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Properties of Polymer Layers Adsorbed on Surfaces under Nonequilibrium Conditions

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ABSTRACT: The properties of polymer coated surfaces which are incompletely saturated are studied using both mean field theory and the scaling theory of polymer adsorption from a semidilute solution (in good solvents), introduced by de Gennes. We obtain theoretical predictions for the force (per unit area) between two such surfaces as a function of interplate separation. We also give the concentration profiles between the surfaces. Both in mean field and in scaling theory the results that we obtain for incompletely saturated surfaces are qualitatively different from those found in the saturated case. In particular: (i) to lowest order in mean field, interactions between incompletely saturated surfaces do not vanish (as happens in the saturated case) but rather are attractive at any interplate separation; (ii) the scaling theory predicts that, in contrast to interactions between saturated surfaces which are always repulsive in good solvents, any surface excess lower than the one corresponding to thermodynamic equilibrium will lead to attractive long distance interactions; we obtain a new set of exponents characterizing this behavior; (iii) the form of the concentration profiles as the interplate separation decreases suggests that, for incompletely saturated surfaces, bridging configurations are more favorable than nonbridging ones: this is not the case for saturated plates. An attempt has been made in this paper to spell out in some detail the experimental conditions under which our results should apply. Experimentally, attractive interplate interactions have been found: these findings agree qualitatively with our results.

1. Introduction

The interactions between polymer solutions and solid surfaces have been the subject of extensive study in recent years.[1-16] They are important in many areas of materials technology: in particular adsorbed layers of polymer are commonly used to control the stability of colloidal dispersions. Interest in this area is heightened by the fact that experimental methods[8-16] are becoming sufficiently refined to probe in detail and in a quantitative way the properties of the solid–solution interface.

Much effort has gone toward formulating theoretical treatments capable of predicting the outcome of experimental investigations. For semidilute solutions a considerable step forward in this direction occurred when de Gennes[2] extended to this problem the Cahn[17] model for interfacial tension and wetting in simple fluids. The de Gennes approach gives, in terms of a limited number of parameters, the concentration profile in proximity of the interface and the force between two polymer adsorbed surfaces. The prediction for the force plays a special role:

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this is because the result is very sensitive to the type of assumptions made in the theory and because direct measurements of the forces between polymer-coated plates can be performed by using the mica technique initiated by Tabor and Israelachvili.[18]

In his work, de Gennes considered situations, where, before performing the force measurements, the surfaces are allowed to reach thermodynamic equilibrium with the solution (saturated surfaces): in a recent paper[7] we used the de Gennes scaling approach to examine the effect of incomplete saturation. We found that the interactions between polymer coated plates in the unsaturated case are qualitatively different from those predicted by de Gennes for saturated surfaces. In particular, while the scaling theory predicts that the interactions between saturated surfaces are always repulsive, we found that any surface excess lower than the one corresponding to saturation leads to attractive long distance interactions. We also gave a new set of exponents characterizing the long-range attraction and the position of the attractive minimum in this regime. This paper describes further results that we obtained for the unsaturated case: in particular, we give the form of the concentration profile and compare the predictions of the scaling theory with those obtained from the corresponding mean field treatment.

In order to clarify what we mean by unsaturated surfaces let us consider the force measurement experiment in detail. We assume that the experiment has been prepared according to the following three-stage model history. In the first stage (incubation) the plates are placed in a dilute polymer solution. In the second stage (washing) the solution is replaced with pure solvent at the same temperature. At the end of this stage, only polymer chains irreversibly attached[19] to the plates remain in the system. These chains may be thought of as being in equilibrium[20] with the pure solvent (i.e. with a polymer solution whose bulk concentration is zero).

We define the surface excess (coverage) Γ on each plate by

$$\Gamma = \int_0^h c(z)\,\mathrm{d}z \tag{1}$$

where $c(z)$ is the concentration profile in the direction z perpendicular to the surface of the plates and $2h$ is the separation between the plates. At the end of the washing stage, one has the largest possible surface excess if the following two conditions are satisfied: (i) throughout the incubation stage the separation $2h$ between the plates was kept large (much larger[21] than the Flory radius of the chains R_F) and (ii) the plates were incubated for a time sufficiently long to allow them to come in thermodynamic equilibrium with the solution. Under these conditions we shall say that the surfaces are saturated. We shall denote with Γ_0 the saturation surface excess at the end of the washing stage. We shall call unsaturated (or incompletely saturated), surfaces whose coverage is lower than Γ_0. Unsaturated surfaces may occur because the incubation time is too short for thermodynamic equilibrium to set in or because the separation of the plates during incubation is smaller than R_F.[22] It should be stressed that, since it is in equilibrium with the pure solvent used to replace the dilute solution, the surface excess Γ at the end of the washing stage does *not* depend on the incubation concentration.[23]

During the third and final stage (measurement) the force is measured for different values of the separation $2h$ between the plates: since the polymer left in the system is irreversibly adsorbed to the plates, it is assumed that throughout this stage the coverage Γ does not change with h: i.e., Γ remains the same as it was at the end of the washing stage.

The prescriptions outlined above have been closely followed in a few[16] of the mica plates experiments reported so far; however, force measurements have also been carried out under different experimental conditions: in particular, often the second stage (washing) is not performed. The theoretical interpretation of experiments done in this way is delicate. Consider in particular, force measurement taken for separations $2h$ smaller[24] than the Flory radius of the chains; for these values of the separation h the motion of chains between the plates is sterically hindered. As a result, surface excesses Γ larger than the saturation coverage Γ_0 are to be expected.[25] However, the precise value of Γ in this situation is essentially beyond control: it depends on how the plates have been brought to their positions and it may also be weakly time dependent.

