Adsorption of Random Copolymers

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ABSTRACT: We discuss the adsorption of copolymer chains where most monomers B are repelled by the surface and a few stickers A distributed regularly along the chain are strongly attracted by the surface. For a single Gaussian polymer chain we calculate the propagator close to a hard wall or a phantom wall. If the adsorption strength is very large, all stickers are on the surface; in a weak adsorption limit the chain may be renormalized to a chain of blobs each containing a single sticker. In this case the propagator is calculated by resummation of a perturbation series. The results are in good agreement with a simple Flory theory. A dilute solution in contact with a wall forms a continuous polymer layer on the wall. We give a geometrical description of this layer in a good solvent in terms of a blob model. When the fraction of stickers decreases from 1 to zero the structure of the layer crosses over smoothly from an adsorbed homopolymer layer to a polymer brush. We finally discuss briefly the interactions between two flat plates coated with copolymers.

I. Introduction

The behavior of polymers close to interfaces has been extensively studied over the last few years, and a broad spectrum of theoretical, numerical, and experimental techniques has been developed to investigate various physical properties of the polymer layers:[1] polymer concentration, surface excess, thickness of the interfacial layer, and elastic response of the layer.

Two mechanisms of interaction between a polymer solution and a surface are in general distinguished, leading to the formation of adsorbed and grafted layers respectively.

(1) Adsorbed layers are built up by polymers where all the monomers are attracted toward the surface. Even in contact with a dilute solution, the interfacial layers are rather diffuse and their thickness is of the order of R_G, the radius of gyration of isolated chains in solution. The layer is made from loops with a broad size distribution that has been described in terms of a self-similar grid.[2]

(2) Grafted layers (sometimes called polymer brushes) are formed by nonadsorbing polymers end-linked to the surface. When the grafted density is large enough to allow overlap, the chains are stretched and the layer thickness is several times thicker than the radius of gyration, R_G.[3,4]

Most studies have been dedicated to homopolymers, but it may sometimes be interesting to use A–B copolymers to form thick layers on a solid surface. A favorable architecture is achieved when one type of monomers A is attracted by the surface and anchors the chain and the other one B is repelled by the surface forming a thick layer. We recently presented a scaling theory of the adsorption of diblock copolymers,[5,6] which are not often used as an alternative way to the covalent cross-links to form grafted layers on solid surfaces. The adsorbing block end-links the chain; the repelled block forms the brush in the solution.

In this paper we are interested in another architecture where the adsorbing monomers are not grouped in a block but are distributed along the chain either in a regular or in a random way. This is an intermediate case between the two situations encountered with homopolymers (grafting and adsorption). When the fraction f of A monomers is close to 1, the interfacial layer is an adsorbed homopolymer layer and is thus formed by many loops on the surface. In the other limit where each chain has only one strongly adsorbing A monomer (to which we will sometimes refer as a sticker), a grafted layer made of extended chains is obtained (even if the sticker is not at the end of the chain, the qualitative structure remains unchanged). We study below the intermediate range $0 \ll f \ll 1$ where we expect a mixed structure where the chains still form loops but are also slightly stretched. We discuss the structure of these loops first for the adsorption of one isolated chain and then for the adsorption of a dilute solution.

A useful picture of the random copolymer is to group monomers into blobs, each of them containing one sticker A. The average number of monomers per blob is $P = f^{-1}$ and the number of blobs per chain is $N = M/P = fM$ where M is the degree of polymerization of the chain. One of our basic assumptions is that the disorder is not a relevant variable and that the adsorption properties of the chain are not very different from that of a chain where all blobs have exactly P ($\gg 1$) monomers. This is certainly true if the variance of the blob size distribution is small compared with the mean size P. We also expect this to be a rather good approximation when the adsorption of A monomers onto the wall is strong and the repulsion of B monomers is large. In cases of weak adsorption or weak repulsion, or close to an adsorption threshold, the disorder might be a relevant variable, its consideration is far beyond the scope of this work.[7,8]

The paper is organized as follows. In section II we review some known results on polymer statistics and Gaussian chain configurations near two different types of interfaces: a phantom and a solid wall. The first corresponds to an attractive interface between two incompatible solvents and the second to a solid–liquid type of interface. In the spirit of the blob model we also first treat the adsorption of one blob (with a single adsorbing monomer). This result is then used in section III to discuss the adsorption of the whole copolymer chain. We use a perturbation expansion that can be resummed to calculate the propagator of an adsorbed Gaussian copolymer. The results are in good agreement with simple Flory arguments. Section IV is devoted to the discussion of the more realistic problem of the adsorption of a dilute solution in a good solvent. A blob model is introduced to describe the geometrical structure of the layer. Our conclusions are presented in section IV.

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II. Statistics of Gaussian Polymer Chains near Interfaces

1. Single-Chain Statistics.[9,10] The fundamental quantity describing the statistics of a Gaussian chain of N monomers of size a is the statistical weight or propagator, $G_N(R,R')$. Within a normalization factor, this is the conditional probability of finding the Nth segment at position R' knowing that the first segment is at R. The determination of the statistical characteristics of the chain (such as the average end-to-end distance or the energy) often involves the knowledge of G_N. As an example, the monomer concentration at a given point R is calculated from

$$c(R) = \frac{\int_0^N \mathrm{d}n \int \mathrm{d}R' \int \mathrm{d}R''\ G_n(R',R)\ G_{N-n}(R,R'')}{\int \mathrm{d}R' \int \mathrm{d}R''\ G_N(R',R'')} \qquad \text{(II.1)}$$

Under the assumption that the chain behaves as a sequence of statistically independent segments under an external potential $U(R)$, the propagator G_N is written as

$$G_N(R,R') = \int D[R(s)] \exp\left[-\int_0^N \mathrm{d}s \left[\frac{3}{2a^2}\left(\frac{\partial R(s)}{\partial s}\right)^2 + \frac{U(R(s))}{T}\right]\right] \qquad \text{(II.2)}$$

where we have chosen temperature units such that the Boltzmann constant is $k_B = 1$ and $R(s)$ is the position of monomer s. This statistical independence between different parts of the chain is expressed by a composition law

$$G_{n+m}(R,R') = \int \mathrm{d}R''\ G_n(R,R'')\ G_m(R'',R') \qquad \text{(II.3)}$$

Under the assumption that the external potential varies slowly, Edwards[11] first showed that the composition law is equivalent to the following differential equation for the propagator:

$$\frac{\partial G_N}{\partial N}(R,R') = \left[\frac{a^2}{6}\nabla_R{}^2 - \frac{U(R)}{T}\right] G_N(R,R') \qquad \text{(II.4)}$$

This equation is the analogue of the Schroedinger equation of quantum mechanics. If the potential does not depend on N, a general solution is found by expansion in eigenfunctions

$$G_N(R,R') = a^3 \sum_k \psi_k{}^*(R')\ \psi_k(R) \exp(-\epsilon_k N) \qquad \text{(II.5)}$$

where $\psi_k(R)$ and ϵ_k are, respectively, the eigenfunctions and eigenvalues of the equation

$$\left[\frac{a^2}{6}\nabla_R{}^2 - \frac{U(R)}{T} + \epsilon_k\right]\psi_k(R) = 0 \qquad \text{(II.6)}$$

The propagator of eq II.5 satisfies the proper boundary condition $G_0(R,R') = \delta(R - R')$.

