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Density Profiles and Interaction between Irreversibly Adsorbed Polymer Layers

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ABSTRACT: The polymer density profiles and the polymer-mediated interaction between parallel walls covered by irreversibly adsorbed polymer layers in good solvents are controlled by the crossover distance between the loops- and tails-regions, and the length of the tails. The relative value of these length scales strongly depends on the adsorbed polymer amount. For extremely over- and undersaturated surfaces (when the scales are well-separated), asymptotic expressions of the force and density profile have been previously obtained, at the mean-field level. We present here numerical results for the more general case of intermediate saturation. The predicted double layer structure of the adsorbed polymers is observed only when the walls are oversaturated. Saturated and oversaturated walls repel each other, while highly undersaturated walls interact only attractively. The interaction between slightly starved walls changes from repulsive to attractive as they come together, the amplitude of the repulsive barrier increasing with the surface coverage.

1. Introduction

The study of solid−liquid interfaces covered by adsorbed macromolecules in solution is an important area in the physics of complex fluids, due both to its practical relevance and to the more fundamental problems that it raises. In many problems of formulation chemistry, for example, one deals with colloidal particles embedded in a polymeric solution. At the level of a macrofluid description, this can be seen as a mixture of three-dimensional colloidal particles and one-dimensional polymer chains. The structure of the system involves length scales related to the two components that may differ by orders of magnitude. The time scales of the diffusive motions can also be very different. In general, it is therefore extremely difficult to treat the two components at the same level of description.

From a colloidal science point of view, if the colloidal particles are large enough, the system can be seen as an effective one component fluid, by mimicking the effect of the polymer chains by an effective interaction potential between particles. The structural and dynamical properties of the colloidal suspension can then be calculated by implementing well-established methods (integral equations theories of simple liquids, many particles Smoluchowski dynamics, etc.). At a more local level, polymer science provides us with the elements for understanding the properties of the "polymeric solvent". There exist in the literature several theoretical approaches for the polymer density profiles and the polymer-mediated interactions between solid−liquid interfaces. These can then be used as an input for the statistical physics of the colloidal fluid. This asymptotic approach assumes that the characteristic length scales of the polymer solution (radius of gyration, correlation length, etc.) are much smaller than the characteristic length scales of the colloidal suspension (particle size, mean distance between particles, etc.). It only gives a qualitative description of the two-components macrofluid when the length scales are comparable, but no unified scheme able to treat simultaneously all the existing correlations seems available at the moment.

In this paper, we consider large adsorbing colloidal particles and smaller polymer chains (still with a very large degree of polymerization N). In this limit, the typical time for one adsorbed chain to leave the gap between colliding particles is several orders of magnitude larger than the collision time. Therefore, after the adsorption equilibrium has been reached, the colloidal particles interact as if they were planar walls covered by irreversibly adsorbed polymer layers. The polymer surface coverage is fixed, but the adsorbed layer structure is not frozen and can reequilibrate freely locally. This configuration has been often considered in the theoretical study of the polymer adsorption onto flat surfaces. The problem is interesting from a fundamental point of view, as it provides an example of confined polymers, but is also interesting because of the practical applications in colloidal stabilization, lubrication, adhesion, residual water treatment, and other industrial fields.

For linear polymers in good solvents, de Gennes has built a scaling theory[1] which predicts a self-similar structure of an adsorbed layer at a solid liquid interface: the dimensionless volume fraction of monomers $\phi(z)$ decays with the distance z from the interface (supposed to be in the xy-plane) as $\phi(z) \propto (a/z)^{4/3}$, where a is the monomer size. The interaction between surfaces coated with polymer scales with the distance h between surfaces as $\beta u(h) \propto (a/h)^2$. The sign of the force and the values of the proportionality constants are not provided by the pure scaling approach. However, it is well-known from experiments[2,3] (supposedly done under constant coverage conditions) that saturated and oversaturated walls repel each other, while undersaturated walls interact attractively.

The earliest attempts to study the interactions between adsorbed polymer layers were based on the mean field approximation (MFA) and on the ground state dominance approximation (GSDA) of the Edwards equa-

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tion for the chain conformations.[4−6] This type of approach ignores the excluded volume correlations and thus leads to slightly erroneous scaling exponents, but it allows for a detailed calculation of the chains conformation and of the interaction between surfaces. The density profile close to an interface is found to decay as $\phi(z) \approx 2/z^2$, and the interaction potential between polymer coated surfaces as $\beta u(h) \approx \pi^2\delta\Gamma/4h^2$ (for the sake of simplicity these quantities are expressed here in rescaled units defined in the body of the paper). Here, $\delta\Gamma$ is a measure of the amount of oversaturation ($\delta\Gamma > 0$), or of undersaturation ($\delta\Gamma < 0$) of the polymer on the surfaces with respect to the equilibrium adsorbed amount Γ_0 that would obtain with infinite polymers. At this level of description the most relevant experimental features are reproduced, but a vanishing interaction is predicted for saturated plates ($\delta\Gamma = 0$). Along the same lines, a rescaled mean field theory was also proposed by de Gennes to take into account the excluded volume correlations. It predicts a repulsive force for saturated layers, and an attractive force at large distances for undersaturated layers.[4−6]

Two important effects must be considered when two adsorbed layers approach each other: first, the reduction of the entropy due to the compression of the polymer coils and, second, the reduction of the energy due to bridge formation (adsorption of a chain onto both interfaces). The entropic effect leads to a repulsion (in a good solvent), and the bridging effect, to an attraction. Their competition results in the total interaction. Moreover, the entropic effect is expected to be dominant for oversaturated layers, and the bridging effect for undersaturated layers. The conformation of a polymer chain in an adsorbed layer is classically described in terms of tails and loops, the tails being the chain sections between the last adsorbed monomers and the free ends (each chain has two tails) and the loops being the section between the tails (including simple loops, trains of loops, and bridges). The classical theory of polymer adsorption accounts correctly for loops, but entirely ignores the tails, which are expected to have an important contribution to the entropy of the system.