As it was pointed out in ref 7, there are several reasons to extend the de Gennes approach to unsaturated surfaces. First, for neutral polymer in good solvent (to which the theory refers) thermodynamic equilibrium is hard to achieve and requires very long incubation times; furthermore, some desorption may take place in the washing stage of sample preparation: as a result coverages slightly below the saturation value are likely to be commonplace. Secondly, since it is possible to carry out experiments where Γ can be chosen to have values smaller than Γ_0, there exists a whole new class of situations which can be used to test our theoretical ideas. Finally, flocculation can be induced in a dispersion of solid colloidal particles by adding a very small amount of polymer.[26] The organization of flocs obtained in this way is currently being investigated by using neutron scattering techniques.[27] A theoretical analysis of the situations studied in this way so far is made difficult by the fact that polyelectrolyte is used and that kinetic effects are probably dominant. Nonetheless, attractive interparticle interactions due to incomplete saturation may play a role in inducing flocculation.

This paper is organized as follows: in the rest of this Introduction we discuss briefly the type of information that can be obtained from the de Gennes approach and the conditions under which it is valid. Section 2 and 3 give the mean field and the scaling theory treatment for unsaturated surfaces, respectively: we obtain results both for the force and the concentration profiles. Conclusions and a brief discussion are given in section 4.

In the de Gennes theory of polymer adsorption one writes the effective surface free energy as a functional of the concentration profile. Under a number of conditions (which are realized reasonably often in practice) this functional can be written in a simple form containing only a limited number of parameters. One obtains measurable quantities such as the concentration profiles or the force between plates by minimizing the functional. As a result the theory does *not* make appeal to a specific adsorption mechanism (type of chain configurations, bridging) and it is global in this sense.

Two characteristic length scales D and R_F[28] enter the problem. D is a measure of the strength of the monomer–surface attraction: only if one looks at an adsorbed chain over distances larger than D, does the energy of sticking associated with that chain exceed[29] kT. The precise definition of D in terms of the other parameters in the theory will be given below. The predictions of the theory are expected to be valid for the range $D < z < R_F$ (central region).

For distances larger than R_F (distal region) the concentration profile falls exponentially to zero (as does the force between two polymer adsorbed plates). For the region $z < D$ (proximal region), computer simulations[3] and enumeration[4] studies suggest a singular behavior[5] for the concentration profile. De Gennes original treatment[2] assumed a regular concentration profile close to the surface and must be modified to deal with this region. Since in this paper we shall only be interested in the range[30] $D < z < R_F$, we shall follow the original de Gennes assumption.

The surface free energy functional, which is the central object in the theory, is written as the sum[31] of a surface and a "bulk" contribution. In general, the surface contribution is expressed as an expansion in powers of the surface volume fraction: the coefficient of each term in the expansion is an additional parameter entering the theory. When the sticking energy associated with a single monomer–wall contact is much smaller than kT, we expect the concentration at the surface to be much smaller than 1. In this case (weak coupling limit) only the linear term in the expansion needs to be retained. To work with the minimum number of parameters, we shall assume weak coupling throughout this paper.

The "bulk" contribution to the surface free energy is an integral over space of a function of the local concentration and its gradient. In de Gennes' theory, this function incorporates the scaling properties of the solution; in mean field theory, it is the simplest possible expansion in the (mean field) order parameter and its gradient (a Landau–Ginzburg expansion): it extends the standard Flory–Huggins picture for polymer solutions to allow for concentration gradients. As anticipated above, the predictions for the force between two polymer adsorbed plates are very sensitive to the detailed form of the surface free energy functional. In particular, for saturated plates, to lowest order in mean field, surface and "bulk" term conspire to give a null force between the plates; scaling theory predicts, instead, a repulsion between the plates at any separation. As we shall see, in both cases, incomplete saturation has the effect of producing an attraction between the plates at large separations: indeed, within the framework of lowest order mean field theory attraction persists at any interplate separation, whereas the scaling description predicts that at small separation repulsion will set in.

The formalism just outlined was developed to treat the case of neutral polymer in good (and Θ) solvents: nonetheless, in the same framework, functionals which are appropriate to certain classes of poor solvent conditions can also be written down:[6] unfortunately, in these cases additional parameters enter the description. Hereafter we shall only deal with neutral polymer solutions above the Θ-point.

2. Mean Field Theory

In this section we work out the results of mean field theory in some detail. This is for two reasons: first it is useful to be able to compare the correct scaling results with those of the more naive mean field approach; secondly these results should describe adequately the "moderately concentrated" regime where mean field averaging[32] is applicable.

In the mean field theory approach to polymer problems where the concentration is variable in space one introduces[33] the mean field order parameter $\psi(z)$ (in the specific case of adsorption from a flat surface, this depends only on the coordinate z perpendicular to the surface) related to the local concentration $c(z)$ and to the volume fraction $\Phi(z)$ by

$$|\psi(z)|^2 = c(z) = \Phi(z)/a^3 \qquad (2)$$

where a is the monomer size. We want to describe the system during the measurement stage of our model history. At this stage there is no exchange of polymer with a reservoir,[34] and we write the free energy (per unit area) γ describing polymer adsorption as

$$\gamma - \gamma_0 = -|\gamma_1|\psi_s^2 a^3 + kT\int_0^h \mathrm{d}z \left[\frac{a^2}{6}\left(\frac{\mathrm{d}\psi}{\mathrm{d}z}\right)^2 + \frac{v}{2}\psi^4\right] \qquad (3)$$

Here γ_0 is the interfacial energy of the pure solvent; γ_1 is a local solute–interface interaction energy per unit area (it is negative for adsorbing walls); ψ_s is the value of $\psi(z)$ at the surface (we have taken $\psi(z)$ to be real); a is the monomer size and v is the excluded volume parameter. Note that three-body and higher order interactions contained in the Flory–Huggins free energy are neglected in (3).