One important feature of eq II.6 is the presence of the factor N in the exponential; in a very large class of problems the sum is dominated by one term, corresponding to the smallest eigenvalue. This is known as the ground-state dominance approximation. The concentration then simply reads

$$c(R) = N|\psi(R)|^2 \qquad \text{(II.7)}$$

2. Single-Chain Adsorption at an Interface. We now briefly review the behavior of homopolymer chains close to a flat interface (the homopolymer chain corresponds to a random copolymer with a fraction of stickers $f = 0$ for a repulsive wall and $f = 1$ to an attractive wall). We first discuss an infinitely repulsive wall and then an attractive wall in the two limits of a phantom wall penetrable by the polymer and a hard wall impenetrable by the polymer. Finally we discuss adsorption of one "blob" of the copolymer where one end is attracted toward the surface and the rest of the polymer repelled by the surface.

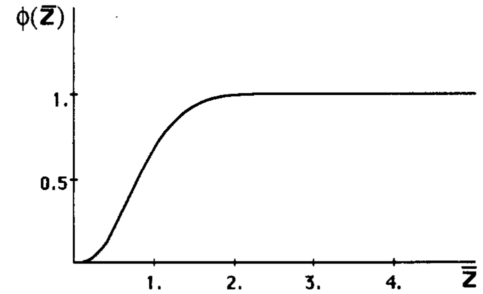

Figure 1. Concentration profile of a Gaussian chain near an impenetrable repulsive wall. $\phi(\bar{z}) = c^i(\bar{z})/c^i(\infty)$. $\bar{z} = (3/2a^2N)^{1/2}z$. The depleted region extends over a distance $\sim N^{1/2}a$.

a. Purely Repulsive Wall. In the vicinity of an infinitely repulsive wall a polymer solution has a depletion layer where the concentration decreases from its bulk value to zero; when a zero concentration is imposed at the wall, the propagator of a Gaussian chain in the direction z perpendicular to the wall is derived[12] from eq II.6

$$G_N{}^i(z,z') = \left(\frac{3}{2\pi N a^2}\right)^{1/2}\left[\exp\left(\frac{3(z-z')^2}{2Na^2}\right) - \exp\left(\frac{3(z+z')^2}{2Na^2}\right)\right] \qquad \text{(II.8)}$$

This leads to a concentration profile

$$c^i(\bar{z}) = \frac{N}{V\left(1 - \left(\frac{2a^2N}{3\pi A}\right)^{1/2}\right)}\left[2 \operatorname{erf}(\bar{z}) - \operatorname{erf}(2\bar{z}) + \frac{4\bar{z}}{\sqrt{\pi}}(\exp(-\bar{z}^2) - \exp(-4\bar{z}^2)) + 8\bar{z}^2\left(\operatorname{erfc}(2\bar{z}) - \frac{1}{2}\operatorname{erfc}(\bar{z})\right)\right] \qquad \text{(II.9)}$$

where we have introduced the dimensionless variable $\bar{z} = (3/2a^2N)^{1/2}z$. erf is the error function defined by erf $(x) = (2/\sqrt{\pi})\int_0^x \mathrm{d}u\ e^{-u^2}$, and erfc is the complementary error function erfc $(x) = 1 - \operatorname{erf}(x)$. A is the total area of the wall and V the volume of the solution.

This profile is shown in Figure 1. As expected the chain avoids a region of order $N^{1/2}a$ near the wall, where its entropy is reduced. For small z the concentration increases as $c^i(z) \simeq (N/V)(z/a)^2$ and reaches, at infinity, the bulk value N/V.

b. Attractive Wall. We distinguish here between a phantom wall penetrable and a hard wall impenetrable by the chain. The potential seen by the polymer chain due to the wall $U(z)$ is purely attractive for a phantom wall. For a hard wall it is attractive for positive values of z but becomes infinitely repulsive on the wall ($z = 0$). We limit the study to short-range attraction potentials with a range b of the order of a monomer length a. At distances smaller than b the details of the concentration profile depend explicitly on the actual shape of the potential; however, the adsorbed layer is in general larger than b and farther away, and the chain configuration is independent of the details of the potential, the only important feature being that this profile has a good matching with the shorter range part $z < b$. This matching imposes the value of the logarithmic derivative of the concentration profile close to the wall. For convenience, in the following we mimic the potential by a δ function for a phantom wall

$$U(z) = -T\frac{\delta a}{6}\delta(z) \qquad \text{(II.10)}$$

For a hard wall, the potential is infinite at the wall and we must shift the attractive well at a distance b from the wall

$$U(z) = -T\frac{\delta a}{6}\delta(z-b) \qquad z > 0$$

$$U(z) = \infty \qquad z < 0 \qquad \text{(II.11)}$$

The use of more realistic potentials would improve the description of the chain conformation in the vicinity of the wall, which is irrelevant for practical purposes.

In both cases the concentration profile is obtained from eq II.7 using the ground-state dominance approximation. Close to a phantom wall, the chain is always confined within a distance D from the surface

$$c(z) = N/AD \exp[-2|z|/D] \qquad \text{(II.12)}$$

The thickness of the layer D decreases with the strength of the potential as

$$D = 2a/\delta \qquad \text{(II.13)}$$

The ground-state dominance approximation is accurate if the distance D over which the chain is confined is smaller than its radius $N^{1/2}a$, i.e.

$$\left(\frac{a}{D}\right)^2\frac{N}{6} \gg 1 \quad \text{or} \quad \delta \gg \left(\frac{24}{N}\right)^{1/2} \qquad \text{(II.14)}$$

We consider here the strong adsorption limit $\delta \sim 1$ for which this condition is always satisfied.

In the presence of a hard wall, the concentration vanishes at the wall and increases up to $z = b$. The bound state of the Schroedinger equation corresponding to an adsorption exists only if the attraction δ is larger than a threshold $\delta_c = a/b \simeq 1$. This threshold is due to the reduction of the entropy of the monomers close to the wall; although their interaction energy with the wall is always negative, their free energy remains positive if $\delta < \delta_c$. Above threshold, the concentration decreases exponentially as $z > b$ according to eq II.12 with a decay length

$$D = a/(\delta - \delta_c) \qquad \text{(II.15)}$$

Below threshold the propagator is not dominated by the ground state and the concentration increases monotonically from the wall to its bulk value. The wall may there be considered as a partially repulsive surface, and the profile shows a depletion layer similar to that of a purely repulsive wall. This depletion profile may also be characterized by its interpolation length D, $1/D = -(2/c)(\mathrm{d}c/\mathrm{d}z)|_b = (1/b)[(\delta_c - \delta)/\delta]$. If there is no attraction $\delta = 0$, the profile is that of Figure 1: D increases with δ and diverges for $\delta = \delta_c$; the profile is then essentially flat, and the attractive part of the potential compensates exactly the repulsive part.

