Can a Polymer Brush Trap a Wetting Layer?

A. Johner and C. M. Marques

Institut Charles Sadron, 67083 Strasbourg CEDEX, France

(Received 14 January 1992)

Grafted polymer layers are well known as stabilizing agents in colloidal dispersions. Here we show how these polymer "brushes" may also deeply modify wetting phenomena by favoring the formation of stable wetting layers of microscopic size. We discuss in particular the influence of a solvated polymer layer on the wetting properties of the substrate by a second minority solvent. In the case where the brush prefers the second solvent, this solvent may be drawn to the interface even if it would not ordinarily wet the substrate. On the contrary, a solvent that ordinarily forms a thick wetting layer may be partially inhibited from doing so (forming a thin trapped layer) if it is a worse solvent for the brush.

A grafted polymer layer, also known as a "brush," is an interfacial structure that can be built by end attachment of homopolymer chains to a surface. For large enough grafting densities the chains interact strongly and stretch out to reduce the excluded-volume energy. The overall properties of the brush thus result from the balance between the osmotic and the stretching energies. As first shown by Alexander and de Gennes [1,2] this balance leads to a conformation where the chains are strongly stretched and the elastic energy per chain is much larger than $k_B T$. Typically the layer thickness ranges from 10 to 100 nm and the elastic energy per chain from $5k_B T$ to $20k_B T$ [3]. Grafted polymer layers are often used to stabilize colloidal dispersions, where a brush corona prevents the hard colloidal core from flocculation that would otherwise occur because of the omnipresent van der Waals interactions [4]. The detailed mechanisms that prevent flocculation have been extensively studied during the last few years and are now well understood. Less attention, however, has been paid to the role of a polymer brush on other interfacial phenomena of major importance, such as the electrical double layer [5] or wetting [6]. In this Letter we address this last problem by considering a wetting film that grows from a mixture of two solvents, on a surface already covered by a polymer brush. As we will show below, the grafted layer may allow the formation of stable thin films.

We first investigate the influence of the wetting film on the polymer layer within the framework of the self-consistent mean-field theory which has recently been proposed to describe the brush structure [7,8]. As a result of strong stretching, fluctuations around the most probable configuration are neglected and the chain path $z(n)$ minimizes the chemical-potential functional $k_B T \int_0^N [(1/2a^2) \times (dz/dn)^2 + v\Phi(z)] dn$. Here, n is a monomer index ranging from 0 at the free end of the chain to N at the wall, $\Phi(z)$ the monomer concentration at a height z from the wall, v an excluded-volume parameter which accounts for the quality of the solvent, and a the size of a monomer (hereafter we will choose units of energy where $k_B T = 1$ and units of length where $a = 1$). Because of the formal equivalence to the Maupertuis principle in classical

mechanics the chain can be mimicked by the trajectory of a fictitious particle moving in the mechanical potential $-U = -v\Phi(z)$, the monomer number n then being the equivalent of time. We assume the brush chains to be monodisperse; the flight time $n(z_0)$ of any particle starting at a distance z_0 from the wall must thus be independent of the starting point z_0 and equal to the polymerization index N. This constrains the potential $U = v\Phi(z)$ to be parabolic, provided that there is a continuous distribution of the chain ends over all the layer thickness. The monomer concentration can then be written as

$$\Phi(z) = \frac{1}{v} \frac{\pi^2}{8N^2}(L_0^2 - z^2), \tag{1}$$

where L_0 corresponds to the layer thickness. The thickness is determined from the monomer conservation, $L_0 = (12/\pi^2)^{1/3} v\sigma^{1/3} N$, with σ the density of chains per unit surface. All the chains whose free ends are at a given distance z_0 larger than z contribute to the total monomer concentration at z; one thus has

$$\Phi(z) = \int_{z_0}^{L} \frac{\rho(z_0) dz_0}{\{2[U(z) - U(z_0)]\}^{1/2}}, \tag{2}$$

from which the distribution of free ends $\rho(z_0)$ can be obtained. The free energy density per unit surface for the brush can be calculated by integrating the chemical potential $NU_0 = Nv\Phi(0)$ from a bare surface to the actual surface density σ:

$$F_0 = \int_0^\sigma U_0(\sigma') d\sigma' = \frac{9}{10} \left[\frac{\pi^2}{12} \right]^{1/3} v^{2/3} N \sigma^{5/3}. \tag{3}$$