In line with our assumption of irreversible adsorption (constant coverage Γ) throughout the measurement stage, we minimize the free energy γ subject to the constraint that the coverage Γ does not change with h. In order to do so we introduce a Lagrange multiplier (pseudochemical potential) μ and look for the extremum of the functional

$$\gamma - \gamma_0 - \mu\Gamma = -|\gamma_1|\psi_s^2 a^3 + \frac{kT}{2}\int_0^h \mathrm{d}z \left[\frac{a^2}{3}\left(\frac{\mathrm{d}\psi}{\mathrm{d}z}\right)^2 + v(\psi^4 - \mu'\psi^2)\right] \qquad (4)$$

where μ' is related to μ by $\mu = kTv\mu'/2$. The Euler–Lagrange equation for $\psi(z)$ is then

$$\frac{a^2}{3v}\left(\frac{\mathrm{d}\psi}{\mathrm{d}z}\right)^2 = \psi^4 - \psi_m^4 - \mu'(\psi^2 - \psi_m^2) \qquad (5)$$

where ψ_m is the value of ψ at the midpoint between the plates. The boundary conditions at the surface are obtained substituting (5) back into (4) and minimizing with respect to ψ_s

$$\left.\frac{1}{\psi_s}\frac{\mathrm{d}\psi}{\mathrm{d}z}\right|_s = -\frac{1}{D_{mf}} = -\frac{6|\gamma_1|a}{kT} \qquad (6)$$

Using (5) and (6) one can write μ' as

$$\mu' = \psi_s^2 + \psi_m^2 - \frac{a^2}{3vD_{mf}^2}\frac{\psi_s^2}{(\psi_s^2 - \psi_m^2)} \qquad (7)$$

Note that since $|\gamma_1|a^2$ is the free energy associated with a single monomer–wall contact, $\delta = (kT/|\gamma_1|a^2)$ is the number of contacts needed to overcome thermal fluctuations. The linear dependence (6) of the length D_{mf} on δ is characteristic of the intersection of a Gaussian chain with a plane. The weak coupling condition implies $D_{mf} \gg a$.

Let us consider the single plate problem (i.e. the limit $h \rightarrow \infty$) in the saturated situation. At the end of the washing stage the surface carrying adsorbed polymer is in thermodynamic equilibrium with pure solvent: therefore, to find the concentration profile in this situation we solve (5) with $\psi_m = 0$ and $\mu' = 0$: using (7) we get

$$c(z) = \frac{a^2}{3v}\frac{1}{(z + D_{mf})^2} \qquad (8)$$

and the corresponding saturation coverage Γ_0 is

$$\Gamma_0 = \int_0^\infty c(z)\,\mathrm{d}z = \frac{a^2}{3vD_{mf}} \qquad (9)$$

Hereafter we shall denote with $c_{s0} = \psi_{s0}^2 = a^2/3vD_{mf}^2$ the value of the concentration on the surface of a single saturated plate (after washing). It is convenient to normalize the concentration with c_{s0}: i.e., to introduce the reduced variable

$$y(z) = \psi(z)/\psi_{s0} \qquad (10)$$

and the reduced pseudochemical potential

$$\tilde{\mu} = \frac{\mu'}{c_{s0}} = y_s^2 + y_m^2 - \frac{y_s^2}{(y_s^2 - y_m^2)} \qquad (11)$$

where y_s and y_m are the surface and midpoint values of $y(z)$, respectively.

The case of a single incompletely saturated plate is also amenable to a simple analytic solution. Letting $\psi_m = 0$ in (5) and (7), one can determine $\tilde{\mu}$ as a function of the surface excess: one finds

$$\tilde{\mu} = -\left(1 - \frac{\Gamma}{\Gamma_0}\right)^2 \qquad (12)$$

and

$$y_s^2 = \frac{\Gamma}{\Gamma_0}\left(2 - \frac{\Gamma}{\Gamma_0}\right) \qquad (13)$$

so that using the notation $\rho = (1 - \Gamma/\Gamma_0)$ and $\kappa_0 = \coth^{-1}(1/\rho)$ one finds

$$y^2(z) = \rho^2 \left(\coth^2 (\kappa_0 + z\rho/D_{mf}) - 1\right) \qquad (14)$$

In general for the two plates problem the behavior of $y(z)$ is given implicitly by the first integral[35] of (5)

$$\frac{z}{D_{mf}} = \int_{y(z)}^{y_s} dy \frac{1}{(y^2 - y_m^2)^{1/2}} \frac{1}{(y^2 + y_m^2 - \tilde{\mu})^{1/2}} \qquad (15)$$

One first finds y_m and y_s in terms of h/D_{mf} and Γ/Γ_0 inverting the relations

$$\frac{h}{D_{mf}} = \int_{y_m}^{y_s} dy \frac{1}{(y^2 - y_m^2)^{1/2}} \frac{1}{(y^2 + y_m^2 - \tilde{\mu})^{1/2}} \qquad (16a)$$

$$\frac{\Gamma}{\Gamma_0} = \int_{y_m}^{y_s} dy \frac{y^2}{(y^2 - y_m^2)^{1/2}} \frac{1}{(y^2 + y_m^2 - \tilde{\mu})^{1/2}} \qquad (16b)$$

Then substituting these results in (15) one can obtain $y(z)$ and the concentration profile $c(z) = c_{s0}y^2(z)$ for given values of the separation and of the surface excess.

The disjoining pressure between the plates is (per unit area)

$$\Pi_d = -\frac{\partial \gamma}{\partial h} = \frac{kTv}{2} c_{s0}^2 y_m^2 (\tilde{\mu} - y_m^2) \qquad (17)$$

Positive (negative) Π_d correspond to repulsive (attractive) forces. Again, using the values of y_m and y_s obtained from (16a) and (16b) one obtains Π_d as a function of h and Γ/Γ_0.

For saturated plates ($\Gamma = \Gamma_0$), it is easy to show[2] that $\tilde{\mu}$ is simply given by[36]

$$\tilde{\mu} = y_m^2 \qquad (18)$$

i.e., for saturated plates, the disjoining pressure Π_d vanishes for any value of the separation $2h$.