c. Chains Adsorbed by One End. As a last example we discuss the behavior of one blob of the copolymer with only one end monomer feeling the attractive part of the potential. Since the potential acts only on the last monomer, the propagator of $N - 1$ first monomers $G_{N-1}{}^0(z,z')$ is that of a free chain

$$\text{phantom wall} \quad G_N{}^0(z,z') = \left(\frac{3}{2\pi Na^2}\right)^{1/2} \exp\left(\frac{3(z-z')^2}{2Na^2}\right)$$

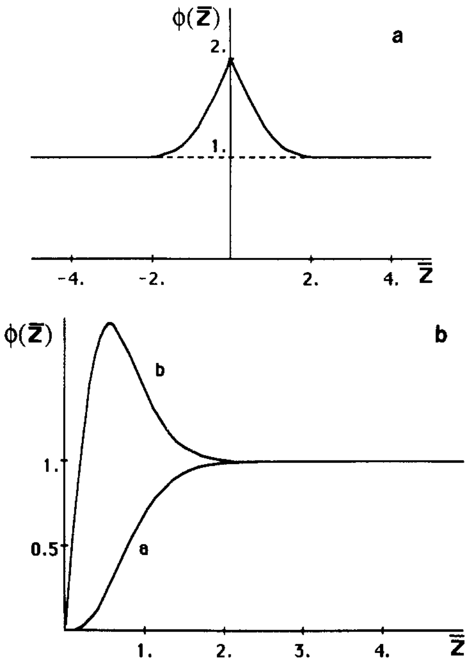

Figure 2. (a) Concentration profile of a Gaussian chain adsorbed by one end on a penetrable wall. $\phi(\bar{z}) = c^i(\bar{z})/c^i(\infty)$. $\bar{z} = (3/2a^2N)^{1/2}z$. The adsorption free energy δ is of order $N^{1/2}$. (b) Concentration profile of a Gaussian chain adsorbed by one end of an impenetrable wall. The adsorption free energy δ is $4N$ in b and $0.5N$ in a.

$$\text{hard wall} \quad G_N{}^i(z,z') =$$

$$\left(\frac{3}{2\pi Na^2}\right)^{1/2}\left[\exp\left(\frac{3(z-z')^2}{2Na^2}\right) - \exp\left(\frac{3(z+z')^2}{2Na^2}\right)\right] \qquad \text{(II.16a)}$$

Adding the adsorbing end simply changes the propagator from its nonperturbed form by a Boltzmann factor

$$G_N(z,z') = G_N{}^0(z,z') \exp[-U(z)/T] \qquad \text{(II.16b)}$$

Using the potentials in eq II.10 and II.11, we obtain

$$\text{phantom wall} \quad G_N(z,z') = G_N{}^0(z,z') + \frac{\delta a}{6}\delta(z)\, G_N{}^0(z,z')$$

$$\text{hard wall} \quad G_N(z,z') = G_N{}^i(z,z') + \frac{\delta a}{6}\delta(z-b)\, G_N{}^i(z,z') \qquad \text{(II.16c)}$$

For a phantom wall the concentration profile is calculated from the propagator

$$c(\bar{z}) = \frac{N}{V + \dfrac{\delta a A}{6}}\left[1 + \frac{\delta}{(6\pi N)^{1/2}}[\exp(-\bar{z}^2) - |\bar{z}| \operatorname{erfc}(|\bar{z}|)]\right] \qquad \text{(II.17)}$$

As soon as the attraction is finite ($\delta a A < V$), the concentration is inversely proportional to the volume, indicating that the chain is not confined to a small region close to the surface. The concentration is slightly higher than its bulk value N/V on the wall and relaxes toward this value over a radius $R_G \sim N^{1/2}a$ (Figure 2a). Only for infinite attraction is the concentration inversely proportional to the area and the chain confined in a radius of thickness R_G. This corresponds to a grafted chain.

The expression for the concentration in the presence of a hard wall is rather lengthy; we only give on Figure 2b the concentration profile for two values of δ. The main new feature is the existence of the depletion layer close to the wall. If $\delta \gg N$, the attraction dominates and the concentration first increases, then shows a maximum, and decreases toward its bulk value. Notice, however, that this does not correspond to the adsorption threshold of the previous section: for finite values of δ, the chain is not constrained in a small region close to the wall and the concentration remains inversely proportional to the volume of the solution.

III. Adsorption of a Random Copolymer

In this section we discuss the adsorption of one chain of $M - N$ monomers B and N monomers A. We first assume a regular distribution of A monomers along the chain, which is then built of blobs of size $P = M/N$, each blob having one A monomer at the end and a tail of $P - 1$ monomers. A and B monomers have thus similar properties in the bulk; only their adsorption behavior is different. We also give one example where the number of monomers per blob fluctuates around an average value P_0.

There are clearly two different limits for the conformation of the chain at the interface. If the adsorption is very strong, all the stickers A are on the surface, the chain is grafted. For a weaker adsorption only a fraction of stickers is in contact with the surface, the others dangling farther away in the solvent. The configuration of the adsorbed chain is then similar to that of an adsorbed homopolymer but with renormalized monomers, the blobs.

1. Strong Adsorption. In the limit of strong adsorption ($\delta \rightarrow \infty$), all the stickers A are on the wall and the chain is made of a succession of loops of B monomers. The concentration profile is obtained by summing the concentration of individual loops with both ends on the surface. Generalizing the results of section II where the blobs only have one sticker, we obtain at a *liquid–liquid* interface

$$c(\bar{z}) = \frac{N}{Aa}\left(\frac{3\pi P}{2}\right)^2 \operatorname{erfc}(2|\bar{z}|) \qquad \text{(III.1)}$$

where we have used the reduced variable $\bar{z} = (3/2a^2P)^{1/2}z$. This profile is plotted in Figure 3a. The chain is confined at the interface over a distance of order $P^{1/2}a$, and the concentration at the origin is of order $NP^{1/2}/Aa$. All the blobs touch the interface and each of them contributes a factor $P^{1/2}$ to the surface concentration (this is due to the Gaussian statistics of each blob).

A true random copolymer would have different blob sizes. Let us assume, for instance, that each blob has P_i monomers with an associated Gaussian probability of average P_0 and root mean square Δ. The monomer concentration is obtained by averaging the concentration profile and is up to second order in Δ

$$\langle c(\bar{z})\rangle \simeq \frac{N}{Aa}\left(\frac{3\pi P_0}{2}\right)^{1/2} \operatorname{erfc}(2|\bar{z}|)\left[1 - \frac{\Delta^2}{8P_0^{\,2}}f(\bar{z})\right] \qquad \text{(III.2)}$$

where the function $f(\bar{f})$ varies slowly from $f(0) = 1$ to $f(\bar{z}) \sim \bar{z}^3$ for $\bar{z} \gg 1$. The power law divergence for large z values is not important since there the concentration decays exponentially. The original assumption over the regularity of the copolymer is then justified if the statistical distribution of the P values is not too broad, i.e., if $\Delta < P_0$. The correction to the concentration profile is of order $(\Delta/P_0)^2$. This result remains valid throughout this section.

