Macromolecules **1997,** *30,* 1479−1489

Interaction between Two Adsorbing Plates: The Effect of Polymer Chain Ends

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Received August 20, 1996; Revised Manuscript Received December 16, 1996[⊗]

ABSTRACT: The interaction between two plates coated by adsorbed polymer layers is considered theoretically in the marginal solvent regime. A novel mean-field approach that takes into account the effect of chain ends is proposed. The approach generalizes the well-known ground-state dominance theory. It is shown that the effect of polymer chain ends is important even if there is no specific interaction between the ends and the adsorbing plates. Both cases of polymer layers in equilibrium with a bulk dilute or semidilute solution and of fixed amount of polymer between the plates are considered. In all the cases the effect of polymer chain ends changes the interaction between the plates from an attraction to a repulsion if the plates are far enough from each other. This additional repulsive interaction can be qualitatively interpreted as being due to an ideal-gas pressure of chain ends.

I. Introduction

The interactions between colloidal particles can be strongly modified by addition of linear polymer to the solution.[1] This is, however, a rather subtle effect, and it has long been recognized experimentally that even the sign of the polymer-mediated interaction between colloidal particles strongly depends on the precise experimental conditions such as the solvent quality for the polymer, the reversibility of the adsorption, or the adsorbed amount of polymer on a colloidal particle. Even when the polymer is adsorbing from a good solvent onto colloidal particles, the force between the particles is repulsive (and is due to the excluded volume interaction between adsorbed layers) if the particles are saturated with polymer, but it is attractive (and is due to bridging by the polymer between different particles) if the particles are starved and do not carry a saturated polymer layer. Polymer-mediated interactions between surfaces also play an important role in various industrial applications such as lubrication or adhesion.

From the theoretical point of view, the interaction between colloidal particles due to a polymer solution results from a balance between the osmotic, excluded-volume interaction and the entropy of the chain conformation. The first theoretical description of the interaction is due to De Gennes.[3] It is a mean-field theory based on the standard ground state dominance approximation for the Edwards equation describing the chain conformation in the gap between the surfaces. One of the main output of De Gennes's work is that the reversibility of the polymer adsorption on the colloid surfaces is a parameter of major importance. If the adsorbed polymer is in thermal equilibrium and can freely exchange with the bulk of the solution, the interaction force is always attractive and decays as a power law of the interparticle distance. In most experimental cases, however, the time scale for chain diffusion outside the gap between particles would be much larger than any experimental time and it is reasonable to assume that the adsorption is irreversible. The simple approximation used by De Gennes is that the amount of polymer trapped in the gap between two particles remains constant and thus that there is no polymer desorption during the approach between two particles. The polymer solution inside the gap is considered in full thermal equilibrium, and the chain conformations can readjust freely. In certain cases, the irreversibility is stronger and the number of monomers on the surface[6] or even the distribution of loops can remain frozen irreversibly (this leads then to the formation of a so-called pseudo-brush which has been studied in detail[4]). We will not consider these cases further in this paper, and we call irreversible adsorption the case where the adsorbed polymer amount (the adsorbance) is frozen. In this case the mean-field theory in the ground state dominance approximation predicts a vanishing force if the surfaces are saturated with polymer, i.e. if the adsorbance is twice the adsorbance of a dilute polymer solution in equilibrium with a single surface.

De Gennes has also extended his results beyond the standard mean-field theory by using a renormalized free energy functional similar to that used in critical phenomena by Widom. Although this approach involves rather uncontrolled approximations, it is supposed to take more correctly into account the excluded volume correlations, and thus it leads to more reliable scaling laws. In the case of reversible adsorption, the force per unit area is attractive and scales with the distance h between the surfaces as $-kT/h^3$ (as can be obtained from dimensional analysis assuming that h is the only relevant length scale in the problem). In the case of irreversible adsorption the renormalized mean-field theory predicts a repulsive force of order kT/h^3 if the surfaces are saturated with polymer. If the surfaces are not saturated, the force is non monotonic, and it is attractive at large distances and repulsive at short distances.[2] These results are in good qualitative agreement with the Scheutjens−Fleer approach[5] which is based on a numerical solution of the full mean-field equations. They also provide an interpretation of most of the experimental data obtained with a surface force apparatus which show a repulsive force due to polymer adsorption.[11]