For incompletely saturated plates, the two limits of large ($h \to \infty$) and small ($h \to 0$) separations are easy to discuss. When h is large $y_m \to 0$, then since $y_s < 1$ for unsaturated plates

$$(\tilde{\mu} - y_m^2) \simeq y_s^2 - 1 \qquad (19)$$

is negative and Π_d is attractive. Separating from the right-hand side of (16a) the part which diverges as $y_m \to 0$, one finds

$$\frac{h}{D_{mf}} \simeq C_1(y_s) + \frac{1}{(1 - y_s^2)^{1/2}} \int_{y_m}^{y_s} \frac{dy}{(y^2 - y_m^2)^{1/2}} \qquad (20)$$

(here $C_1(y_s)$ is constant as $y_m \to 0$). Therefore, y_m vanishes exponentially at large h

$$y_m \sim e^{-\rho h/D_{mf}} \qquad (21)$$

so that, at large separations, the interplate attraction also goes to zero exponentially.

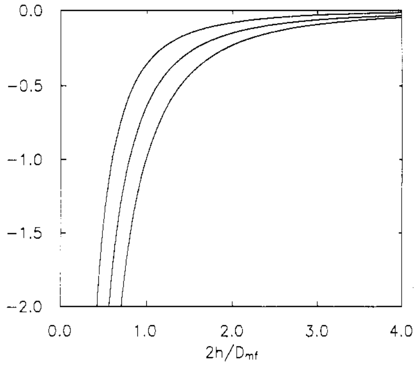

Figure 1. Results for the disjoining pressure in mean field theory: the reduced function $H(2h/D_{mf}) = 2\Pi_d/(kTvc_{s0})$ is plotted vs separation $2h/D_{mf}$ for (from left to right) $\Gamma/\Gamma_0 = 0.1, 0.8$, and 0.5.

For small separations we expect the concentration profile to be nearly flat: so that approximately $c_m \simeq \Gamma/h$ (here c_m is the midpoint concentration. Neglecting the gradient term in the surface free energy functional one gets

$$\gamma - \gamma_0 \simeq -\frac{kTv}{2} D_{mf} c_{s0} c_m \left(1 - \frac{\Gamma}{\Gamma_0}\right) \qquad (22)$$

so that

$$\Pi_d = -\frac{\partial \gamma}{\partial h} \simeq -\frac{kTv}{2} c_{s0}^2 \frac{D_{mf}^2}{h^2} \frac{\Gamma}{\Gamma_0}\left(1 - \frac{\Gamma}{\Gamma_0}\right) \qquad (23)$$

i.e., at small h the force between the plates is attractive and diverges as h^{-2} and

$$\tilde{\mu} \simeq \frac{D_{mf}}{h}\left(2\frac{\Gamma}{\Gamma_0} - 1\right) \qquad (24)$$

For any $\Gamma < \Gamma_0$ the reduced pseudochemical potential $\tilde{\mu}$ is negative at large h. For $(\Gamma/\Gamma_0) > {}^1/_2$, $\tilde{\mu}$ is positive at small h and changes sign as the separation increases. For $(\Gamma/\Gamma_0) < {}^1/_2$, $\tilde{\mu}$ is negative at any separation. A positive (negative) $\tilde{\mu}$ indicates that the coverage is larger (smaller) than it would be if the polymer adsorbed on plates, kept a distance h apart, was in thermodynamic equilibrium with the pure solvent.

Two comments are in order about our result (23) for the force. First at short distances, the (negative) disjoining pressure is symmetric in the coverage around $(\Gamma/\Gamma_0) = {}^1/_2$: at small h the attraction is largest when $(\Gamma/\Gamma_0) = {}^1/_2$. This result can be understood observing that as (Γ/Γ_0) decreases, the attraction per unit amount of polymer becomes stronger and stronger but there is less and less polymer in the system. Secondly the infinite attraction described by eq 23 is unphysical: as h decreases and the concentration between the plates increases, three-body interactions (i.e., the c^3 term in the Flory–Huggins free energy which was neglected in eq 3) become important and give a short distance repulsion between the plates.

Our numerical results for the force, obtained from (16) and (17), are shown in Figure 1: we find that any surface excess lower than the one corresponding to saturation gives an attractive interaction between the plates at any separation. In general, there is no symmetry around $(\Gamma/\Gamma_0) = {}^1/_2$ and the attraction is stronger for $(\Gamma/\Gamma_0) > {}^1/_2$ than for the corresponding symmetric value of the coverage.

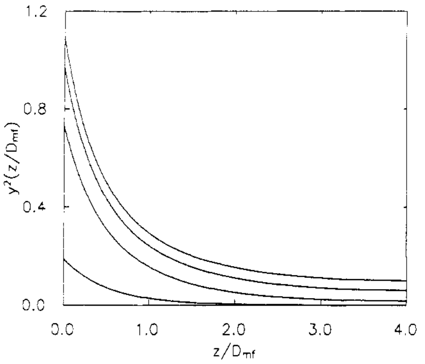

Figure 2. Mean field theory predictions for the reduced concentration profiles for interplate separation $h = 4D_{mf}$. The curves refer (from top to bottom) to Γ/Γ_0 = 1.0, 0.8, 0.5, and 0.1.

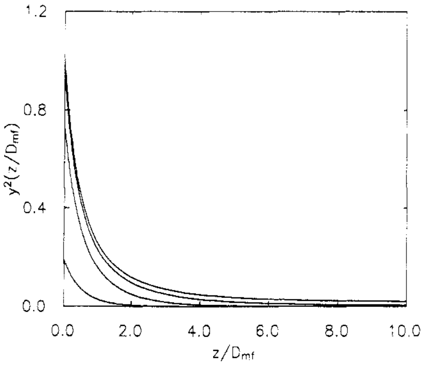

Figure 3. Same as in Figure 2 but for interplate separation $h = 10D_{mf}$.