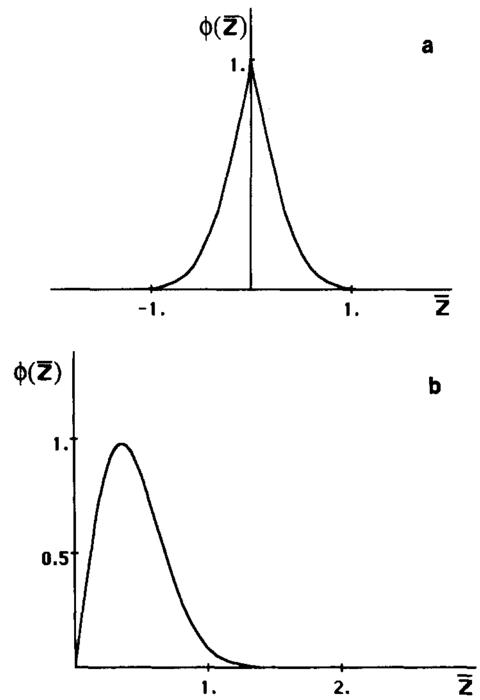

Figure 3. Concentration profile of a Gaussian copolymer chain grafted on a wall: (a) phantom wall, (b) hard wall. $\phi(\bar{z}) = c^i(\bar{z})/c^i_{\max}$. $\bar{z} = (3/2a^2P)^{1/2}z$.

Close to a *solid wall*, the concentration profile can be determined as before, the Green function for each loop of P monomers being $G_P{}^i(b,b)$ (eq II.8). The profile is displayed in Figure 3b. Its mean characteristics are similar to those of a copolymer chain grafted on a phantom surface: thickness of confinement of order of $P^{1/2}a$ and maximum of concentration of order $NP^{1/2}/Aa$. We already noticed in section II.2.c. that for the grafted chain geometry the existence of an impenetrable wall introduces a depletion region of the order of $P^{1/2}a$, the radius of gyration of the loop. In contrast to the depletion layer of a purely repulsive wall (eq II.9), the concentration increases here linearly from its vanishing interfacial value to reach its maximum at $z \simeq P^{1/2}a$ and decreases again to zero over a length $P^{1/2}a$.

2. Weak Adsorption. a. Flory Theory. In the opposite limit of weak adsorption the stickers A have a finite adsorption strength δ. There is then a distribution of the positions of monomers A along the z axis, two successive stickers being connected by a free chain of $P - 1$ monomers B. In terms of blobs this means that only a fraction of the blobs touch the interface, all the others dangling in the solvent. Let D be, as above, the size of confinement of the chain. D may be estimated from a usual Flory argument that balances the loss of entropy due to confinement with the adsorption energy gained by contact with the surface. In the case of a liquid–liquid interface, this reads

$$\left.\frac{F}{T}\right|_{\text{chain}} = -(\delta/P)\varphi M + (a/D)^2 M \qquad \text{(III.3)}$$

In the first term, on the right-hand side, $\varphi = a/D$ is the fraction of monomers in contact with the surface, a fraction $1/P$ of those (the monomers A) being able to gain an energy $-\delta$. The second term is the loss of entropy of a Gaussian chain of M monomers confined in a size D. Minimizing this energy with respect to D leads to

$$D \sim aP/\delta \qquad \text{(III.4)}$$

which naturally recovers eq II.13 in the limit $P = 1$. From eq III.4 we thus expect the adsorbed random copolymer to have loops extending P times further in the solvent than a simple homopolymer. This Flory argument is easily extended to the case where the chain is in a good solvent. The only term that we need to change is the entropic contribution[10] that becomes $M(a/D)^{5/3}$; the minimization leads to

$$D \sim a(P/\delta)^{3/2} \tag{III.5}$$

In a good solvent, the increase of the thickness of the adsorbed chain is even more important.

A similar scheme may be applied to the adsorption on a hard wall, but two new difficulties arise. First, the existence of a finite threshold is not predicted by the Flory argument, which simply takes into account the adsorption free energy γ gained by contact of the monomers with the surface. This free energy is the difference from the threshold $\gamma = \delta - \delta_c$. Second, as we have seen before, there is a depletion layer close to the wall over a distance of order $P^{1/2}a$. The concentration increasing as a quadratic function from the wall, $c(z) \sim (M/DA)(z^2/Pa^2)$, the fraction of monomers within a distance b from the wall is thus $\varphi = (a/DP)(b/a)^2$. Substituting this in the Flory energy and minimizing with respect to D, we obtain

$$D \sim aP^2/\gamma \tag{III.6}$$

In a good solvent a similar argument leads to

$$D \sim a(P^2/\gamma)^{3/2}(a/b)^{5/2} \tag{III.7}$$

Notice, however, that this ignores proximal effects, which to our knowledge have not been studied for such copolymers.[13,14]

b. Perturbation Theory. To go beyond these simple Flory arguments and calculate the detailed concentration profile, we need to compute the propagator of the copolymer. We first notice that the potential $U(z)$ which acts on the A monomers is now N dependent, and we cannot use the expansion in eigenfunctions of eq II.5. One natural approach would be to renormalize the monomers to blobs and try to derive a Schroedinger equation from the composition law between successive stickers

$$G_{(n+1)P}(R_0,R_{(n+1)P}) = \int \mathrm{d}R_{nP}\, G_{nP}(R_0,R_{nP})\, G_P(R_{nP},R_{(n+1)P}) \tag{III.8}$$

The major problem with this approach is that the solution ignores the details on length scales smaller than $P^{1/2}a$ and thus does not correctly account for the boundary condition at the wall. An alternative approach is to build the propagator recursively from the individual blobs using the composition law and the propagator of the blobs given by eq II.16. This is equivalent to a diagrammatic expansion of the propagator shown in Figure 4: we sum over all the configurations that take the chain from z to z'; each configuration is a succession of flights of nP monomers starting and ending on the surface. A configuration of m flights is trapped by the potential $m - 1$ times and is thus weighed by a factor $(\delta/6)^{m-1}$. The final expression of the Green function of the Nth sticker is, for a liquid–liquid interface

$$G_N(z,z') = \left[1 + \frac{\delta a}{6}\delta(z)\right]\left[1 + \frac{\delta a}{6}\delta(z')\right][G_N{}^0(z,z') + \Delta G_N(z,z')] \tag{III.9}$$

with

$$\Delta G_N(z,z') = \sum_{r=1}^{N-1}\left(\frac{\delta a}{6}\right)^r \sum_{i_1=1}^{N-r}\ \sum_{i_2=1}^{N-r+1-i_1} \cdots \sum_{i_r=1}^{N-i_1-i_2-\ldots1} G_{i_1}{}^0(z,0)\, G_{i_2}{}^0(0,0)\ldots G_{i_r}{}^0(0,0)\, G_{N-i_1-\ldots i_r}{}^0(0,z') \tag{III.10}$$