Recently, a theoretical approach that accounts for both loops and tails has been proposed.[7,8] It is still a mean field theory, but it differs from the classical theory in the approximation used to solve the Edwards propagator equation. Instead of considering only the bound eigenstate associated to the ground state energy of this equation, the contribution of the free eigenstates is resummed in the limit of very high molecular weights. This allows to take into account the leading contribution of the tails of the chains to the concentration profiles and to the free energy. The results agree quantitatively with the large molecular weight limit of the self-consistent mean field numerical theory of Scheutjens and Fleer[9] that explicitly solves numerically the Edwards propagator equation for adsorbing polymers. The properties of the adsorbed layers are characterized by two length scales: the composition crossover distance z^* between the loops and the tails regions, and the adsorbed layer thickness, which corresponds to the length of the tails λ. Analytical expressions of the concentration profile $\phi(z)$, and of the interaction between polymer coated surfaces $u(h)$ were obtained in the limit where $z^* \ll \lambda$. The polymers were found to adsorb in a double layer array formed by an inner layer ($z < z^*$) dominated by loops, and by an outer layer ($z > z^*$) dominated by tails. In these two regions, the polymer volume fraction shows a power law decay $\phi(z) \propto (a/z)^2$. The interaction between irreversibly adsorbed layers has been calculated for oversaturated surfaces. The scaled interaction energy is $\beta u(h) \approx 1670/(3h^3)$ when only the outer layers overlap, $h \gg z^*$, and $\beta u(h) \approx \pi^2\delta\Gamma/4h^2$ when the inner layers overlap, $h \ll z^*$. This suggests a nonmonotonic interaction for undersaturated surfaces. However, in that case we expect layers mainly formed by loops, which may be inconsistent with the condition $z^* \ll \lambda$.

The aim of this paper is to study the interaction between irreversibly adsorbed polymer layers in all the possible range of surface coverage, within this mean field approach. To do that, we release the ratio z^*/λ from constraints and solve the chain partition function equations by implementing numerical methods. In particular, we put special interest in the study of slightly starved interfaces. Here, a nonmonotonic interaction is found that goes from repulsive to attractive as the plates come closer. The amplitude of the repulsive barrier increases with the surface coverage. As far as we know, such behavior has not been experimentally observed. It could be due to the difficulties inherent to the control of the adsorbance (the phenomenon is predicted for $|\delta\Gamma| \lesssim 1\%$). However, its existence would open new possibilities for applications.

The paper is organized as follows. The next section presents in details the self-consistent mean field theory of polymer adsorption. Then, our results for the density profiles and the interaction between irreversibly adsorbed polymer layers are presented; only good solvents and infinite bulk dilutions are considered. Finally, the last section contains some concluding remarks.

2. Mean Field Theory of Polymer Adsorption

Within a mean field approach, the basic quantity characterizing the chain statistics is the statistical weight (or partition function) of a chain of N steps with one-end point at the position $\mathbf{r}$; $G(\mathbf{r},N)$. As first shown by Edwards, $G(\mathbf{r},N)$ satisfies the Schrödinger-like equation

$$\left[\frac{\partial}{\partial N} - \frac{a^2}{6}\nabla^2 + \beta U_{\mathrm{e}}(\mathbf{r})\right]G(\mathbf{r},N) = 0 \qquad (1)$$

Equation 1 is obtained by considering one Gaussian chain in a fixed external potential $U_{\mathrm{e}}(r)$ which is supposed to be either a smooth function of $\mathbf{r}$,[10] or very small as compared with β^{-1}.[1] The interaction between monomers (of the same chain or of different chains) is treated at the mean−field level by writing $U_{\mathrm{e}}(\mathbf{r}) = U_{\mathrm{w}}(\mathbf{r}) + U_{\mathrm{mf}}(\mathbf{r})$, where $U_{\mathrm{w}}(\mathbf{r})$ is the wall−monomer adsorbing potential, and $U_{\mathrm{mf}}(\mathbf{r})$ the mean−field excluded volume potential acting on one monomer and due to all the other monomers. This is given by the local excess chemical potential $\mu^{\mathrm{ex}}(\mathbf{r})$, which is the derivative of the local free energy density $f^{\mathrm{ex}}(\mathbf{r})$ with respect to the local concentration $c(\mathbf{r})$: $\mu_{\mathrm{ex}}(\mathbf{r}) = \partial f^{\mathrm{ex}}(\mathbf{r})/\partial c(\mathbf{r})$. If the polymer is in a good solvent, $f^{\mathrm{ex}}(\mathbf{r})$ is in a first approximation proportional to the local density of particle-pairs[1]

$$\beta U_{\mathrm{mf}}(\mathbf{r}) \approx vc(\mathbf{r}) = \phi(\mathbf{r}) \qquad (2)$$

The repulsive interactions between monomers are characterized here by the second virial coefficient or excluded volume $v > 0$. The local volume fraction of monomers

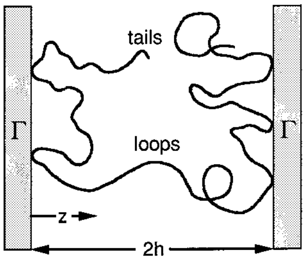

Figure 1. Simple picture of the studied systems: two parallel planar walls covered by irreversibly adsorbed polymer layers. The tails are the parts of the chains between the last adsorbed monomers and the free ends (each chain has two of them), and the loops are the part between the tails (including simple loops, trains of loops, and bridges).

is defined by $\phi(\mathbf{r}) = vc(\mathbf{r})$, and can be written as

$$\phi(\mathbf{r}) = C\int_0^N \mathrm{d}M\ G(\mathbf{r}, N - M)G(\mathbf{r}, M) \tag{3}$$

where the adsorbed polymers are considered as consisting of two sub-chains of M and $N - M$ steps, $M \le N$.