Concentration profiles for $h = 4D_{mf}$ and $h = 10D_{mf}$ are shown in Figures 2 and 3, respectively. As the interplate separation increases, eq 14 describes correctly the concentration profile in a wider and wider region extending from the surface of the plates towards the middle of the interplate region: at a given value of the separation this region is wider the lower Γ/Γ_0 is.

3. Scaling Theory

In the scaling theory of polymer adsorption the surface free energy functional has the form[2]

$$\gamma - \gamma_0 = -|\gamma_1|\Phi_s + \alpha kT\int_0^h \mathrm{d}z\, \frac{1}{\xi^3(\Phi)}\left[1 + \left(m\frac{\xi(\Phi)}{\Phi}\,\frac{\mathrm{d}\Phi}{\mathrm{d}z}\right)^2\right] \tag{25}$$

Here Φ_s is the value of the polymer volume fraction $\Phi(z)$ at the surface; $\xi(\Phi) = a\Phi^{-3/4}$ is the local correlation length;[1] $m = 8am_0/3$ has dimension of length; α and m_0 are numerical constants.

Again we implement the constraint of constant coverage Γ, by introducing a Lagrange multiplier (pseudochemical potential) μ and minimizing $(\gamma - \gamma_0 - \mu\Gamma)$. To simplify the algebra, we define a new field $f = \Phi^{3/8}$ and a reduced pseudochemical potential μ' such that $\mu = \alpha kT\mu'$. Then

$$\gamma - \gamma_0 - \mu\Gamma = -|\gamma_1|f_s^{8/3} + \frac{\alpha kT}{a^3}\int_0^h \mathrm{d}z\left[f^6 - \mu' f^{8/3} + \left(m\frac{\mathrm{d}f}{\mathrm{d}z}\right)^2\right] \tag{26}$$

where f_s is the value of f on the plates. The Euler–Lagrange equation for $f(z)$ obtained from (26) is

$$m^2\left(\frac{\mathrm{d}f}{\mathrm{d}z}\right)^2 = f^6 - f_m^{\,6} - \mu'(f^{8/3} - f_m^{\,8/3}) \tag{27}$$

Here f_m is the value of f at the midpoint between the plates. The boundary condition at the surface, obtained substituting (27) back into (26) and minimizing with respect to f_s, is

$$\frac{8}{3}\,\frac{1}{f_s}\,\frac{\mathrm{d}f}{\mathrm{d}z}\bigg|_s = \frac{1}{D}\left(\frac{f_s}{f_{s0}}\right)^{2/3} \tag{28}$$

where we have defined D so that

$$\frac{1}{D} = \frac{32|\gamma_1|a^3 f_{s0}^{\,2/3}}{9\alpha kTm^2} \tag{29}$$

and f_{s0} is the value that f takes at the surface of a single saturated plate.

Solving (4) with $f_m = 0$ and $\mu' = 0$ one has the standard scaling result[2] for a single saturated plate

$$\Phi(z) = \left(\frac{m}{2(z + 4D/3)}\right)^{4/3} \tag{30}$$

Therefore

$$f_{s0} = (3m/8D)^{1/2} \tag{31}$$

and

$$a^3\Gamma_0 = \frac{3m}{2}f_{s0}^{\,2/3} = 4D\Phi_{s0} \tag{32}$$

Note that now $D/a \sim (kT/|\gamma_1|a^2)^{3/2}$ which is characteristic of the intersection of a self-avoiding walk with a (transparent) plane. The need to account for the fact that the plates on which polymer adsorbs cannot in fact be crossed is at the origin of the singular behavior in the proximal region[3-5] which was mentioned in the Introduction.

As in mean field theory, it is convenient to introduce a reduced variable y such that

$$f = f_{s0}y^{3/2} \tag{33}$$

and a reduced pseudochemical potential $\tilde{\mu}$ which, using (27) and (28), can be written in terms of $y_s = (f_s/f_{s0})^{2/3}$ and $y_m = (f_m/f_{s0})^{2/3}$ as

$$\tilde{\mu} = \frac{\mu'}{f_{s0}^{\,10/3}} = \frac{(y_s^{\,9} - y_m^{\,9} - y_s^{\,5})}{(y_s^{\,4} - y_m^{\,4})} \tag{34}$$

From (27) one gets that $y(z)$ is given by

$$\frac{z}{4D} = \int_{y(z)}^{y_s}\mathrm{d}y\left(\frac{y}{y^9 - y_m^{\,9} - \tilde{\mu}(y^4 - y_m^{\,4})}\right)^{1/2} \tag{35}$$

Again, as in mean-field, one first finds y_m and y_s for given values of the separation $2h$ and of the coverage (i.e., of the ratio Γ/Γ_0) using the relations

$$\frac{h}{4D} = \int_{y_m}^{y_s}\mathrm{d}y\left(\frac{y}{y^9 - y_m^{\,9} - \tilde{\mu}(y^4 - y_m^{\,4})}\right)^{1/2} \tag{36a}$$

$$\frac{\Gamma}{\Gamma_0} = \int_{y_m}^{y_s}\mathrm{d}y\left(\frac{y^9}{y^9 - y_m^{\,9} - \tilde{\mu}(y^4 - y_m^{\,4})}\right)^{1/2} \tag{36b}$$

Substituting these results in (35) one can obtain $y(z)$ and the volume fraction profile $\Phi(z) = f_{s0}^{\,8/3}y^4(z)$. From the results for y_m and y_s obtained from (36a) and (36b), one also finds the disjoining pressure (per unit area)

$$\Pi_d = -\frac{\partial\gamma}{\partial h} = \frac{\alpha kT}{a^3}(\mu'\Phi_m - \Phi_m^{\,9/4}) \tag{37}$$