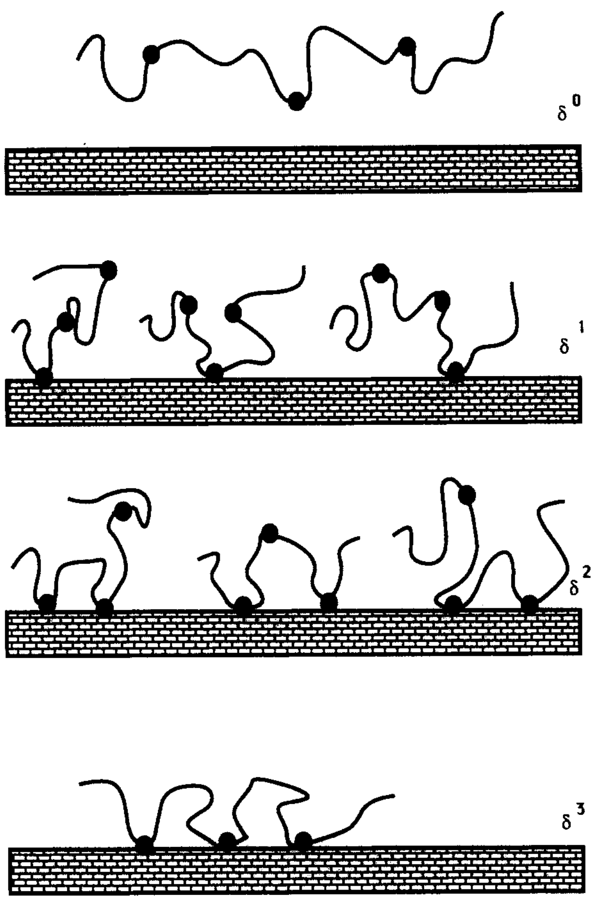

Figure 4. Diagrammatic expansion for the propagator of a chain of four blobs. The sum has eight terms in this case. Each term of the sum for which j stickers touch the surface is weighed by a factor $(\delta/6)^j$.

This same approach also may be used for a solid–liquid interface if one substitutes all the Gaussian statistical weights at the surface $G_i{}^0(0,0)$ by the corresponding propagators $G_i{}^i(b,b)$ for an impenetrable wall and the δ functions at the origin by the δ functions centered at a distance b from the wall.

The perturbation series eq III.10 can be summed by Laplace transformation over N leading to

$$\Delta G_s(z,z') = \int_0^\infty \Delta G_N(z,z') e^{-sN}\, \mathrm{d}N \simeq \frac{\delta a}{6}\frac{1}{1 - g_s(0,0)} g_s(z,0)\, g_s(0,z') \tag{III.11}$$

where $g_s(z,z') = (\delta a/6)\int_1^\infty \mathrm{d}N\, e^{-sN}\, G_{NP}{}^0(z,z')$. The propagator is then calculated by inverse Laplace transformation. In the limit of a very long chain ($N \rightarrow \infty$), there are two different contributions to the inverse Laplace transform of eq III.11. The first corresponds to the existence of a branch point at $s = 0$, the second one is the pole s_c corresponding to $g_{s_c}(0,0) = 1$. The ground-state dominance approximation is equivalent to neglecting the contribution of the branch point; the pole corresponds to the smallest eigenvalue.

For a penetrable interface the explicit form of $g_s(z,z')$ is

$$g_s(\bar{z},\bar{z}') = \frac{\delta}{6}\left(\frac{3}{2P}\right)^{1/2}\{[e^{-2(\bar{z}-\bar{z}')s^{1/2}} \operatorname{erfc}[s^{1/2} - (\bar{z} - \bar{z}')] + e^{2(\bar{z}-\bar{z}')s^{1/2}} \operatorname{erfc}[s^{1/2} + (\bar{z} - \bar{z}')]]/2s^{1/2}\} \tag{III.12}$$

The pole exists for all positive values of δ. This gives a threshold for adsorption $\delta_c = 0$. Figure 5 displays the concentration profile as calculated from eq II.1. Note that eq III.9 only gives the stickers's statistical weight; the complete propagator for a chain with an arbitrary length $r = nP + s$ must be calculated from the composition law (eq II.3)

$$G_{nP+s}(z,z') = \int_{-\infty}^{\infty} dz''\, G_{nP}(z,z'')\, G_s^{0}(z'',z') \qquad \text{(III.13)}$$

with $G_{nP}(z,z'')$ calculated above and $G_s^{0}(z'',z')$ the usual Gaussian propagator.

At larger distances $z > P^{1/2}a$ the concentration decays exponentially according to eq II.12 with a decay length

$$D = 2aP/\delta \qquad \text{(III.14)}$$

in agreement with the Flory argument (eq III.4). In the limit $P \rightarrow 1$ this reproduces the homopolymer result (eq II.14). Since there is only a fraction $f = 1/P$ of monomers contributing to the adsorption energy, the ground-state dominance approximation holds only for adsorption strengths P times larger than that of a homopolymer, the validity condition (eq II.13) becomes

$$f\delta \gg (24/M)^{1/2} \qquad \text{(III.15)}$$

Geometrically this corresponds to a confinement length D smaller than the radius of the chain R_G.

For a solid–liquid interface $g_s(z,z')$ is given by

$$g_s(\bar{z},\bar{z}') = \frac{\delta}{6}\left(\frac{3}{2P}\right)^{1/2} \frac{1}{2s^{1/2}}[e^{-2(\bar{z}-\bar{z}')s^{1/2}} \operatorname{erfc}[s^{1/2} - (\bar{z} - \bar{z}')] + e^{2(\bar{z}-\bar{z}')s^{1/2}} \operatorname{erfc}[s^{1/2} + (\bar{z} - \bar{z}')] - e^{-2(\bar{z}-\bar{z}')s^{1/2}} \operatorname{erfc}[s^{1/2} - (\bar{z} - \bar{z}')] - e^{2(\bar{z}-\bar{z}')s^{1/2}} s + (\bar{z} - \bar{z}')] \qquad \text{(III.16)}$$

The pole s_c exists for $\delta \geq \delta_c = aP/b\beta(P)$ where the function $\beta(P)$ is defined by $\beta = \operatorname{erf}(\bar{b}) - [(1 - e^{-\bar{b}})/\pi^{1/2}b]$ with $\bar{b} = (3/2a^2P)^{1/2}b$. In the limit where P is unity $\delta_c \sim a/b$. If P is much larger than unity the threshold is $\delta_c = (\pi/6)^{1/2}(a/b)P^{3/2}$. The threshold value is large, and the perturbation theory might be questionable in this case. We expect, however, these results to be qualitatively correct. The concentration profile of the adsorbed chain onto the solid wall is sketched in Figure 5b. It decays exponentially at large distances. When δ is slightly larger than δ_c, the decay length D is written as

$$D = \frac{aP}{\beta(P)^2(\delta - \delta_c)} \qquad \text{(III.17)}$$

and the asymptotic behavior for $P \gg 1$ is

$$D = \frac{\pi P^2}{6(\delta - \delta_c)}\left(\frac{a}{b}\right)^2 a \qquad \text{(III.18)}$$

in agreement with the Flory arguments presented above.