To introduce the volume fraction of loops and tails monomers, we divide the chain conformations into two subsets; the adsorbed conformations with a statistical weight $G^{\mathrm{a}}(\mathbf{r},N)$, where at least one monomer of the chain is adsorbed (and interacts directly with the surface), and the free conformations with a statistical weight $G^{\mathrm{f}}(\mathbf{r},N)$, where no monomer of the chain is adsorbed. The partition function is then split as

$$G(\mathbf{r}, N) = G^{\mathrm{a}}(\mathbf{r}, N) + G^{\mathrm{f}}(\mathbf{r}, N) \tag{4}$$

The volume fraction of monomers belonging to loops $\phi_l(\mathbf{r})$, or to tails $\phi_t(\mathbf{r})$, can then be written as

$$\phi_{\mathrm{l}}(\mathbf{r}) = C\int_0^N \mathrm{d}M\ G^{\mathrm{a}}(\mathbf{r}, N - M)G^{\mathrm{a}}(\mathbf{r}, M) \tag{5}$$

$$\phi_{\mathrm{t}}(\mathbf{r}) = 2C\int_0^N \mathrm{d}M\ G^{\mathrm{a}}(\mathbf{r}, N - M)G^{\mathrm{f}}(\mathbf{r},\mathrm{M})$$

The local volume fraction of chain-end monomers is proportional to the statistical weight; $\phi_{\mathrm{e}}(\mathbf{r}) = 2CG(\mathbf{r},N)$. We consider throughout the paper that there are no free chains, so that the total volume fraction is $\phi(\mathbf{r}) = \phi_{\mathrm{l}}(\mathbf{r}) + \phi_{\mathrm{t}}(\mathbf{r})$.

Figure 1 shows a schematic picture of the kind of systems we study: two infinite planar surfaces at a distance $2h$ with irreversibly trapped polymer between. The total amount of polymer per unit area in the gap is 2Γ; Γ is thus the surface coverage of one plate. The two plates system is invariant by translation along the plates, and the relevant quantities are symmetric with respect to the midplane, so that it is enough to consider only half of the slab. The proportionality constant C can then be determined by integrating the end-points volume fraction over the coordinate z perpendicular to the plates; $C = v\Gamma/NZ$. Here, $Z = \int_0^{\mathrm{h}} \mathrm{d}z\ G(z,N)$, and $2Z$ is the total partition function of a chain in the slab. In the vicinity of the walls, the wall-monomer adsorbing potential becomes dominant, and as we are not interested in the molecular details, its effects can be replaced by an effective boundary condition on the partition function:

$$\left.\frac{\partial G(z, N)}{\partial z}\right|_0 = -\frac{G(0, N)}{b} \tag{6}$$

Here, the phenomenological length b measures the strength of the adsorbing potential; in the strong adsorption limit, it is of the same order of magnitude as the step size a (an equivalent approach is to replace $U_{\mathrm{w}}(z)$ by a δ-function potential). Thus, the partition function satisfies the same eq 1 as in the absence of the wall potential, $U_{\mathrm{w}}(z) = 0$, but with the boundary conditions $G'(0,N) = -G(0,N)/b$ on the adsorbing surface, and $G'(h,N) = 0$ at the midplane. The initial condition is $G(z,0) = 1$, assuming an arbitrary normalization and a uniform distribution of free monomers. The prime denotes a derivative with respect to z.

The partition function $G(z,N)$ can be calculated as an expansion over the eigenstates of the Schrödinger-like equation

$$G(z, N) = \sum_i K_i\psi_i(z)\mathrm{e}^{-\beta\epsilon_i N} \tag{7}$$

Here, $\{\psi_i(z)\}$ is demanded to be a complete orthonormal set of eigenfunctions in $[0,h]$. The initial condition on $G(z,N)$ imposes the value of the constants K_i:

$$K_i = \int_0^h \mathrm{d}z\ \psi_i(z) \tag{8}$$

In the limit of infinite molecular weights, the eigenfunction expansion is dominated by the first term (ground state dominance approximation). We thus write

$$G(z, N) = K_0\psi_0(z)\mathrm{e}^{-\beta\epsilon_0 N} \tag{9}$$

This approximation introduces two new restrictions in our treatment. On the one hand, the adsorption has to be weak enough so that there is only one bound state[15] (of energy ϵ_0). On the other hand, the polymers must be of a very large molecular weight so that $|\beta\epsilon_0 N| \gg 1$. The eigenstate equation for $\psi_0(z)$ reads

$$\frac{a^2}{6}\frac{\mathrm{d}^2\psi_0(z)}{\mathrm{d}z^2} - \beta[U_{\mathrm{mf}}(z) - \epsilon_0]\psi_0(z) = 0 \tag{10}$$

with the boundary conditions

$$\left.\frac{\mathrm{d}\psi_0(z)}{\mathrm{d}z}\right|_0 = -\frac{\psi_0(0)}{b} \quad \text{and} \quad \left.\frac{\mathrm{d}\psi_0(z)}{\mathrm{d}z}\right|_h = 0 \tag{11}$$

The constant C can be calculated within this approximation as

$$C = \frac{v\Gamma}{N\,K_0^{\,2}\mathrm{e}^{-\beta\epsilon_0 N}} \tag{12}$$

In the ground state dominance approximation only the bound state is considered and the partition function for the adsorbed conformations is also given by eq 9. The volume fraction of monomers belonging to loops is then $\phi_{\mathrm{l}}(z) = v\Gamma_{\mathrm{l}}\psi_0^{\,2}(z)$, where Γ_{l} denotes the contribution of loop-monomers to the adsorbance.[16]