At large separations ($h \to \infty$), for any $\Gamma/\Gamma_0 < 1$, the force between the plates is attractive.[7] In fact, when $h \to \infty$ the midpoint volume fraction Φ_m vanishes and so does y_m. Equation 34 then becomes

$$\tilde{\mu} = y_s(y_s^4 - 1) \tag{38}$$

Consider first the case $(\Gamma - \Gamma_0)$ finite: then y_s is smaller than 1 and μ' is finite and negative. The expression for the force in the rhs of (37) is then dominated by the first term (the one containing μ') so that the force is attractive. Separating from the rhs of eq 36a the part which diverges as $y_m \to 0$ one has

$$\frac{h}{D} \to \int_{y_m}^{y_s} \frac{\mathrm{d}y}{(-\tilde{\mu}y^3)^{1/2}} \sim (-\tilde{\mu}y_m)^{-1/2} \tag{39}$$

Therefore as $h \to \infty$, one gets $y_m \sim h^{-2}$ so that $\Phi_m \sim y_m^4 \sim h^{-8}$. Correspondingly for the (negative) disjoining pressure one has $\Pi_d \sim h^{-8}$, instead of the exponential decay found in mean field.

Consider now the limit $\Gamma \to \Gamma_0$ and $h \to \infty$, in this limit $\tilde{\mu}$ vanishes. Defining $g = \tilde{\mu}/y_m^5$, it is easy to see[2] that, as $h \to \infty$, for $\Gamma = \Gamma_0$, g is finite[37] and larger than 1. Then the two terms in the rhs of eq 37 are of the same order (both vanish as $\Phi_m^{9/4}$), and since $g > 1$, the force is repulsive. In this case one finds that $\Pi_d \sim h^{-3}$ for large h. Strictly speaking if Γ is not exactly equal to Γ_0, then $g(h \to \infty) \to -\Phi_m^{-5/4}$, i.e., for sufficiently large h the force is attractive and one is back to the situation leading to eq 39. However, the issue becomes physically irrelevant, once it involves attractive tails at h larger than the Flory radius of the chains R_F. As it was pointed out in the Introduction, the scaling theory applies only if $h < R_F$; i.e., if there is a certain overlap between the adsorbed polymer layers. If $h > R_F$, the polymer concentration profile in the distal region decays exponentially towards the bulk value (zero in this case), and the disjoining pressure falls exponentially to zero.

At small separations ($h \to 0$) the concentration profile between the plates is nearly flat and $\Phi_m \simeq a^3\Gamma/h$. The interfacial energy is dominated by the first term in the integral appearing in the rhs of eq 25

$$\gamma \simeq \alpha kT\Phi_m^{9/4}h/a^3 \tag{40}$$

Therefore the force is repulsive and is given by

$$\Pi_d \simeq \frac{5}{4}\frac{\alpha kT}{a^3}\Phi_{s0}^{9/4}\left(\frac{\Gamma}{\Gamma_0}\frac{4D}{h}\right)^{9/4} \tag{41}$$

which should be compared with the mean field result eq 23. Contrary to what was found in mean field, the reduced pseudochemical potential $\tilde{\mu}$ is always positive at small separations and it is given by

$$\tilde{\mu} \simeq {}^9/_4\Phi_m^{5/4} \tag{42}$$

Although our arguments leading to eq 41 use the original de Gennes assumption of regular behavior in the proximal region, the power-law dependence of Π_d on h and Γ given in eq 41 is unchanged in the modified version of the theory, which tries to account for the proximal singularity.[5] Nonetheless, such behavior may be difficult to detect experimentally: as h decreases, the concentration between the plates increases (see Figure 7) and soon one reaches the "moderately concentrated" regime described by mean field theory.[32]

Since, for $\Gamma < \Gamma_0$ the interplate interaction is attractive at large separations and repulsive when h is small, one expects a minimum of the attraction at some finite h. Indeed, solving numerically for y_s and y_m in eq 36 and substituting the results in eq 37, one obtains for the disjoining pressure the behavior shown in Figure 4. As the coverage decreases the attraction minimum becomes deeper and it is found at lower and lower interplate separations. Even for values of the coverage considerably below the saturation value (see, for example, the curve for $\Gamma/\Gamma_0 = {}^1/_2$) the attraction minimum is very flat, and it is found at rather high values of h/D. Nonetheless, a coverage lower than Γ_0 has the effect of reducing very significantly the extent of the repulsion.

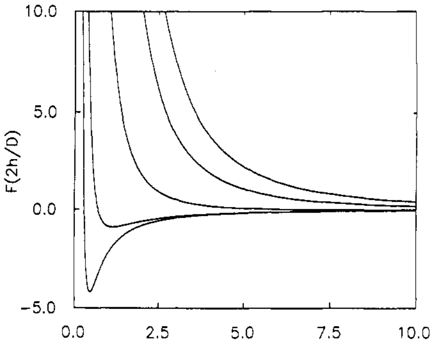

Figure 4. Results for the disjoining pressure in scaling theory: the reduced function F is plotted vs separation $2h/D$ for (from left to right) Γ/Γ_0 = 0.25, 0.3, 0.5, 0.8, and 1.0 (the function F is related to the disjoining pressure Π_d by $a^3\Pi_d = \alpha kTf_{s0}^6F$).

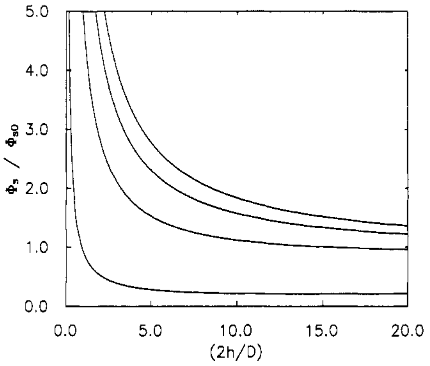

Figure 5. Scaling theory predictions for the reduced surface concentration as a function of interplate separation $h/2D$. The curves refer (from top to bottom) to Γ/Γ_0 = 1.0, 0.8, 0.5, and 0.1.