The previous approximations break down if δ is too large. A necessary condition for their validity is that the thickness of the layer D be larger than the blob size; i.e., $\delta < P^{1/2}$ (liquid–liquid interface) or $\delta - \delta_c < P^{3/2}$ (solid–liquid interface). At larger values of δ the concentration profile smoothly crosses over to the strong adsorption limit given in the previous section.

Throughout this section we have presented results for the adsorption of a copolymer in two extreme limits for the interface, which we have called liquid–liquid and solid–liquid situations. Practically, this led us to use two different statistical weights to describe the behavior of the nonadsorbed monomers: the Gaussian propagator G^0 for blobs at a liquid–liquid interface and the propagator G^i of an impenetrable wall for the blobs close to the solid–liquid interface. As mentioned at the end of section II the actual situations are often intermediate, the nonadsorbed monomers see a small attraction near a solid surface or a small depletion close to the liquid–liquid interface. The propagator for that intermediate situation may be approximated by[15]

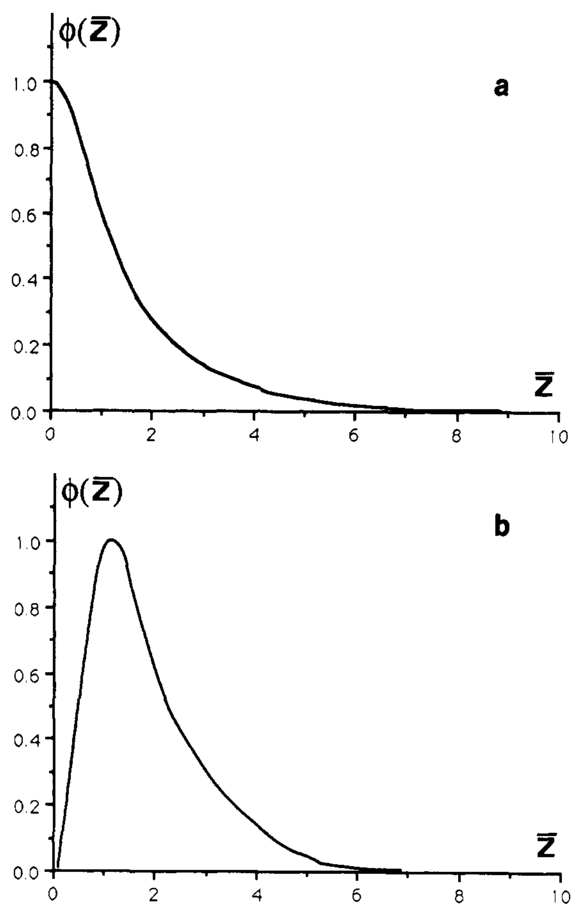

Figure 5. (a) Concentration profile of an adsorbed copolymer chain on a penetrable wall. The profile has been calculated numerically. $\phi(\bar{z}) = c^i(\bar{z})/c^i_{\max}$. $\bar{z} = (3/2a^2P)^{1/2}z$. The adsorption free energy is smaller than T, and the profile decays exponentially over a distance several times larger than $P^{1/2}a$. (b) Sketched concentration profile for the copolymer chain adsorbed on an impenetrable wall.

$$G_N^{i}(z,z') = \left(\frac{3}{2\pi N a^2}\right)^{1/2}\left[\exp\left(\frac{3(z - z')^2}{2Na^2}\right) - \exp\left(\frac{3(z + z' + 2D_B)^2}{2Na^2}\right)\right] \qquad \text{(III.19)}$$

where the interpolation length is $D_B = b\delta^B/(\delta_c^{\,B} - \delta^B)$, δ^B being the strength of the interaction acting on the nonadsorbed monomers. The size of confinement of the copolymer in the presence of a partially repulsive wall has a form similar to eq III.17

$$D = \frac{aP}{\Gamma(P)^2(\delta - \delta_c)} \qquad \text{(III.20)}$$

with $\Gamma = \operatorname{erf}(\bar{b} + \bar{D}_B) - [(1 - e^{-(\bar{b}+\bar{D}_B)}/[\pi^{1/2}(b - D_B)]]$ and $\delta_c = aP/b\Gamma(P)$ where $\bar{D}_B = (3/2a^2P)^{1/2}D_B$. Notice that when the interaction with the loops is such than $D_B \rightarrow \infty$ ($\delta^B \rightarrow \delta_c^{\,B}$), *we recover the phantom-wall situation* of eq III.14 with a zero threshold. On the other hand, if there is no interaction ($\delta^B = 0$), the wall is purely repulsive, $\Gamma(P) = \beta(P)$, and eq III.20 reduces to eq III.17. The introduction of a single parameter D_B allows a description of the crossover between a purely repulsive wall and a phantom surface.

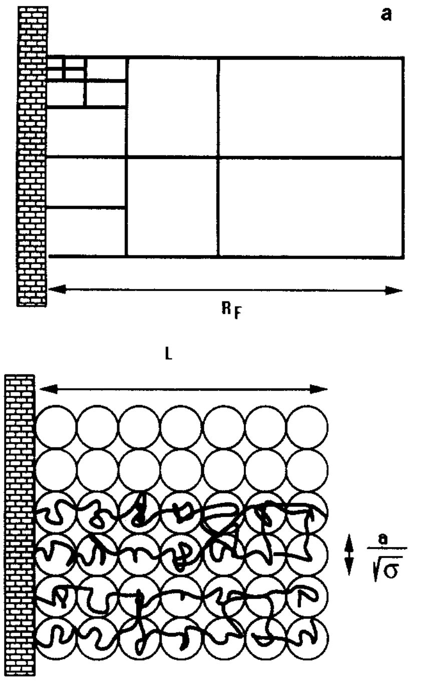

Figure 6. (a) Self-similar grid of a homopolymer solution adsorbed on a solid wall. (b) Brush of grafted polymer chains with excluded-volume interactions. Circles represent the blobs.

IV. Adsorption from a Dilute Solution

A single copolymer chain adsorbed on a wall makes a layer much thicker than a homopolymer, forming loops larger than the blob size $P^{1/2}a$. However, even if the bulk concentration of the solution in equilibrium with the wall is very small (way below the overlap concentration c^*), different chains overlap and form a continuous polymer layer. Isolated adsorbed chains turn out to be almost impossible to observe in the limit of large molecular weight. We now discuss the adsorption of copolymers from a dilute solution in the so-called plateau regime of the adsorption isotherm when the copolymer is in a good solvent. As mentioned in the introduction, this creates a somewhat intermediate structure between the so-called self-similar and grafted layers of homopolymers. These two configurations have been described in terms of blob models. We extend here these models to describe the copolymer layer. We then briefly discuss the interactions between two plates coated by copolymers.

1. **Adsorbed Layer.** An adsorbed homopolymer layer may locally be viewed as a semidilute solution but with a correlation length $\xi(z)$ that depends on the distance from the wall. The blob size $\xi(z)$ varies with the local volume fraction of monomers $\phi(z)$ as $\xi(z) \sim a\phi(z)^{-3/4}$. The self-similar structure proposed by de Gennes[2] and sketched on Figure 6a corresponds to $\xi(z) \sim z$, i.e., to a decay of concentration $\phi(z) \sim (a/z)^{4/3}$. The size of the layer is the size of the largest loops of the order of the radius of gyration of isolated chains $R_F \sim M^{3/5}a$ (M being the degree of polymerization).

