{N_B \alpha^2} + \frac{1}{2} \nu_B N_B^2 \sigma^2 \quad (4)$$

The first term is the chain elasticity, the second term is the excluded volume free energy.

The anchor layer is a semidilute layer where the local volume fraction  $\phi$  of A monomers decays with the distance  $z$  from the wall. The free energy functional of such layers is conveniently written in terms of the order parameter  $\psi = \phi^{1/2}$ ,<sup>15</sup>

$$\frac{F_A \alpha^2}{T} = -\gamma \phi_s + \int_0^\infty \left[ \frac{\alpha^2}{6} \left( \frac{d\psi}{dz} \right)^2 + \frac{\nu_A}{2} \psi^4 \right] dz \quad (5)$$

The first term, where  $\phi_s$  is the surface concentration, is the energy gain due to the contact of the polymer with the wall. In a strong adsorption limit, the monomer adsorption free energy  $\gamma$  is of order unity. The gradient term takes into account the polymer elasticity, and the last term is the excluded volume between A monomers. Because A and B chains are connected in a block copolymer, the number of chains per unit surface is the same in the two layers

$$\sigma = \frac{1}{N_A} \int_0^\infty \phi(z) \frac{dz}{a} \quad (6)$$

In order to take this constraint into account, we introduce a Lagrange multiplier  $\lambda$  and minimize

$$\Omega' = \Omega - \lambda T \alpha^{-2} \left[ \sigma - \frac{1}{N_A} \int_0^\infty \phi(z) \frac{dz}{a} \right] \quad (7)$$

with respect to the three independent variables  $\sigma$ ,  $L$ , and  $\psi$ . Minimizing  $\Omega'$  with respect to  $L$ , we obtain the usual brush size  $L$  and free energy  $F_B$  (the external pressure  $\Pi_{\text{ex}}$  always has a small contribution)

$$\begin{aligned} L &= k_0 N_B \sigma^{1/3} \nu_B^{1/3} \alpha \\ F_B \alpha^2 / T &= k_1 N_B \sigma^{5/3} \nu_B^{2/3} \end{aligned} \quad (8)$$

where  $k_0$  and  $k_1$  are numerical constants of order unity.

Minimization with respect to  $\sigma$  gives a relation between  $\lambda$  and  $\sigma$

$$\frac{5}{3} k_1 N_B \sigma^{2/3} \nu_B^{2/3} - \left( \frac{\mu_{\text{ex}}}{T} + \lambda \right) = 0 \quad (9)$$

The minimization with respect to  $\psi$  is made by using an Euler-Lagrange equation

$$\frac{a^2}{6} \frac{d^2 \psi}{dz^2} = \nu_A \psi^3 + \frac{\lambda}{N_A} \psi \quad (10)$$

As  $z$  becomes large, in the brush, the concentration of monomers A becomes small, the homopolymers being highly incompatible;<sup>13</sup> we approximate it by zero:  $\lim_{z \rightarrow \infty} \psi = 0$ . The boundary condition on the solid surface is obtained by minimizing the free energy with respect to the surface order parameter  $\phi_s$

$$\frac{1}{\psi_s} \frac{d\psi}{dz} \Big|_{z=0} = -\frac{1}{2b} = -\frac{6\gamma}{a} \quad (11)$$

The size of the proximal region  $b$  is, in the case of strong adsorption ( $\gamma \sim 1$ ) which we consider here, of the order of the monomer length  $a$ .

The solution of eq 10 with these boundary conditions is

$$\psi(z) = \frac{a}{d(3\nu_A)^{1/2}} \frac{1}{\sinh(z + z_0/d)} \quad (12)$$

where the size of the anchor layer  $d$  is given by

$$d = a(N_A/6\lambda)^{1/2} \quad (13)$$

The length  $z_0$  is given by eq 11 as

$$\coth(z_0/d) = d/2b \quad (14)$$

In the limit of strong adsorption  $b \ll d$  and  $z_0 = 2b$ .