The volume fraction of monomers belonging to tails can be obtained from eq 5: $\phi_t(z) = (2v\Gamma/NK_0)\psi_0(z)\varphi(z)$, with $\varphi(z) \equiv \int_0^{\mathrm{N}} \mathrm{d}M\ G^{\mathrm{f}}(z,M)\ \mathrm{e}^{\beta\epsilon_0 M}$. The integration of the Edwards equation for $G^{\mathrm{f}}(z,M)$ over the molecular weight provides the equation for $\varphi(z)$

$$\frac{a^2}{6}\frac{d^2\varphi(z)}{dz^2} - \beta[U_{mf}(z) - \epsilon_0]\varphi(z) = -1 \qquad (13)$$

with boundary conditions

$$\varphi(0) = 0 \quad \text{and} \quad \left.\frac{d\varphi(z)}{dz}\right|_h = 0 \qquad (14)$$

The total volume fraction can then be calculated as a function of the two order parameters $\psi_0(z)$ and $\varphi(z)$ as

$$\phi(z) = v\Gamma_l\left[\psi_0^2(z) + \frac{2}{NK_0}\,\psi_0(z)\,\varphi(z)\right] \qquad (15)$$

This allows a self-consistent calculation of the mean field potential $U_{mf}(z)$, and thus of the concentration profiles. The energy ϵ_0 of the ground state is here determined by imposing the monomer adsorbed amount Γ.

To calculate the force between the two surfaces mediated by the polymer, we first write the free energy of the polymer solution in half of the gap between the two surfaces. The partition function of a solution of $\aleph = \Gamma/N$ independent and indistinguishable chains in a fixed external potential $U_{mf}(z)$ is

$$Z_{tot} = \frac{1}{\aleph!}\,[Z]^{\aleph} \qquad (16)$$

where Z is the total partition function of one chain defined above. The free energy of this reference system is $\beta F_0 = -\ln Z_{tot}$. In the mean field approach that we use, the mean field potential acting on one monomer is due to the interactions with the other monomers. The entropy of the chains is the same as the entropy of the reference system, but the interaction energy is only half of the interaction between the monomers and the external field. Correcting for this double counting, we thus write the mean field free energy of the solution as

$$\beta F = \left(\ln\frac{C}{v} - 1\right)\aleph - \frac{1}{2v}\int_0^h \beta U_{mf}(z)\,\phi(z)\,dz \qquad (17)$$

The interaction force between the two surfaces is obtained by derivation of the free energy at constant surface coverage Γ: $f(h) = -\partial F/\partial h|_\Gamma$. The explicit derivation has been performed in reference.[8] It turns out to be useful to notice that the equilibrium concentration profile can be obtained by minimization of F with respect to the order parameters $\psi_0(z)$ and $\varphi(z)$ with the constraint that Γ is constant. This constraint can be taken into account by introducing a Lagrange multiplier. The final result for the force per unit area is expressed as a function of the volume fractions at the midplane ($z = h$):

$$v\beta f(h) = -\frac{1}{2}\,\phi^2(h) + \phi_e(h) + \beta\epsilon_0\phi(h) - v\aleph\psi_0{}^2(h) \qquad (18)$$

The interaction energy $u(h)$ can then be obtained by integration of the force.

To perform explicit calculations, it is convenient to write the mean field equations in a dimensionless form. We first use units such that $a\sqrt{6}$, and β are equal to unity. We then change the normalization of the order parameters and define $\psi(z) \equiv \sqrt{v\Gamma_l}\,\psi_0(z)$ and $K \equiv \sqrt{v\Gamma}K_0$. As can be seen from eq 15, the natural length scale of the adsorption problem is $l \equiv (2v\Gamma/NK)^{-1/3}$. This corresponds to the length at which the volume fraction of tails becomes important as compared with the volume fraction of loops. We choose in the following l as the unit length and use the coordinate $\tilde{z} = z/l$. The rescaled order parameters are defined as $\tilde{\psi} = l\psi$ and $\tilde{\varphi} = \varphi/l^2$, and the rescaled volume fraction is $\tilde{\phi} = l^2\phi$. The mean field equations then read

$$\begin{aligned}&\tilde{\psi}''(\tilde{z}) - [\tilde{\phi}(\tilde{z}) - \epsilon]\,\tilde{\psi}(\tilde{z}) = 0;\\ &\qquad\tilde{\psi}(0) + \tilde{b}\tilde{\psi}'(0) = 0,\ \tilde{\psi}'(\tilde{h}) = 0,\\ &\qquad\tilde{\varphi}''(\tilde{z}) - [\tilde{\phi}(\tilde{z}) - \epsilon]\,\tilde{\varphi}(\tilde{z}) = -1;\quad \tilde{\varphi}(0) = 0,\\ &\qquad\tilde{\varphi}'(\tilde{h}) = 0,\quad \tilde{\phi}(\tilde{z}) = \tilde{\psi}^2(\tilde{z}) + \tilde{\psi}(\tilde{z})\,\tilde{\varphi}(\tilde{z})\end{aligned} \qquad (19)$$

where $\tilde{b} = b/l$, $\tilde{h} = h/l$ and $\epsilon = \beta\epsilon_0 l^2$. We also define a reduced force as $\tilde{f} = v\beta l^4 f$

$$\tilde{f}(\tilde{h}) = -\frac{1}{2}\,\tilde{\phi}^2(\tilde{h}) + \tilde{\psi}(\tilde{h}) + \epsilon\tilde{\phi}(\tilde{h}) - \frac{1}{2}\frac{K}{\tilde{\Gamma}}\,\tilde{\psi}^2(\tilde{h}) \qquad (20)$$

where the reduced surface coverage is defined as $\tilde{\Gamma} = vl\Gamma$.

In the rest of the paper, we consider only the rescaled quantities, and for the sake of simplicity we do not write the tilde symbols. One must stress that l depends both on Γ and h. This dependence is however very weak in the range of parameters that we discuss below, and l can be considered as roughly constant. Moreover, due to historical reasons we always compare with $z^* = 2.04l$, instead of l, and call it the crossover distance.