When an external potential $f(z)$ acts on the monomers, the total potential does not reduce to the osmotic contribution $v\Phi(z)$; one has instead

$$U = v\Phi(z) + f(z). \tag{4}$$

In the case where $f(z)$ is a small perturbation the brush properties can be derived from the linear response theory recently proposed by Marko and Witten [9]. We consider here situations where $f(z)$ is much larger than $v\Phi(z)$, and one then needs to work beyond linear response. The

brush properties can, however, be derived as for the free brush, as long as the resulting chain end distribution remains positive. This is the case if the slope of the external field $df(z)/dz$ is everywhere larger than the slope of the parabolic potential (note that the parabolic slope is negative) so that the monomer concentration profile decreases monotonically from the surface. Otherwise there is an exclusion zone where no chain ends are present and where the total potential is no longer parabolic. The relevant external potential for the wetting problem that we consider is, in the sharp-kink approximation [10], of the form $f(z) = \epsilon\Theta(z-d)$, a step function of amplitude ϵ and length d, where ϵ is given by the difference of the chemical potentials of the polymer in the two solvents, $\epsilon = \chi_w - \chi$ (χ_w being the Flory interaction parameter of the polymer with the wetting solvent). For negative values of ϵ the concentration profile always decreases from the surface, with a discontinuity at d. The concentration profile and brush thickness read in this case

$$\Phi(z) = \frac{1}{v}\frac{\pi^2}{8N^2}(L^2-z^2) - \epsilon\Theta(z-d), \qquad (5)$$

$$L = L_0\left[1 + \frac{3}{2}\frac{\epsilon}{U_0}\frac{d}{L_0}\right]^{1/3}. \qquad (6)$$

Equations (5) and (6) hold for small enough values of the step strength $|\epsilon|$ and thickness d. In this regime the chain ends are only partially confined inside the region of the external potential. If we increase the step thickness at constant strength we reach a point where the brush and the step thickness are identical [line b in the parametric plane (ϵ,d) of Fig. 1]. For a larger step length the brush height remains fixed at d until it reaches its natural length L_0. In this regime all the chain ends are confined inside the external potential region and the free energy difference $\Delta F = F - F_0$ is given by

$$\Delta F = F_0\left[\frac{5}{9}\frac{L_0}{d} + \frac{5}{9}\left(\frac{d}{L_0}\right)^2 - \frac{1}{9}\left(\frac{d}{L_0}\right)^5 + \frac{N\sigma\epsilon}{F_0} - 1\right].$$

$$(7)$$

For still larger values of d the grafted layer is not perturbed.

When the external field is positive ($\epsilon > 0$) an exclusion regime exists in the (ϵ,d) phase diagram. We first address the case where the step length is small enough (or the interaction strength ϵ strong enough) to totally exclude the chain ends from the wall up to the distance d. In the outer region, where the step potential vanishes, we can invert Eq. (2) to evaluate the end density from which
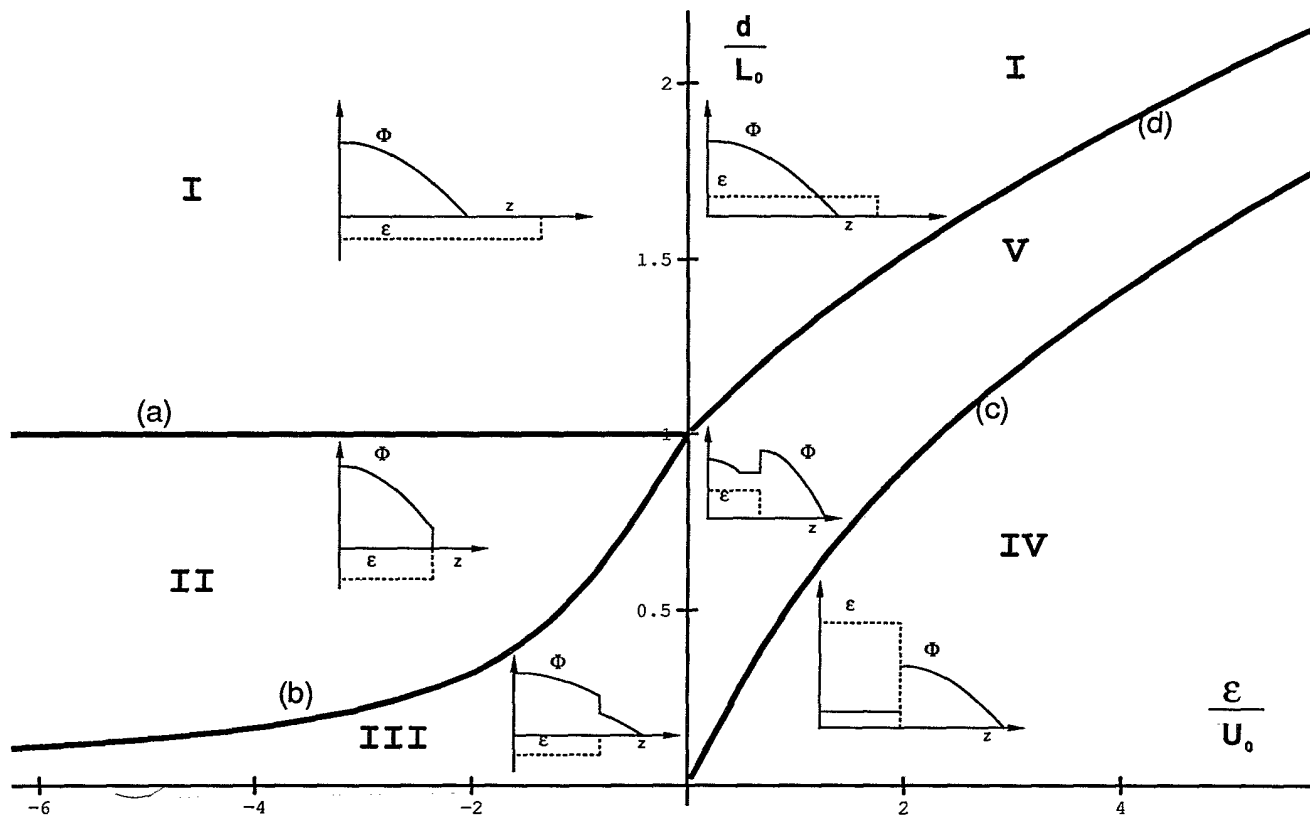