Close to the solid surface ( $z + z_0 \ll d$ ) the concentration profile is the same as the concentration profile of a pure homopolymer A adsorbed layer

$$\phi(z) = \frac{1}{3\nu_A} \left( \frac{a}{z + z_0} \right)^2 \quad (15)$$

The presence of the B block reduces the number of adsorbed chains (the brush free energy is positive); however, it does not change the concentration profile. Only the thickness of the adsorbed layer is reduced from the homopolymer radius  $R_A$  to  $d$ . At distances larger than  $d$ , the concentration profile decays exponentially with  $z$ .

Inserting the concentration profile  $\phi(z)$  in eq 6 gives a relation between the surface density  $\sigma$  and the anchor thickness  $d$

$$1 - \frac{2b}{d} = \sigma N_A \frac{6b\nu_A}{a} \quad (16)$$

Combining eq 16, 13, and 9, we obtain an equation giving the surface density  $\sigma$

$$\frac{\mu_{\text{ex}} \alpha}{N_A} = \frac{\alpha' \beta^2}{N_A^{2/3}} y^{2/3} - (1 - y)^2 \quad (17)$$

where we have introduced the reduced density  $y = (6b/a)\nu_A \sigma N_A$  and the numerical constants of order of unity  $\alpha$  and  $\alpha'$  such that  $\alpha = a/(6b\nu_A)$  and  $\alpha' = {}^5/3 [k_1 \nu_B^{2/3} / (3\nu_A)^{5/3}] (a/2b)^{5/3}$ . In general, since no mesophases are expected, the chemical potential term is negligibly small in eq 17 if the bulk polymer concentration  $\phi_b$  has a finite value ( $\phi_b \gg \exp(-N_A)$ ). We now distinguish two regimes

according to the value of the radius ratio  $\beta$ .

(1) Whenever  $\beta \ll N_A^{1/3}$  we obtain  $y = 1$  or a surface density

$$\sigma = \frac{a}{6bv_A} \frac{1}{N_A} \left[ 1 - \frac{\beta}{N_A^{1/3}} \alpha'^{1/2} \right] \quad (18)$$

The thickness of the anchor A layer may then be calculated from eq 16

$$d = \frac{2bN_A^{1/3}}{\beta\alpha'^{1/2}} \sim \frac{N_A^{5/6}}{N_B^{1/2}} \quad (19)$$

The thickness  $L$  of the brush is

$$L = \alpha'' N_B^{2/3} a \beta^{2/3} \sim N_B / N_A^{1/3} \quad (20)$$

It may be directly checked that  $\sigma R_B^2 \sim \beta \gg 1$ , and the chains in the brush are effectively stretched. The thickness  $d$  of the A layer scales with the mass of the anchor A with a higher power than the gaussian radius of gyration  $R_A$ . However, the radius ratio  $\beta$  is larger than 1 and  $d < N_A^{1/3} a < R_A$ . As explained earlier, the constraint introduced by the confinement of the B chains does not change the concentration profile in the A layer, it only diminishes the thickness of the layer, which becomes smaller as  $\beta$  is increased.

(2) When the asymmetry of the chain,  $\beta$ , is larger than  $N_A^{1/3}$ , eq 17 leads to a surface density

$$\sigma \approx \frac{a}{6v_A b \alpha'^{3/2}} \frac{1}{\beta^2} \quad (21)$$

This result, however, does not seem to be very meaningful; it leads to a distance between junction points of the copolymer D much larger than the chain radius  $R_A$  and a thickness of the adsorbed A layer of the order of a monomer size  $a$ . The continuous semidilute picture of the anchor layer that we have adopted in eq 5 is not appropriate for this regime; we will discuss it further with more accurate approximations in section IV.