3. Results

We now discuss the behavior of the density profiles and of the force between the two surfaces as functions of the polymer surface excess, and of the distance between plates. We first summarize the asymptotic results obtained by Semenov et al. in the limit of large oversaturation, which corresponds here to $|\epsilon_\infty| \ll 1$, with ϵ_∞ being the asymptotic value of ϵ at infinite distances (isolated plates). The concentration profiles are[7]

$h \to \infty$	$\phi_l(z)$	$\phi_t(z)$
$b \ll z \ll z^*$	$2/z^2$	$(4z/z^{*3})\ln(z^*/z)$
$z^* \ll z \ll \lambda$	$1800z^{*6}/z^8$	$20/z^2$
$\lambda \ll z \ll R$	$\propto (z^{*6}/\lambda^8)\exp(-2z/\lambda)$	$\propto (1/\lambda^2)\exp(-z/\lambda)$

(21)

where $z^* = 2.04$ and $\lambda \equiv 1/\sqrt{|\epsilon_\infty|}$. In this limit, the value of the surface coverage is

$$\Gamma \approx \Gamma_0 + 3.47 - \frac{7.24}{\lambda} + \dots \qquad (22)$$

Here, $\Gamma_0 = 2/b$ is the classical value of the adsorbance that would obtain for one wall in equilibrium with a very dilute bulk solution of infinite chains. We call it the saturation value, and $\delta\Gamma = \Gamma - \Gamma_0$ is referred to as the oversaturation or the undersaturation, depending on its sign. The adsorbance Γ given by eq 22 is at a maximum when $\lambda \gg 1$, and the limit $|\epsilon_\infty| \ll 1$ indeed corresponds to strongly oversaturated systems. Furthermore, eq 21 shows that the adsorbed polymers structure in a double layer array formed by an inner layer ($z < z^*$) dominated by loops and an outer layer ($z > z^*$) dominated by tails; in both layers the volume fraction decays as a power law $\phi(z) \propto (a/z)^2$. The volume fractions of monomers

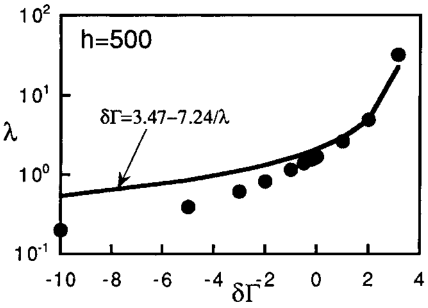

Figure 2. Variation of the adsorbed layer thickness λ as a function of the saturation $\delta\Gamma$. The continuous line is the asymptotic prediction of eq 22.

belonging to loops and tails are equal at a distance $z_0 \approx 1.43$. Due to the finite size of the polymers, the density profiles decay exponentially for $z \gg \lambda$. Thus, λ can be interpreted both as the length of the tails and as the layer thickness.

The force $f(h)$ between the surfaces mediated by the polymer is given by[8]

	$f(h)$
$b \ll h \ll z^*$	$\pi^2\delta\Gamma/2h^3$
$z^* \ll h \ll \lambda$	$1670/h^4$
$\lambda \ll h \ll R$	$\propto (1/\lambda^4)\exp(-2h/\lambda)$

(23)

Thus, the interaction between oversaturated plates is repulsive at all distances. However, the properties of the inner layer are in a first approximation independent of the tail structure, so that the short distances expression of the force, $f(h) \approx \pi^2\delta\Gamma/2h^3$, is also valid for undersaturated systems (provided that the undersaturation is not too large and that the end-points contribution to the force, the second term in eq 20 can be neglected). In fact, this expression is obtained whenever the force in eq 20 is dominated by the interaction between loops.

A brush-like structure with small loops and large tails is expected in strongly oversaturated systems ($\lambda \gg 1$), as inferred from eq 21. In the opposite case, when the walls are strongly undersaturated ($\lambda \ll 1$), the adsorbed layers are essentially made of loops, and the classical ground state dominance theory of polymer adsorption is expected to account for their physical properties. In most experimental situations however the surface coverage is in the neighborhood of the saturation value, and $\lambda \sim 1$. To study such systems, it is therefore necessary to solve eq 19 without any limitations on the value of λ. This is the subject of this paper, and this is done by implementing finite differences numerical methods[11] to solve the mean field equations. Typical values of b in these systems are between 0.05 and 0.1, in scaled units, we take here however a somehow smaller value, $b = 0.01$ ($\Gamma_0 = 200$), which allows us to have well-separated regimes in z and h and to sort out the various physical phenomena involved. The volume fraction profile $\phi(z)$ and the force profile $f(h)$ are then evaluated for several values of the distance h and of the surface excess Γ. Let us first discuss the concentration profiles.

The thickness λ of the adsorbed layer is plotted in Figure 2 as a function of $\delta\Gamma$ and compared to the asymptotic result of eq 22. For the numerical calculations we take walls separated by the distance $h = 500$, which can be considered as isolated. At the maximum oversaturation λ diverges, and ϵ_∞ vanishes. We find numerically a maximum adsorbed amount 203.185 ± 0.005, which is somehow smaller than the prediction of eq 22, namely 203.47. The value 1.427 ± 0.001 is found for the distance z_0 at which the volume fractions of monomers belonging to loops and tails are equal, when Γ is at a maximum.

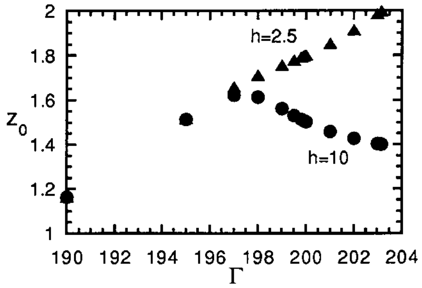

Figure 3. Composition crossover distance z_0 as function of the adsorbance Γ for two systems with $h = 10$ and 2.5.