In our recent papers,[9,10] we have shown that the ground state dominance approximation[7,8] correctly accounts for the concentration of monomers belonging to

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

S0024-9297(96)01263-6 CCC: $14.00

the loop sections of the chains, but that it entirely ignores the contribution of monomers belonging to the tail sections at the end of the chains. As pointed out by Scheutjens and Fleer,[5] this is a poor approximation in the outer part of an adsorbed polymer layer where most monomers belong to tails. We have constructed a new mean-field theory that correctly accounts for the tails in polymer adsorption on a single solid surface.[9,10] This theory gives the asymptotic limit of the Scheutjens−Fleer theory for large molecular weights. We have also quantitatively compared our results to the numerical self-consistent field approach in a recent paper.[12] The aim of this paper is to extend this new mean-field theory to describe the polymer adsorption between two surfaces and to calculate the interaction between the surfaces. A short account of the essential results in the case of reversible adsorption has already been published.[13]

The paper is organized as follows. In the next section, we give the general framework of the mean-field theory with two order parameters; we derive formal expressions for the free energy and the force between surfaces. Section 3 is devoted to reversible adsorption (in equilibrium with a bulk polymer solution) and section 4 to irreversible adsorption (with the constraint of constant coverage). The last section presents some concluding remarks.

II. Mean-Field Theory and Ground State Dominance Approximation

In this section we present the mean-field theory with two order parameters that allows to description of the structure of an adsorbed layer in terms of tails and loops. We first establish the general equations that determine the monomer concentration profile between two surfaces. We then derive the free energy of the solution and the force between the two plates mediated by the polymer solution.

A. Partition Functions. We study a semidilute polymer solution with concentration ϕ. In the mean-field approximation, the interaction free energy between the monomers is given by a virial expansion that we truncate at second order, $\mathcal{F}_{\text{int}} = (v/2)k_BT\phi^2 = (v/2)\phi^2$ where v is the monomer-excluded volume. Here and below we use the thermal excitation k_BT as the energy unit. This virial expansion provides a good description of semidilute solutions in the so-called marginal solvent regime.[14]

The solution is confined in a slab between two adsorbing solid surfaces (at $z = 0$ and $z = 2h$), and it is in equilibrium with a bulk solution of concentration ϕ_0. The total adsorbance (number of monomers between the plates per unit area) is $\Gamma = \int_0^{2h}\phi(z)\mathrm{d}z$ where $2h$ is the distance between the plates.

The attraction of the monomers to the plates is described by a short range surface−monomer interaction $U_s(z)$ localized near the plates. The statistics of each chain inside the slab is driven by the total mean-field potential $U_{\text{tot}} = U_s + U_{\text{mol}}$, where $U_{\text{mol}}(z) = \partial\mathcal{F}_{\text{int}}/\partial\phi = v\phi(z)$ is the molecular field.

The conformation and the partition function of one polymer chain in the solution are the same as those of an isolated polymer chain in the external potential U_{tot}.[8,15,10] If each chain comprises N monomers, we call $Z(N, z)$ the partition function of a chain with one end point fixed at position z. The concentration of chain ends in the solution in the gap between the two plates, $\rho(z)$, is proportional to this partition function: $\rho(z) = CZ(N, z)$. The equilibrium with the bulk implies that the constant C is the same in the slab and in the bulk solution, so that $C = \rho_0/Z_0$, where $\rho_0 = 2\phi_0/N$ is the bulk chain end concentration and $Z_0 = e^{-v\phi_0N}$ is the bulk partition function ($v\phi_0$ is the monomer chemical potential in the bulk). Thus $\rho(z) = (2\phi_0/N)Z(N, z)/Z_0$. As the total number of chain ends in the slab, $\int\rho(z)\mathrm{d}z$, is equal to $2\Gamma/N$, we obtain the total adsorbance in terms of the single chain partition function $Z(N) = \int_0^{2h}Z(N, z)\mathrm{d}z$ as