### III. Scaling Theory

The mean-field theory of block copolymer adsorption is expected to give a qualitatively good description of the adsorbed copolymer layer; however, it does not take into account correctly the concentration correlations induced by the excluded volume, and we thus do not expect it to give quantitative results. The power law dependences must be corrected to take into account the excluded volume effects. In a good solvent, the natural radius of the polymer chains is the Flory radius  $R_{FA} = N_A^{3/5} a$  and  $R_{FB} = N_B^{3/5} a$ . We thus change the definition of the radius ratio

$$\beta = \frac{R_{FB}}{R_{FA}} = \left( \frac{N_B}{N_A} \right)^{3/5}$$

In the grand canonical free energy  $\Omega'$  which governs the structure of the adsorbed copolymer layer (eq 7), the free energies of both layers,  $F_A$  and  $F_B$ , must be modified. Alexander<sup>7</sup> has proposed a blob model to calculate the free energy of a grafted polymer brush in a good solvent. For a grafted brush with a chain density  $\sigma$  this leads to

$$\begin{aligned} \frac{F_B a^2}{T} &\sim N_B \sigma^{11/6} \\ L &\sim N_B a \sigma^{1/3} \end{aligned} \quad (22)$$

In this section we are interested only in scaling laws of the relevant parameters  $N_A$ ,  $N_B$ , and  $\sigma$ , and we will ignore

systematically the numerical coefficients. The brush size  $L$  has the same scaling behavior as in mean-field theory. The dependence of the free energy in  $\sigma$  is slightly modified.

de Gennes<sup>14</sup> has proposed a modified free energy functional which explicitly takes into account correlations in an adsorbed layer. In the anchor layer this is written as

$$\frac{F_A a^2}{T} = -\gamma \phi_s + \int_0^\infty \frac{\alpha a^2}{\xi^3} \left[ 1 + \left( m \frac{\xi}{\phi} \frac{d\phi}{dz} \right)^2 \right] dz \quad (23)$$

$\phi$  is the local monomer A concentration in the anchor layer,  $\xi$  is the local correlation length (in a good solvent  $\xi \sim \phi^{-3/4}$ ), and  $m$  and  $\alpha$  are two numerical constants of order unity.

The minimization of the free energy  $\Omega'$  (eq 7) with respect to the chain density  $\sigma$  gives

$$\lambda + \frac{\mu_{\text{ex}}}{T} = N_B \sigma^{5/6} \quad (24)$$

with the external chemical potential  $\mu_{\text{ex}}$  being a small contribution when the external solution is dilute.

The concentration profile in the anchor layer is obtained by minimization of  $\Omega'$  with respect to  $\phi$ . Close to the wall, at a distance  $z$  smaller than the layer thickness  $d$ , the Lagrange multiplier term is small in eq 7, and we obtain the usual self-similar profile in an adsorbed polymer layer

$$\begin{aligned} \xi(z) &= z \\ \phi(z) &\sim z^{-3/4} \end{aligned} \quad (25)$$

The thickness of the layer is reached when the Lagrange multiplier term  $(\lambda/N_A) \int \phi dz$  becomes equal to the two terms of eq 23. The thickness of the adsorbed layer is then

$$d = (N_A/\lambda)^{3/5} a \quad (26)$$

As in the mean-field theory, the concentration profile in the A layer is the same as in a homopolymer A adsorbed layer. The confinement of the B chains only reduces the thickness of the layer.

At distances larger than  $d$  the concentration profile of the A chains decays rapidly to zero:  $\phi(z) \sim 1/\lambda^4 z^6$ . It is not clear, however, whether the Cahn-de Gennes free energy of eq 23 retains a meaning in this regime.

Inserting the concentration profile in the copolymer constraint,<sup>6</sup> we obtain

$$N_A \sigma = 1 - (a/d)^{1/3} \quad (27)$$

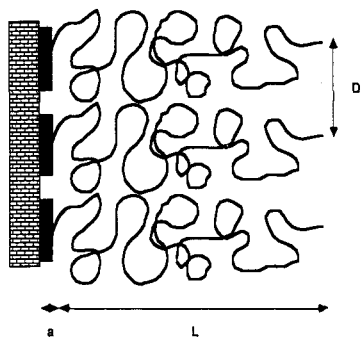
The geometrical characteristics of the adsorbed layer are given in this scaling theory by eq 24, 26, and 27. We will consider them here only on the limit where the radius ratio  $\beta$  is smaller than  $N_A^{1/2}$  for which this continuous description has a meaning

$$\begin{aligned} \sigma &\sim 1/N_A \\ d &\sim N_A^{1/2}/\beta \\ L &\sim N_B^{2/3} \beta^{1/3} \sim N_B N_A^{-1/3} a \end{aligned} \quad (28)$$

These results are quite similar to what was obtained in the mean-field approximation although the thickness of the anchor layer shows a different scaling behavior and is somewhat larger.