FIG. 1. Phase diagram for a grafted layer which interacts with an external potential of the form of a step function with amplitude ϵ and length d. (I) Unperturbed regime. (II) Total confinement of the chain ends. (III) Partial confinement. (IV) Total exclusion of chain ends. (V) Partial exclusion. The situations discussed in the text correspond to regimes IV (thin trapped layer) and II (thick trapped layer). This last regime lies in practice very close to line a.

the value of the potential in the exclusion zone can be obtained:

$$\frac{\epsilon}{U_0} = \frac{2}{\pi}\left[1+\frac{U-U_0}{U_0}\right]\arctan\left[\frac{U-U_0}{U_0}\right]^{1/2}$$
$$+\frac{2}{\pi}\left[\frac{U-U_0}{U_0}\right]^{1/2}, \quad z<d. \tag{8}$$

Equation (8) shows that the total potential U is uniform over the entire exclusion zone and discontinuous at d. We measure the discontinuity by the increment $\eta = U - U_0$. For small values of the field strength ϵ this increment is quadratic in ϵ, $\eta \simeq \pi^2\epsilon^2/16U_0$ (the discontinuity of the concentration profile is stronger, of order ϵ) and approaches ϵ, $\eta \simeq \epsilon$, for arbitrarily large values of the field strength (the discontinuity of the concentration profile then approaches U_0/v). In order to calculate the free energy increase of the brush we consider a particular chain with a free end at the tip of the exclusion zone. This chain needs $d/\sqrt{2\eta}$ steps to cross the exclusion zone at a potential $U_0+\eta$ and thus has $N = d/\sqrt{2\eta}$ monomers dangling just behind d (in the potential U_0). The total free energy difference $\Delta F = F - F_0$ is therefore given by

$$\Delta F = d\int_0^\sigma \sqrt{2\eta(\sigma)}\,d\sigma. \tag{9}$$

When ϵ is too small (or d too large) the exclusion zone does not start at the wall but there is, close to the wall, a region where the potential is parabolic. At the threshold of total exclusion the few "parabolic" chains dangling on the wall are in chemical equilibrium with the excluded ones, which locates the crossover line at $d_c = N\sqrt{\eta/2}$ (line c in the phase diagram). On the other hand, when the step length is very large the brush is unperturbed. The transition to the unperturbed regime (line d) occurs for $d > L_0$: The chains stretch in order to escape the high potential region. This separating line can again be determined by the argument of equal chemical potential which leads to

$$d = \tfrac{1}{2}L_0\{[(\epsilon/U_0)^{1/2}+(U_0/\epsilon)^{1/2}]\arctan(\epsilon/U_0)^{1/2}+1\}.$$

The detailed description of the concentration profiles and of the free end distributions in the partial and total exclusion regimes can be obtained from the equal-time requirement; the derivation is, however, quite lengthy and will be presented elsewhere [11]. We next use these results to discuss the influence of the polymer brush on wetting.

The main contribution of the grafted polymer layer to the wetting growth (up to a small contribution from the headgroups that only shifts the transition point) arises from the interaction of the wetting layer with the polymer brush and is measured by the parameter ϵ introduced above. Note that ϵ is positive when the polymer is less soluble in the wetting layer than in the majority solvent. Considering a van der Waals disjoining pressure we can

write for the relevant contributions to the interfacial free energy,

$$F = -S+A/12\pi d^2+F_{\text{int}}, \tag{10}$$

where the first term stands for the spreading power, the second term accounts for the nonretarded van der Waals interactions with the wall, and the third term is for the interaction with the brush. If the two solvents are not at coexistence, an extra term proportional to the shift of the chemical potential must be added [10]. Depending on the relative signs of the Hamacker constant A, of the spreading power S, and of the relative quality of the solvents ϵ, one may consider several situations. In the following we discuss two configurations where the wetting layer can be trapped by the polymer brush.