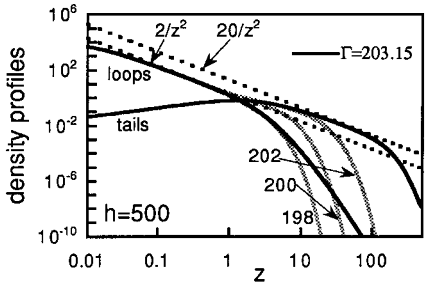

Figure 4. Density profiles of four systems with $\Gamma = 203.15$, 202, 200, and 198 and $h = 500$. The black lines represent $\varphi_l(z)$ and $\varphi_t(z)$, and the gray lines $\varphi(z)$. The dashed lines correspond to the analytical results for $\lambda \gg z^*$.

When the two surfaces are at a finite distance, z_0 is a function of both Γ and h, as shown in Figure 3. In undersaturated systems, z_0 is small because the layers are very thin. When Γ increases, both loops and tails grow, and z_0 increases. For relatively large distances, $h = 10$ for example, a maximum value of z_0 as a function of Γ is reached, and beyond this value, the tails increase at the expense of the loops and z_0 decreases. The opposite behavior is observed at smaller distances, $h = 2.5$ for example, where the size of the tails is strongly limited by the small separation between walls and the loop concentration increases faster with Γ than the tails volume fraction. In addition, $\phi_l(z)$ and $\phi_t(z)$ never cross for very small values of h, and consequently, z_0 does not exist. The effective adsorption energy ϵ (not shown here) is negative for large values of h ($\gg\lambda$), and positive for small values of h ($\ll\lambda$). At distances smaller than λ, ϵ is on the order of the chemical potential of a polymer solution at the volume fraction $\phi(h)$: $\epsilon \approx \mu^{ex}(h) \approx \phi(h)$. At distances of order b, the concentration is roughly constant, $\phi \approx \Gamma/h$, and $\epsilon \approx \Gamma/h$. At larger distances, the effective adsorption energy only weakly depends on Γ and decays as h^{-2}.

Figure 4 shows the loops and tails volume fractions, $\phi_l(z)$ and $\phi_t(z)$, on a log−log scale for a system with $\Gamma = 203.15$ and $h = 500$ (full lines). At this separation, the walls are expected to behave as if they were isolated. In addition, the value 203.15 is very close to the maximum coverage, so that our results are in good agreement with the analytical expressions for $\lambda \gg 1$, which are represented in the figure by dashed lines. The

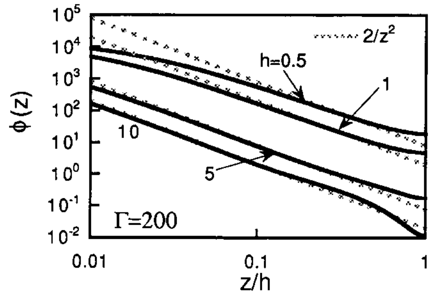

Figure 5. Total volume fraction $\phi(z)$ as function of z/h for four systems with $h = 10$, 5, 1, and 0.5 and $\Gamma = 200$. The dashed gray lines represent the asymptotic loops behavior $2/z^2$.

double layer structure of the adsorbed polymers is clearly observed, as well as the exponential tail for $z \gg \lambda$. Here, the values of z_0 and λ are 1.427 and 32.14, respectively. The gray lines in Figure 4 correspond to the total volume fractions $\phi(z)$ of systems with $\Gamma = 202$ ($z_0 \approx 1.437$ and $\lambda \approx 4.89$), $\Gamma = 200$ ($z_0 \approx 1.502$ and $\lambda \approx 1.677$) and $\Gamma = 198$ ($z_0 \approx 1.614$ and $\lambda \approx 0.823$), in the same decreasing order. Since $\lambda < 1$ in the undersaturated system, the volume fraction profile directly crosses over from the loops regime to an exponential tail. In fact, the double layer structure is characteristic only of oversaturated systems. The word double layer is however more an academic expression than a measurable effect, since the density of the tails layer is several orders of magnitude smaller than the density of the loops layer. The loops show a similar structure for all values of Γ, as if they were independent of the tails. From the rescaling of the previous section, we know that Figure 4 actually shows $l^2\phi(z)$. Typical values of l are between 10^1 and 10^2, so that the real volume fractions reach unphysical values for $z \leq 0.1$. This is a consequence of using the second virial approximation $U_{\mathrm{mf}}(z) \approx \phi(z)$ when many-body interactions become important. Thus, we expect our results to be correct for $z \geq 0.1$, when the unscaled volume fraction $\phi(z)$ becomes appreciably less than 1. At smaller distances, molecular details may become relevant.

Figure 5 shows the volume fraction $\phi(z)$ vs z/h between two saturated walls for $h = 10$, 5, 1, and 0.5. The gray dashed lines represent the asymptotic loops contribution $2/z^2$, which provides an excellent approximation in the whole range $[0,h]$. In the case $\lambda \sim 1$, the same decaying power law is observed for $\phi(z)$ as in the under- and oversaturated cases. The tendency of the curves to be flat observed in Figure 5 by decreasing h is expected to lead to a uniform distribution $\phi = \Gamma/h$ for very small distances. In fact, this law describes well the numerical results for $h \lesssim 0.1$, until close packing is reached.