The brush configuration is obtained by grafting the chains by one end on the surface with a density σ such that $\sigma(R_F/a)^2 \gg 1$. In the blob model proposed by Alexander[3] each chain is a linear chain of blobs of size $\xi \sim a\sigma^{-1/2}$ (Figure 6b). This leads to a brush thickness $L = Ma\sigma^{1/3}$. The concentration in the grafted layer is a constant all over the layer, except in a region of size D on the outside. The more refined model of Milner et al.[4] gives a precise description of the concentration profile, which is not constant over the layer. It gives, however, the same scaling behavior, and we use here the simpler blob model.

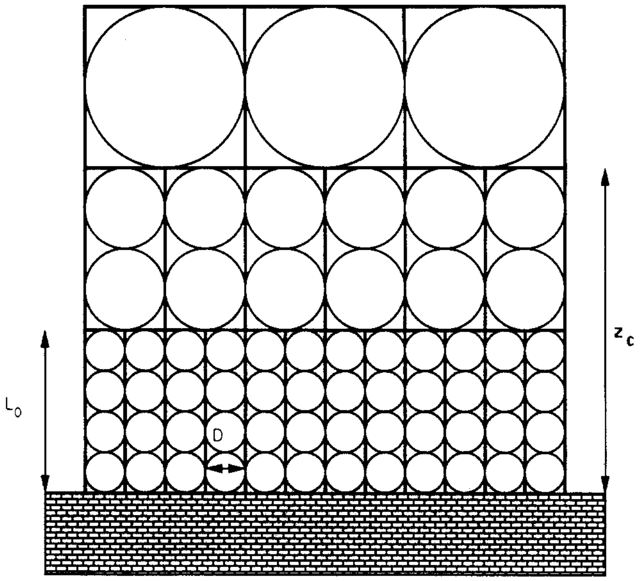

Figure 7. Blob picture for a random copolymer chain adsorbed from a dilute solution. For distances smaller than z_c the chains are stretched. On the outer side of this region the chains build a self-similar grid.

We now construct a blob model for a copolymer layer on a solid wall with preferential adsorption sites, i.e., sites to which the stickers of the polymer bind. In the very strong adsorption limit each of these sites must be in contact with a monomer A (notice that not all A monomers need to be on the surface). This for instance might be a good model for adsorption on silica colloidal particles where polymers adsorb on polar sites. The density between adsorbed sites σ_0 is chosen such that the distance between two of these neighboring sites is smaller than the size of a blob ($\sigma_0 P^{6/5} \gg 1$). The first layer of blobs made by the blobs in contact with the surface has thus a structure very similar to a brush: this layer obviously contains blobs where the two ends are on the wall; they also are in a brush configuration and behave as two chains with a degree of polymerization $P/2$ end-grafted on the wall. If we forget about numerical constants, the thickness of this layer is

$$L_0 = Pa\sigma_0^{1/3} \qquad \text{(IV.1)}$$

On top of this first blob layer there is a second generation of blobs, which are also in a brush configuration. The surface density σ_1 in this second layer is, however, smaller than that in the first layer: some blobs of the first layer have their two stickers on the wall and are not linked to a blob of the second layer; they do not contribute to the surface density in the second layer. Paralleling the construction of the self-similar grid, we assume that a finite fraction k of blobs does not make such small loops. We then build the layer recursively (Figure 7) by assuming that the ith generation has a surface density $\sigma_i = k\sigma_{i-1}$. The thickness of the ith blob layer is thus

$$L_i \sim k^{i/3}\sigma_0^{1/3}P \qquad \text{(IV.2)}$$

The thickness of the stack at the ith layer is

$$z_i = \sum_{j=0}^{i} L_j = Pa\sigma_0^{1/3}\frac{1 - k^{i/3+1}}{1 - k^{1/3}} \qquad \text{(IV.3)}$$

The concentration in the ith layer $\phi_i = \sigma_i^{2/3}$ may then be expressed as a function of the distance z from the wall

$$\phi(z) = \left(\frac{\sigma_0}{k}\right)^{2/3}\left[1 - (1 - k^{1/3})\frac{z}{Pa\sigma_0^{1/3}}\right]^2 \qquad \text{(IV.4)}$$

When the density σ_i in the ith layer becomes such that $\sigma_i P^{6/5} \ll 1$, individual blobs are not stretched any more and this construction reduces to the self-similar grid. This occurs at a thickness z_c

$$z_c = \frac{Pa}{1 - k^{1/3}}\sigma_0^{1/3}\left[1 - \frac{1}{P^{2/5}}\left(\frac{k}{\sigma_0}\right)^{1/3}\right] \simeq L_0 \qquad \text{(IV.5)}$$

of the order of a few times L_0.

At larger distances, the concentration decays as $z^{-4/3}$. The correct scaling form is obtained by imposing the good crossover at $z = z_c$

$$\phi(z) = \left(\frac{a}{z - z_c + P^{3/5}a}\right)^{4/3} \qquad \text{(IV.6)}$$

Notice that this self-similar region exists only if the chain is long enough

$$M > M_C \sim P^{5/3}\sigma_0^{5} \qquad \text{(IV.7)}$$

The thickness of the layer is $L \sim P\sigma_0^{1/3}$ if $M < M_C$ and $L \sim R_G \sim M^{3/5}$ if $M > M_C$.

If the surface does not have specific adsorption sites but attracts the A monomers with a finite free energy $-T\delta$, the surface density is obtained by minimizing the free energy of the layer

$$\frac{F}{T} = -\frac{\delta\sigma_0}{a^2} + \frac{F_{\text{conf}}}{T} \qquad \text{(IV.8)}$$

where F_{conf}/T is the conformational free energy of the chains. Its scaling behavior is obtained by integrating the excluded-volume free energy from the surface

$$\frac{a^2 F_{\text{conf}}}{T} \sim \int_0^\infty \phi^{9/4}\frac{\mathrm{d}z}{a} \sim P\sigma_0^{11/6} \qquad \text{(IV.9)}$$

The equilibrium surface density is

$$\sigma_0 = (\delta/\mathrm{P})^{6/5} \qquad \text{(IV.10)}$$

If the adsorption energy is smaller than T ($\delta \ll 1$), the regime where the chains are stretched does not exist ($\sigma_0 P^{6/5} \ll 1$). The concentration profile is given by eq IV.6 and $z_c \sim P^{3/5}a$. If the adsorption energy is larger than T ($\delta \gg 1$), the chains are extended close to the surface and form a self-similar grid at larger distances.

2. Interaction between Plates. We now briefly discuss the interaction between two flat plates coated by copolymers. This is a model for the interactions between colloidal particles and could also be compared to experiments with a mica force apparatus.[16] The plates are first put far apart and coated with the copolymer in a good solvent. The two layers are then approached by applying a force per unit surface Π_{ex}. We assume here that the adsorption is irreversible and that the total number of adsorbed copolymer molecules remains constant. The distance $2z$ between the plates at mechanical equilibrium is such that the osmotic pressure at the midplane $\Pi(z)$ is equal to Π_{ex}.