The first case concerns the formation of a wetting layer of a poorer solvent of the polymer (ϵ is positive) that spreads onto the wall (S is positive) and has an intermediate polarizability between the wall and the exterior solvent (A is then positive). The interaction energy with the polymer brush is given by Eq. (9) and the thickness d of the wetting layer is obtained by minimization of the free energy (10); when the difference in the quality of the two solvents is finite ($\epsilon N^3 \gg 1$) we have

$$d = [A/6\sqrt{2}\pi]^{1/3}\sigma^{-1/3}\epsilon^{-1/6}. \tag{11}$$

The wetting layer thus extends over a distance of a few correlation lengths of the polymer in the brush. It may typically range from 30 to 100 Å (ϵ, which may in principle vary from 0 to 1, has a small influence on the final result). The correlation length, also known as the "blob size," scales as $\sigma^{-1/3}$ in a mean-field calculation. It is well known, however, that the proper blob size in a brush, when deviations from mean field are accounted for, is the distance D between attachment points which scales instead as $\sigma^{-1/2}$ [2]. A simple Flory argument gives the scaling behavior $d \simeq A^{1/3}\sigma^{-1/2}(\epsilon/U_0)^{-1/5}$ which gives an exponent to ϵ close to the mean-field result (11). Note that the stability of the layer is easily ensured since for the usual situations one has $S \sim k_BT/a^2 \gg A/D^2$.

A second "trapping" configuration arises when the wetting layer (a) has a larger polarizability than the wall or a smaller polarizability than the solvent of reference (the Hamacker constant A is negative and the disjoining pressure tends to prevent the formation of a wetting layer); (b) is a better solvent of the polymer than the solvent of reference (ϵ is then negative). We calculate the equilibrium thickness of the wetting layer from Eqs. (7) and (10). For finite solvent quality differences ($|\epsilon|N^3 \gg 1$) the layer thickness is equal to the unperturbed brush size L_0 (up to corrections of order AN^{-3}); in this configuration the wetting liquid layer extends over the whole brush. These two configurations, which are more likely to be observed experimentally, correspond to regime IV and regime II, close to line a, in the (ϵ,d) phase diagram.

In summary, we have shown how the presence of a

polymer grafted layer onto a surface may induce large qualitative changes on the wetting of this surface by a simple liquid. In particular it is possible, with the appropriate choice of the polymer and the two solvents, to constrain inside the polymer brush a wetting layer which would otherwise grow to a macroscopic size. The thickness of this inhibited layer is mainly controlled by the grafting density and is of the order of the spacing between grafting points. The brush then imposes a large energy scale allowing for a detailed study of the wetting transition itself when coexistence is approached at fixed temperature or when the transition is induced by a temperature change at coexistence. In any case the presence of a strong interaction of the wetting liquid with the polymer can in principle be a factor for widening the gap (in temperature or chemical potential) where the transition can be experimentally monitored. In nonwetting conditions a forced layer with a thickness of the order of the brush size can also be obtained. Finally it is worth noting that the results presented above hold not only for wetting of simple liquids but also, to a certain extent, for wetting by a second polymer in a poor solvent. More generally they show that an exclusion zone may appear in any problem where a repulsive, monotonically decreasing potential acts on the brush. This could be in particular relevant for grafted layers of charged polymers [5].

[1] S. Alexander, J. Phys. (Paris) **38**, 983 (1977).
[2] P. G. de Gennes, J. Phys. (Paris) **37**, 1443 (1976).
[3] P. Auroy, L. Auvray, and L. Léger, Phys. Rev. Lett. **66**, 719 (1991).
[4] D. H. Napper, *Polymeric Stabilization of Colloidal Dispersions* (Academic, London, 1983).
[5] P. A. Pincus, Macromolecules **24**, 2912 (1991).
[6] A. Halperin and P. G. de Gennes, J. Phys. (Paris) **47**, 1243 (1986).
[7] S. Milner, T. Witten, and M. Cates, Europhys. Lett. **5**, 413 (1988).
[8] E. B. Zhulina and T. M. Birshtein, Vysokomol. Soedin. Ser. A **28**, 2589 (1986).
[9] J. F. Marko and T. A. Witten, Phys. Rev. Lett. **66**, 1541 (1991).
[10] M. Schick, in *Liquids at Interfaces*, edited by J. Charvolin, J. F. Joanny, and J. Zinn-Justin (North-Holland, Amsterdam, 1990).
[11] J. F. Marko, A. Johner, and C. M. Marques (to be published).