Figure 6 shows the interaction force between the two surfaces; the absolute value of $f(h)$ is plotted on a log–log scale for three systems with $\Gamma = 203.15$, 200, and 198. The first system (black line) corresponds to a value close to the maximum oversaturation, so that our results agree with the asymptotic expressions in eq 23, represented by dashed lines. The second system ($\Gamma = 200$) corresponds to $\lambda \sim 1$. As expected, the force is repulsive. However, the decaying power law is no longer -3, as in the under- and oversaturated cases, but -1. The interaction between loops vanishes in this case and, even at short distances, one must include the first correction due to the end points given by the second term on the right-hand side of eq 20. As the order parameter at the midplane decays as $\psi(h) \propto h^{-1}$, the force is

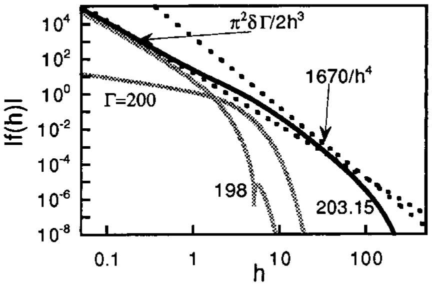

Figure 6. Absolute value of the interaction force $f(h)$ for three systems with $\Gamma = 203.15$, 200, and 198. The dashed lines correspond to the analytical results for $\lambda \gg z^*$.

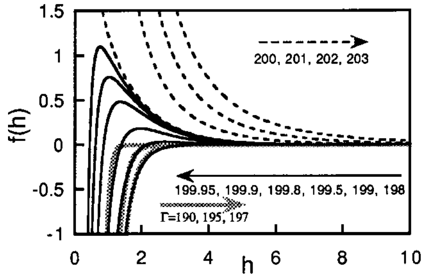

Figure 7. Saturated and oversaturated walls repel each other (dashed lines), while high undersaturated walls interact only attractively (gray lines). The interaction between slightly starved walls (black lines) changes from repulsive to attractive as they come together, the amplitude of the repulsive barrier increases with the surface coverage.

$$f(h) \approx \frac{\pi^2 \delta\Gamma}{2h^3} + \frac{\alpha}{h} \tag{24}$$

where α is a numerical constant. In the last system ($\Gamma = 198$), the force is attractive at short distances ($h < 1$), and varies as $\pi^2\delta\Gamma/2h^3$, with $\delta\Gamma = -2$, as expected. For $h \gtrsim 5$, the force is repulsive (see the discontinuity in the exponential tail). The interaction varies therefore nonmonotonically with h. We now study this phenomenon in detail.

The variation of the force is displayed in Figure 7 for a broader range of values of the saturation $\delta\Gamma$. For strongly undersaturated systems ($\Gamma \lesssim 197$), the force is purely attractive (gray lines). The range of the force increases with Γ, due to the increasing size λ of the layer, which makes easier the formation of bridges between walls. In addition, at smaller distances the curves cross and the force becomes more attractive for larger undersaturation, as predicted by eq 24. This is shown in Figures 8 and 9. At large distances, the force decays exponentially, as shown in Figure 9. We cannot discard here the possibility of a very shallow maximum, but the repulsive part of the force would correspond to extremely weak values, and would be therefore negligible. For weak undersaturation ($198 \lesssim \Gamma \lesssim 200$), we observe a nonmonotonic force (black lines) changing from repulsive to attractive as the plates come closer to each other. The repulsion appears when the tails of the adsorbed chains reach the midplane between the plates. Then, further compression leads to a reduction of the entropy of the system. However, when the first tails penetrate the opposite layer and reach the wall, adsorption on both surfaces takes place, leading to a lowering of the energy. The attraction appears when

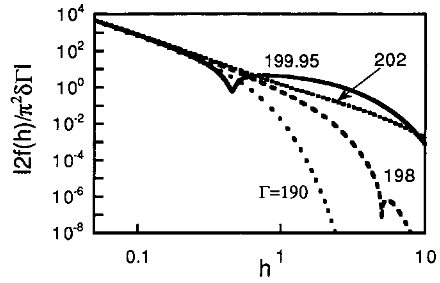

Figure 8. Short distance force between surfaces. As predicted by eq 24, the force f is proportional to the saturation $\delta\Gamma$ and the curves corresponding to various adsorbances superimpose at short distances. The various curves correspond to $\Gamma = 190$, 198, 199.5, and 202.

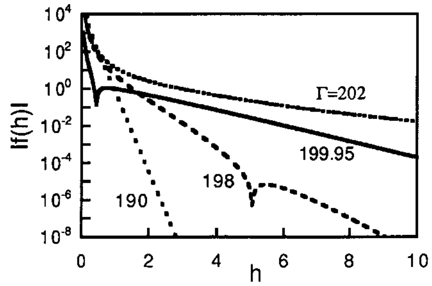

Figure 9. Long distance behavior of the force. The force f decays exponentially with the distance h as shown by the semilogarithmic plot. The values of Γ are the same as in Figure 8.

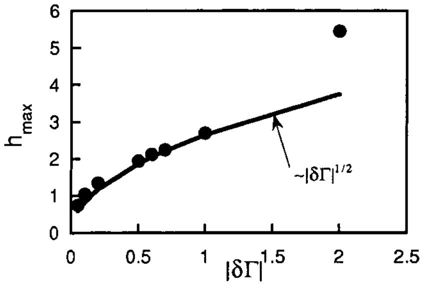

Figure 10. Variation of the distance where the force is a maximum, $h_{\max}$, as a function of the saturation $\delta\Gamma$. The numerical results are compared to the scaling prediction of eq 24.

this effect dominates over the entropic repulsion. The attraction is also well described by eq 24 (see Figure 8). The position of the maximum repulsive force, as predicted by eq 24, behaves as $h_{\max} \propto |\delta\Gamma|^{1/2}$. This scaling law is tested in Figure 10, and found to be valid for small undersaturation, when the maximum occurs well into the loop-dominated region. At larger undersaturation, no scaling law can be proposed. The repulsive force at large distances decays exponentially with h, with a range of the order of λ. When the plates are saturated (first dashed line from left to right in Figure 7) the interpenetration rarely produce a bridge, so that the interaction is purely repulsive (this justifies a posteriori the use of the term saturation for the classical result $\Gamma_0 = 2/b$). For oversaturated plates ($\Gamma > 200$), the range of the repulsion increases with Γ (see the other dashed lines), because the tails become larger. The nonmonotonic behavior of the force is observed for $|\delta\Gamma| \lesssim 1\%$, and the repulsive barrier may be arbitrarily high (limited only by the strong repulsion at $h \lesssim 0.1$.