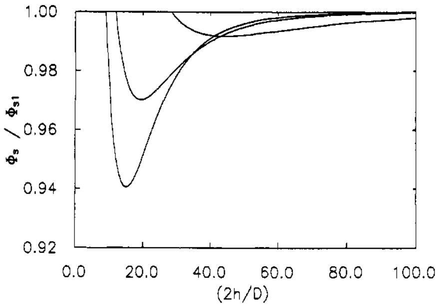

Figure 6. Scaling theory predictions for the surface concentration at large interplate separations. The plot shows the ratios Φ_s/Φ_{s1}, where $\Phi_{s1} = \Phi_s(h \to \infty)$. The curves refer to (from left to right) Γ/Γ_0 = 0.1, 0.3, and 0.5.

At a given plate separation there is a value of the surface excess for which the attraction is largest: this value becomes smaller as the separation decreases. This fact might play a role in determining the organization of flocs precipitated from colloidal suspensions. At low values of Γ/Γ_0, two new exponents control the location $x_{\min}$ and the strength $y_{\min}$ of the attraction minimum: we find $x_{\min} \sim (\Gamma/\Gamma_0)^5$ and $y_{\min} \sim (\Gamma/\Gamma_0)^{-9}$. However, "proximal" corrections will become important when $x_{\min} < D$, so that the location and strength of the minimum, for Γ/Γ_0 small, will be affected.

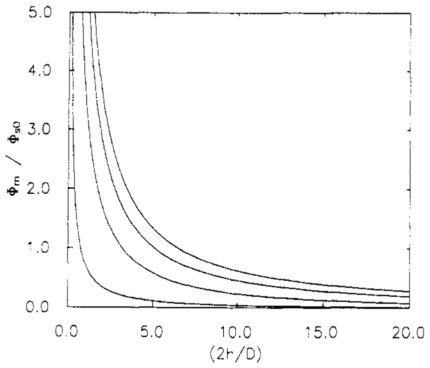

Figure 7. Scaling theory predictions for the reduced midpoint concentration as a function of interplate separation $h/2D$. The curves refer (from top to bottom) to Γ/Γ_0 = 1.0, 0.8, 0.5, and 0.1.

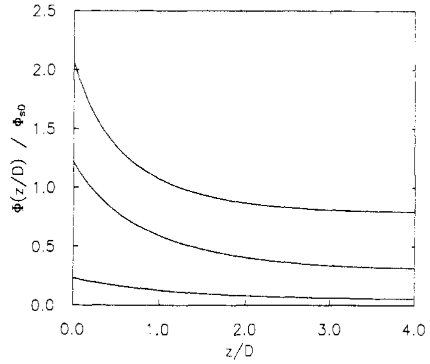

Figure 8. Scaling theory predictions for the reduced concentration profiles for interplate separation $h = 4D$. The curves refer (from top to bottom) to Γ/Γ_0 = 1.0, 0.5, and 0.1.

Figure 5 shows the reduced surface concentration as a function of plate separation. As detailed in Figure 6, the surface concentration has a shallow minimum at finite h (the minimum falls outside the range of Figure 5 for all curves except for Γ/Γ_0 = 0.1). Indeed, with use of eq 39, one finds

$$\frac{dh}{dy_s} \sim \frac{5y_s^4 - 1}{(-\tilde{\mu}y_m)^{1/2}} \tag{43}$$

namely, as $h \rightarrow \infty$, for $y_s^4 > {}^1/_5$, $(dy_s/dh) \rightarrow 0^+$ so that Φ_s increases asymptotically to its limiting value $\Phi_{s1} = \Phi_s(h \rightarrow \infty)$ and must have a minimum at finite h. For $y_s^4 < {}^1/_5$, which corresponds to $\Gamma/\Gamma_0 < 0.091$, Φ_s has both a minimum (at some finite h) and a shallow maximum further out, and then it decreases to its asymptotic value Φ_{s1}.

It is tempting to ascribe the behavior described above to a bridging effect. As the plates are brought closer, the polymer chains rearrange themselves from the surface toward the middle of the interplate region as bridges are formed. As a result, the concentration at the surface decreases; eventually, as the volume available gets smaller and smaller, the surface concentration starts increasing again. The same effect is found in mean field,[38] and it is slightly more pronounced there. For saturated surfaces there is no minimum in Φ_s. Bridges will occur even in this case; however, these configurations are not so favored to produce a significant rearrangement of polymer from the surface to the middle.

The reduced midpoint concentrations is plotted in Figure 7: it decreases monotonically as h increases and, for low values of the coverage, it remains quite low up to relatively small values of h/D. Finally, Figures 8, 9, and 10 show the full concentration profiles for h/D = 4, 10, and 50, respectively. It is seen that, as the separation decreases, the concentration profiles flatten out more quickly for lower values of the surface excess.

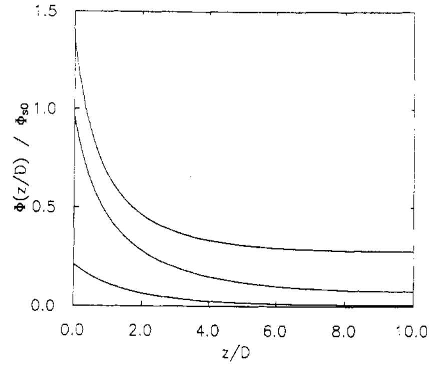

Figure 9. Same as in Figure 8 but for interplate separation $h = 10D$.

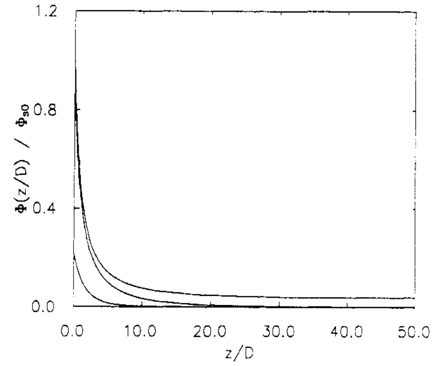

Figure 10. Same as in Figure 8 but for interplate separation $h = 50D$.