$$\Gamma = \phi_0Z(N)/Z_0 \tag{1}$$

The partition function of a chain with its n-th monomer fixed at position z is $Z(n, z)Z(N - n, z)$, where the two factors correspond to the two independent chains starting from monomer n. The total monomer concentration due to $\mathcal{N} = \Gamma/N$ independent chains is

$$\phi(z) = \frac{\Gamma}{N}\int_0^N\frac{Z(n, z)Z(N - n, z)}{Z(N)}\,\mathrm{d}n \tag{2}$$

The concentration depends on the total mean-field potential U_{tot} through the partition function $Z(n, z)$. In order to get the *conformational* free energy of the solution in the slab, we must subtract the potential energy from the total free energy $-\mathcal{N}\ln Z(N)$:

$$\tilde{F}_{\text{conf}} = -\mathcal{N}\ln Z(N) - \int U_{\text{tot}}(z)\phi(z)\mathrm{d}z \tag{3}$$

The partition function, $Z(n, z)$, satisfies the following master equation[10,8,15]

$$\frac{\partial Z}{\partial n} = Z'' - U_{\text{tot}}Z, \quad Z(0, z) = 1, \qquad Z(n, 0) = Z(n, 2h) = 0 \tag{4}$$

It can be decomposed in terms of eigenfunctions as

$$Z(n, z) = \sum_s K_s\psi_s(z)e^{-E_sn} \tag{5}$$

where ψ_s and E_s are the eigenfunctions and the eigenvalues of the associated Edwards−Schrödinger equation, $-a^2\psi'' + U_{\text{tot}}\psi = E\psi$. The constant K_s is defined as $K_s = \int\psi_s(z)\mathrm{d}z$ and the eigenfunctions are normalized, $\int|\psi_s(z)|^2\,\mathrm{d}z = 1$. Note that only even eigenstates, which are symmetric with respect to the transformation $z \rightarrow 2h - z$, are relevant.

The chain statistical segment is here defined as $a6^{1/2}$, so that the mean square end-to-end distance of a chain of n monomers is $\langle R_n^2\rangle = 6na^2$. In the following, we choose a as the unit length.

The effect of the surfaces can be taken into account by effective boundary conditions which replace the hard-wall boundary conditions $\psi(0) = \psi(2h) = 0$:[16]

$$(\psi'/\psi)_{z=+0} = -1/b, \quad (\psi'/\psi)_{z=2h-0} = 1/b \tag{6}$$

The length b is the so-called extrapolation length; it characterizes the strength of the wall attraction and becomes smaller as the attraction gets larger. With these new boundary conditions, we rewrite the eigenstate equation as

$$-\psi'' + U\psi = E\psi \tag{7}$$

where the potential is now the molecular field $U = U_{\text{mol}}(z)$. The chain partition function $Z(N, z)$, is dominated by the ground-state which has the lowest eigenvalue E_0 if the energy gap between E_0 and the other eigenvalues is large enough, $\epsilon = E_1 - E_0 \gg 1/N$. The energy gap depends both on the bulk concentration ϕ_0 and on the distance $2h$. In the limit where the distance between plates $2h$ is much smaller than the Gaussian coil size $R = N^{1/2}a$ the energy gap can be estimated as $\epsilon \gtrsim 1/h^2$, so that the ground state dominance condition is satisfied. Thus, in a first approximation, we can write up to an exponentially small correction