For undersaturated systems, our calculations predict an attractive force at short distances. One should however point out that at short distances the volume fraction is very high, and that higher order terms in the virial expansion can become important. If we include the third virial contribution, the mean field potential reads (in the original nonrescaled units) $U_{\mathrm{mf}}(z) = \phi(z)+w\phi^2(z)$, where w is dimensionless, and of order 1. The correction to the interaction force due to this term treated as a perturbation is repulsive at short distances. Its value in dimensionless units is $\delta f \propto l^{-2}h^{-6}$, which clearly dominates over $\pi^2\delta\Gamma/2h^3$ if h is small enough, and one thus expects a repulsive force for $h \ll 1$. We have observed this numerically when the third virial interaction is included. The force is then repulsive at short distances, attractive at intermediate distances, and eventually repulsive again at large distances, due to the effect of the tails. Furthermore, the density may become so high at small distances that not only the third virial coefficient may be relevant but also all the higher order terms. This could be taken into account by using locally the standard Flory free energy that includes, at least qualitatively, all these higher order terms.

4. Conclusions

We have calculated numerically the polymer density profiles and the polymer mediated interaction force between two very large colloidal particles modeled as planar surfaces in the limit where the adsorption is irreversible and where the adsorbed amount is imposed on each surface. This corresponds to what is usually done in a surface force apparatus where the polymer is first adsorbed on the surfaces and then the polymer solution is washed and replaced by pure solvent.[17] The adsorbed amount is then controlled by the concentration in the adsorbing polymer solution and more importantly by the adsorption kinetics (the incubation time of the surfaces in the polymer solution). It is in general observed that the desorption is small even in contact with pure solvent. Our approach is based on a mean field theory and thus ignores the excluded volume correlations that play an important role in good solvents. It does however take into account both the monomers belonging to the loop and tail sections of the chains, and thus explicitly the effect of the chain ends. We also assume that the chain conformation can reequilibrate freely, and that the system is at local thermodynamic equilibrium; stronger irreversibilities (fixed loop structure) have been considered by other authors.[12]

When the surfaces are oversaturated, our results are in good agreement with the scaling results recently published by Semenov et al.[7,8] For undersaturated surfaces, we obtain an attraction at small distances and eventually a repulsion at large distances due to the tails of the chains. The magnitude of the repulsion can be very large in the limit of vanishing undersaturation and can thus constitute a strong potential barrier against aggregation. This nonmonotonic behavior is in qualitative agreement with recent force measurements between magnetic emulsions.[13] The short distance attraction between undersaturated layers is due to a strong bridging and has already been predicted using scaling theories.[4-6] As explained in the previous section, at very short distances, the density is very high and the force is repulsive because of the strong repulsive excluded volume interaction.

In the loops region ($h < 1$), the force decays as a power law of the distance. In the tails region ($h > 1$) and for strongly oversaturated systems, a repulsive power law decay is also expected, but our numerical results indicate that this asymptotic power law is very rarely observed and that crossover effects play an important role. For most practical purposes the large distances exponential decay (either attractive in cases of undersaturation or repulsive in cases of oversaturation) will be observed at rather small distances (of order λ, or l, which in many cases are comparable and of the order of 10 nm or less). This is consistent with many experimental results, and in particular with recent force measurements done in Bordeaux,[14] which systematically show a repulsive exponential decay of the force at large distances.

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References and Notes

(1) de Gennes, P. G. *Scaling Concepts in Polymer Physics;* Cornell: Ithaca, NY, 1985.
(2) Klein, J. In *Liquids at interfaces*; Charvolin, J., Joanny, J. F., Zinn-Justin, J., Eds.; North-Holland: Amsterdam, 1990.
(3) Fleer, G.; Cohen-Stuart, M.; Scheutjens, J.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces;* Chapman and Hall: London, 1993.
(4) de Gennes, P. G. *Macromolecules* **1981**, *14*, 1637.
(5) de Gennes, P. G. *Macromolecules* **1982**, *15*, 492.
(6) Rossi, G.; Pincus, P. A. *Macromolecules* **1989**, *22*, 276.
(7) Semenov, A. N.; Bonet-Avalos, J.; Johner, A.; Joanny, J. F. *Macromolecules* **1996**, *29*, 2179.
(8) Semenov, A. N.; Joanny, J. F.; Johner, A.; Bonet-Avalos, J. *Macromolecules* **1997**, *30*, 1479.
(9) Johner, A.; Bonet-Avalos, J.; van der Linden, C. C.; Semenov, A. N.; Joanny, J. F. *Macromolecules* **1996**, *29*, 3629.
(10) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics;* Clarendon Press: Oxford, England, 1986.
(11) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes;* University Press: Cambridge, England, 1989.
(12) Guiselin, O. *Europhys. Lett.* **1992**, *17*, 225.
(13) Bibette, J. Private communications.
(14) Mondain-Monval, O.; Espert, A.; Omarjee, P.; Bibette, J.; Leal-Calderón, F.; Philip, J.; Joanny, J. F. *Phys. Rev. Lett.* **1998**, *80*, 1778.
(15) This assumption can be relaxed to some extent.
(16) We only have to distinguish between the total adsorbance Γ and Γ_1 in the leading term of the adsorbance; otherwise, we use the total adsorbance Γ throughout.
(17) The case of colloids is actually more complex since only internal modes of the layer faster than the collision time relax, slower modes being frozen. A more repulsive force is thus anticipated during fast collisions.

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