4. Conclusion

The theoretical analysis presented above extends current standard theories of adsorption from polymer solutions to cover the case of unsaturated surfaces. In an actual experiment measuring the forces between unsaturated polymer adsorbed surfaces (starting from the good solvent regime), both the scaling and mean field descriptions might be relevant. Specifically, as long as the interplate concentration remains low, scaling predictions should be valid; however, when the plates are brought sufficiently close together for the "moderately concentrated" regime to be reached, the mean field description should apply. In practice, there is probably a fairly wide crossover region between the two regimes.[39] The results presented in Figures 5 and 7 show that at lower values of the coverage the interplate concentration remains quite low even at small separations, so that the range where the scaling description applies should be wider.

Only two[15,16] of the force experiments (in nonaqueous solvent) reported so far in the literature were performed above the Θ-point. The long-range attraction described in ref 16 for unsaturated surfaces[40] is in qualitative agreement with the results presented here; our results also confirm that considerable desorption takes place in the experiment described in ref 15. However, both experiments were performed so close to Θ-conditions that a direct comparison with the scaling results is unwarranted. Rather, in analyzing these situations the mean field description should be used and it should include the three-body interactions which were neglected in the treatment of section 2. It should also be remarked that equilibrium statistical mechanics underlies the theoretical assumptions used here: in view of the strong restrictions imposed on the movement of the chains as the interplate separation decreases, one should be aware of the fact that actual statistical equilibrium might be very hard to achieve in practice.

In conclusion, we have obtained theoretical predictions for the properties of unsaturated surfaces in the framework of mean field and scaling theory. In both cases, we find that the interactions between two polymer adsorbed surfaces and the properties of the concentration profiles close to the surfaces are *qualitatively* different from those found in the saturated case. Experimental methods to measure interplate interactions are becoming increasingly reliable, and neutron reflectivity data should soon provide quantitative information on the concentration profiles in thin adsorbed layers. We hope that the work presented here will turn out to be useful in interpreting this new wealth of data.

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(19) A polymer chain is irreversibly attached if its adsorption free energy is much greater than kT.

(20) The chains present in the system are allowed to explore all available configurations and are in statistical equilibrium in this sense.

(21) Practical experimental considerations require that during incubation, the plates be kept at a distance several order of magnitude larger than the Flory radius the chains. This is because equilibrium is reached in a reasonable amount of time, only if the kinetics of the chains is convection rather than diffusion limited: convection is inhibited unless the interplate separation is very large.

(22) This has two effects. (i) The first effect is kinetic: the amount of time needed to reach equilibrium is (inordinately) increased since the motion of chains between the plates is strongly hindered (see also previous note). (ii) The second effect is that, even if one waits for a time sufficiently long for thermodynamic equilibrium to set in, the total amount 2Γ of polymer between the plates, left after the washing stage, is less than it would be, had the plates been kept a distance $2h \gg R_F$ apart, during incubation.

(23) Of course this is not the case if the incubation concentration is so low that the total amount of polymer present is less than $2\Gamma_0$. It is unrealistic to contemplate working at such low concentration in the mica plates experiment; however, the total amount of polymer present can be the limiting factor in colloidal suspension where the surface available for adsorption is large.

(24) In principle (see ref 21 and 22), for separations $2h$ much larger than R_F one is in conditions of reversible adsorption; however, for such large separations the forces between the plates are very small (and difficult to measure). These values of h correspond to the distal regime where the concentration profile decays exponentially towards the bulk value.

(25) Provided that the plates were incubated a large distance apart and thermodynamic equilibrium with the solution was allowed to set in.

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(28) Since we are dealing with zero bulk concentration, the Flory radius R_F, rather than the bulk correlation length, characterizes the onset of the distal region.

(29) A weak monomer-surface attraction corresponds to large values of D, since many contact points between the chain and the wall are required to give a sticking energy of order kT. Conversely, if the monomer–surface attraction is strong, only a few contacts will be sufficient to overcome thermal disorder, these will occur within a relatively small length scale D.

(30) We assume that $D \ll R_F$; of course, if the attraction is so weak that D is comparable with R_F, one cannot avoid dealing with the proximal behavior.

(31) The assumption that long-range tails in the van der Waals attraction can be neglected is hidden in this separation into a surface and a "bulk" part: see ref 2.

(32) This occurs when the interplate concentration is sufficiently high for the swelling length (i.e., the size of a "thermal blob") to be comparable to the correlation length. Obviously, if one is sufficiently close to (just above) the Θ-point, this condition is satisfied at any concentration.

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(34) This would add a ψ^2 term to the integrand in the rhs of eq 3.

(35) The equation satisfied by $y(z)$ is a standard differential equation for Jacobian elliptic functions: see: Gradshtheyn, I. S.; Ryzhik, I. M. *Table of integrals, series and products*; New York, 1965. See also: Jones, I. S.; Richmond, P. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1062.

(36) In this case the reduced concentration profile is

$$y^2(z) = y_m^2\left(1 + \tan^2\left(\frac{y_m(h - z)}{2D_{mf}}\right)\right)$$

and y_m is related to h by

$$(h/D_{mf}) = (2/y_m) \arctan (1/y_m)$$

(37) The value of $g_c = g(h \to \infty, \Gamma = \Gamma_0)$ that we find numerically is marginally lower than the one reported in ref 2. We get $g_c = 2.1914$, versus de Gennes' $g_c = 2.234$.

(38) In this case (see eq 20), as $h \to \infty$, $(\mathrm{d}y_s/\mathrm{d}h) \to 0^+$ for any coverage $0 < \Gamma/\Gamma_0 < 1$.

(39) The scaling and mean field treatment agree on the repulsive (attractive) character of the long distance interaction in the saturated (unsaturated) situations: therefore, the same behavior should be expected in the crossover region between the two regimes.

(40) Note, however, that replacement of the solution with pure solvent (washing) was not carried out in this experiment.