### IV. Discontinuous Layer: Dilute and Semidilute Regime

The previous results are meaningful only if the adsorbed layer is continuous and may be considered locally as a semidilute solution. This requires in particular that the thickness of the A layer on the wall is much larger than a monomer size  $a$ . This is obviously the case when the



**Figure 2.** Discontinuous regime. For very asymmetric chains the A layer forms a discontinuous pancake patchwork in contact with the wall. The B chains are always stretched, except for very low bulk concentrations.

block copolymers are moderately asymmetric but ceases to be true for very asymmetric polymers ( $\beta > N_A^{1/2}$ ), which we discuss below. We first consider the case where the radius ratio  $\beta$  is extremely large. The adsorbed copolymer layer breaks then into a patchwork of individual chains as shown in Figure 2. As for homopolymer single-chain adsorption, the A block forms a flat two-dimensional pancake on the surface with a thickness  $d$  of the order of a monomer size (and decreasing with the adsorption energy  $\gamma$ ). The radius of these pancakes is the radius of an excluded volume polymer chain in two dimensions

$$R_A = N_A^{3/4}a \quad (29)$$

The A chains are not close packed on the surface and form a two-dimensional dilute solution only if the A chain concentration is smaller than the overlap concentration

$$\sigma^* = \frac{a^2}{R_A^2} = N_A^{-3/2} \quad (30)$$

The B blocks are dangling in the solution and form a brush as soon as  $\sigma(R_{FB}^2/a^2) \gg 1$ ,  $R_{FB}$  being the Flory radius. If  $\sigma(R_{FB}^2/a^2) \ll 1$ , the buoy layer is also discontinuous.

The grand canonical free energy, which governs the structure of the adsorbed layer, reads in this geometry

$$\Omega = F_A + F_B + F_{\text{trans}} - \mu_{\text{ex}}\sigma a^{-2} \quad (31)$$

$\mu_{\text{ex}}$  is the external chemical potential given by eq 2, and we have neglected the external pressure contribution.  $F_{\text{trans}}$  is the translational entropy of the chains on the surface

$$F_{\text{trans}}a^2/T = \sigma \ln \sigma \quad (32)$$

$F_B$  is the brush stretching energy given by eq 22, and  $F_A$  is the adsorption free energy of the A blocks. The adsorption energy of one chain is proportional to the number of monomers  $N_A$

$$F_A a^2/T = -\delta \sigma N_A \quad (33)$$

$\delta$  being a number of order unity depending on the monomer adsorption energy  $\gamma$ .

When  $\sigma R_{FB}^2 \ll 1$ , the brush energy is small and

$$\sigma = \exp(N_A \delta + \mu_{\text{ex}}/T) \sim \phi_b e^{\delta N_A} \quad (34)$$

This is possible only when the monomer external concentration  $\phi_b$  is extremely small

$$\phi_b < (N_B^{6/5})^{-1} \exp(-N_A \delta) \quad (35)$$

As soon as the external concentration is finite, the buoy layer B becomes continuous (although the anchor layer might be discontinuous), and the translational energy  $F_{\text{trans}}$  and the external chemical potential  $\mu_{\text{ex}}$  are negligibly small in eq 31.