For polymer brushes, in between the plates the concentration is roughly constant and at short distances ($z < L = Na\sigma^{1/3}$) the force between plates varies with the distance z as

$$\Pi_{\text{ex}}(z) = (T/a^3)\sigma^{3/2}(L/z)^{9/4} \qquad \text{(IV.11)}$$

At larger distances the force is exponentially small.

For adsorbed polymer layers, locally the correlation length ξ is equal to z so that

$$\Pi_{\text{ex}}(z) = T/z^3 \qquad \text{(IV.12)}$$

Copolymer layers behave as brushes at short distances $z < L_0$. At large distances ($L_0 < z < z_c$) we obtain

$$\Pi \simeq \frac{T}{a^3}\left(\frac{\sigma_0}{k}\right)^{3/2}\left[1 - (1 - k^{1/3})\frac{z}{Pa\sigma_0^{1/3}}\right]^{9/2} \qquad \text{(IV.13)}$$

At larger distances this crosses over to the self-similar grid behavior

$$\Pi_{\text{ex}}(z) = \frac{T}{(z - z_c + P^{3/5}a)^3} \qquad \text{(IV.14)}$$

V. Conclusions

We have studied the adsorption of copolymers with stickers regularly distributed along the chain but otherwise repelled by the surface.

For a single Gaussian copolymer we found two regimes; a very strong adsorption regime where all the stickers are bound to the surface and where the chain makes small loops with a size equal to the blob size, and a weak adsorption regime where the chain may be viewed as a renormalized chain of blobs with the usual adsorption behavior.

The results of the simpler Flory theory are easily generalized to a chain in a good solvent. However, we have ignored the so-called proximal effects close to the hard wall, which for homopolymer strongly modify the adsorption behavior. They would certainly deserved a detailed study for copolymers.

Another major assumption is that we neglected the disorder of the copolymer chemical sequence: even for Gaussian chains it might be a relevant factor in some limits. It would also be interesting to see how it affects the proximal effects.

For the adsorption of a dilute solution in a good solvent, we proposed a blob model that crosses over smoothly between the self-similar structure and the brush behavior. This description is quite rough, and a more detailed study is certainly needed: we were not able to write down explicitly a free energy of the polymer layer that would give both the brush and the self-similar limit; this would be a first step toward a more precise description of copolymers layers.

On the experimental side we are not aware of any detailed quantitative study in the limit considered here. Our main result seems to be the existence of a large distribution of loops which could perhaps be observed by measuring the hydrodynamic thickness of copolymer layers adsorbed on colloidal particles. One could also make direct measurements with a mica force apparatus to probe the structure of the layer; the force between two flat plates has been discussed in section IV.2.

The adsorption of a single chain does not seem accessible experimentally; however, computer simulations could be useful to test some ideas presented here and to study the influence of disorder along the chain.

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Slow Spreading of Polymer Melts

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ABSTRACT: We discuss the precursor film profiles expected to be encountered during the spreading of large N polymer melts. We introduce a new control parameter: the ratio f of bulk to substrate monomer mobility. As a function of f, a variety of shapes are encountered. For $f \approx 1$, the "sliding" profile of Brochard and de Gennes is recovered. With increasing f the macroscopic "foot" predicted by Brochard and de Gennes diminishes in height and eventually vanishes. For large f, the precursor is found to spread by a new mechanism: reptation instead of hydrodynamic flow. The new precursor profile is characterized by a shoulder or step with a height on the order of the radius of gyration of the polymers.

I. Introduction

The macroscopic properties of drops of low-viscosity fluids spreading over dry and smooth substrates are well understood.[1] The drop has the shape of a hemispherical cap whose radius increases with time and whose contact angle θ with the substrate decreases with time (Figure 1). The spreading velocity U of the drop is determined by a competition between the capillary pressure, favoring spreading, and viscous losses. This competition is expressed in Hoffman's law: $U \propto (\gamma/\eta)\theta^3$, with η the viscosity and γ the surface tension. Importantly, this spreading velocity is *not* dependent on the difference in surface energy of a wet and a dry surface. A measure of that difference is the spreading pressure S, defined by

$$S = \gamma_{sv} - \gamma_{sl} - \gamma \tag{1}$$

with γ_{sv} and γ_{sl} respectively the energy per unit area of the dry and the wet substrate. Of course, a positive value for S (wetting) is a necessary condition for spreading. For negative S (nonwetting), the contact angle is fixed by Young's law[2] $\gamma \cos(\theta) = \gamma_{sv} - \gamma_{sl}$.

It has been known since the days of Hardy that ahead of the macroscopic drop there exists a microscopically thin precursor film. This precursor film is due to the film-thickening "disjoining" pressure exerted by van der Waals forces between substrate and film. The driving force for the spreading is the combined effect of gradients in the capillary pressure and the disjoining pressure. The height profile $\zeta(x)$ of the precursor film was predicted, by Joanny and de Gennes[1,3] (JG), to be proportional to $1/x$, with x a coordinate along the substrate and perpendicular to the contact line (see Figure 1). The precursor film starts when the thickness of the droplet has fallen below a height a_0/θ, with $a_0 = (A/6\pi\gamma)^{1/2}$ a microscopic length (A is the Hamaker constant). Naively, we should have expected the drop to spread until its height has been reduced to that of a monolayer. JG predicted instead that due do the disjoining pressure, there should be a minimum height $e \approx a_0(\gamma/S)^{1/2}$, such that ζ cannot drop below e.

The spreading properties of drops of polymer melts are of particular intereres for technical applications (lubrification, paints, etc.). Because they are nonvolatile and because of their slow spreading velocities, large N polymer melts (with N the degree of polymerization) would be expected to provide us with a test case for the JG theory of precursor films. However, already the macroscopic spreading properties of polymer melt droplets offer unexpected features: the spreading velocity sometimes exceeds Hoffman's law[4] and deviations from the macroscopic drop shape have been noted.[5,6]

Recently, polarized reflection microscopy by Ausserre et al.[7] of drop profiles of large N (10^4–10^6) poly(dimethylsiloxane) (PDMS) melts, spreading over smooth silica surfaces, confirmed Hoffman's law. Detailed ellipsometry measurements by Leger et al.[8,9] showed that the drop thins out to a limiting thickness that is in fair agreement with the predicted value of e. They did find a precursor film, but the measured profile was in clear disagreement with the calculated profiles.[10]

Brochard and de Gennes[11] (BG) noted that we indeed should expect the precursor profiles of polymer melt droplets to be unusual. Because large N polymers are entangled with each other, polymer melts will resist shear flow. A precursor film spreading under a pressure gradient normally can only do so by shear flow because the flow velocity at the substrate is assumed zero. For large N melts, this is an unlikely scenario. One would rather expect[12] a thin melt film subjected to a pressure gradient to slip and slide over the substrate. If k is the friction coeffi-

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