**Table I**  
Conformation of the Copolymer as a Function of the Asymmetry Ratio  $\beta = R_B/R_A$

$\beta$	3D regime $1 < \beta < N_A^{1/2}$	2D semidilute $N_A^{1/2} < \beta < N_A^{3/4}$	2D dilute $\beta > N_A^{3/4}$
$\sigma \approx$	$N_A^{-1}$	$\beta^{-2}$	$\beta^{-2}$
$d \approx$	$(N_A^{1/2}/\beta)a$	$a$	$a$
$L \approx$	$N_B N_A^{1/3} a$	$N_B^{3/5} N_A^{2/5} a$	$N_B^{3/5} N_A^{2/5} a$

The surface density then depends strongly on the radius ratio  $\beta$

$$\sigma = \beta^{-2} \quad (36)$$

The A layer forms thus a two-dimensional dilute solution if the asymmetry  $\beta$  is larger than  $N_A^{3/4}$ . When  $\beta < N_A^{3/4}$  the A blocks form on the solid surface a semidilute two-dimensional layer whose properties have been discussed in details by Bouchaud and Daoud.<sup>17</sup> Although the A blocks start to form large loops and to build up the self-similar fluffy layer, the average thickness of the A layer remains of order of a monomer length. The chain density in this semidilute layer is given by eq 36. The semidilute regime crosses over smoothly to the continuous regime of the previous section when  $\beta = N_A^{1/2}$ . In the case of adsorbed homopolymer A studied by Bouchaud and Daoud, the two-dimensional semidilute regime is obtained for extremely low bulk concentrations, which are inaccessible experimentally. The study of adsorbed diblock copolymer layers in a nonselective solvent might make this regime accessible by an accurate choice of the asymmetry of the copolymer. Finally, both in the dilute and semidilute regimes the size of the buoy layer increases with the buoy molecular mass slower than linearly

$$L = N_B^{3/5} N_A^{2/5} a \quad (37)$$

Although this is much smaller than a stretched chain, it is much larger than the Flory radius of the B chains due to the  $N_A$  dependence.

## V. Discussion

Although the simplest way to coat a colloidal particle with a polymer brush seems to be the adsorption of diblock copolymers in a highly selective solvent, the results presented here show that such layers also form in a nonselective solvent where the two incompatible blocks are in a good solvent, one block being strongly attracted by the surface and the other one strongly repelled.

At thermodynamic equilibrium, when the adsorption is made from a dilute solution, the structure of the adsorbed layer is governed essentially by the asymmetry of the copolymer, which we have measured here by the radius ratio  $\beta$ . A summary of our results for the conformation of the copolymers as a function of  $\beta$  is given in Table I.

When  $\beta$  is smaller than  $N_A^{1/2}$  the A layer in contact with the surface is a continuous fluffy layer where the concentration profile decays in the same way as in an adsorbed homopolymer layer. The existence of the buoy dangling in the solution prevents this layer from reaching the equilibrium surface coverage of a homopolymer layer and reduces the number of adsorbed chains. The thickness of the adsorbed layer is thus smaller for block copolymers than for homopolymers. The external layer is, as required, a polymer brush with a thickness  $L$  scaling linearly with the molecular mass of the B block of the copolymer.

When  $\beta$  is larger than  $N_A^{1/2}$  the anchor layer has a thickness of the order of a monomer size  $a$  and forms a quasi-two-dimensional polymer solution which is either dilute or semidilute, the crossover between these two regimes occurring for  $\beta = N_A^{3/4}$ .

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,<sup>18</sup> Klein and co-workers,<sup>19</sup> and Hair and co-workers.<sup>20</sup> 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.

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## Polymer Adsorption and Electron Binding on Rough and Fractal Surfaces

Martin Blunt,\* William Barford,† and Robin Ball

*Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, England. Received December 23, 1987; Revised Manuscript Received July 21, 1988*

**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 problem 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.<sup>1,2</sup> Some recent work by Hone et al.<sup>3</sup> 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.<sup>4,5</sup>

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

First, though, we shall briefly introduce the Edwards<sup>8</sup> mean-field approach to polymer statistics, which we use

here to formulate the problem. The reader is referred to de Gennes<sup>9</sup> or Doi and Edwards<sup>10</sup> for a more comprehensive treatment.

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

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

$G(\mathbf{r}, \mathbf{r}', L)$  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  $\delta$  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  $k_B T$ ; 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.

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

\* Present address: BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, England.

† Present address: Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, England.