$$Z(N, z) = K_0\psi_0(z)e^{-E_0N}, \quad Z(N) = K_0^2e^{-E_0N} \tag{8}$$

However, the terms neglected by this pure ground state dominance approximation are important for the partition function $Z(n, z)$ of a short chain section containing $n \ll N$ monomers. We write

$$Z(n, z) = e^{-E_0n}[K_0\psi_0(z) + r(n, z)] \tag{9}$$

where the rest function is defined as

$$r(n, z) = \sum_{s>0}K_s\psi_s(z)e^{-(E_s - E_0)n} \tag{10}$$

Equation 9 just amounts to rewriting the partition function of eq 5 in a different form. Physically the first term in eq 9 roughly corresponds to the adsorbed states (many contacts of the chain with the walls) and the second term to the free states (no contacts). This point is discussed further in ref 10 and in the Appendix. The monomer concentration is obtained by inserting eqs 8, 9 into eq 2 as a sum of three terms proportional to ψ_0^2, $\psi_0 r$, and r^2. However, the last term is proportional to $e^{-\epsilon N}$ and thus is negligible. Physically this means that there are no free chains in the slab. Keeping only the first two terms, the monomer concentration reads

$$\phi(z) = \Gamma\psi_0^2(z) + \frac{2\Gamma}{NK_0}\psi_0(z)r(z) \tag{11}$$

where $r(z) \equiv \int_0^N r(n, z)\, dn$. The upper boundary in the integral defining $r(z)$ can be extended to ∞ as $r(n, z)$ is exponentially small for $n > N$. We thus redefine $r(z)$ as

$$r(z) = \int_0^\infty[e^{E_0n}Z(n, z) - K_0\psi_0(z)]dn \tag{12}$$

Taking into account that $Z(0, z) \equiv 1$, it can be directly checked that $r(z)$ satisfies the following equation

$$-r'' + (U - E_0)r = 1 - K_0\psi_0(z) \tag{13}$$

The boundary conditions for $r(z)$ are also given by eq 6. Equation 12 also implies that the functions $r(z)$ and $\psi_0(z)$ are orthogonal:

$$\int_0^{2h}r(z)\psi_0(z)dz = 0 \tag{14}$$

We now return to the real solution of interacting chains and we impose the self-consistency condition:

$$U = U_{\mathrm{mol}} = v\phi(z) \tag{15}$$

The total adsorbance Γ is not an independent variable; it is related to E_0 and ψ_0 via eqs 1, 8,

$$\Gamma = \phi_0K_0^2e^{\epsilon_bN} \tag{16}$$

where $\epsilon_b = v\phi_0 - E_0$ is the effective adsorption energy per monomer which was denoted ϵ in ref 10. Note that the adsorbance is determined here from the ground state dominance approximation. This is legitimate since it is dominated by the vicinity of the adsorbing surface where the loops are dominant; the other contributions to the concentration profile only lead to small corrections to the adsorbance.

The novel ground state dominance formalism is completely specified by these equations together with the Edwards equation for the order parameter $\psi_0(z)$,

$$-\psi_0'' + U\psi_0 = E_0\psi_0 \tag{17}$$

They allow determination of the two order parameters $\psi_0(z)$ and $r(z)$ and then the concentration profiles. The classical ground state dominance theory is recovered if the second-order parameter, $r(z)$, is formally set equal to zero. This roughly amounts to neglecting the tail contribution to the concentration and to keep only the loop and bridge contributions. The formalism presented here is slightly different from the one developed in ref 10 (we use here the rest function $r(z)$ instead of the free chain partition function $\varphi(z)$). The connection between the two approaches is discussed in the Appendix.

B. Free Energy. The total free energy of the solution in the slab (per unit area) can be written as the sum of the interaction, conformational, surface, and combinatorial contributions:

$$F = F_{\mathrm{int}} + \tilde{F}_{\mathrm{conf}} + \int U_s(z)\phi(z)dz + \ln(\mathcal{N}!)$$

The interaction free energy is

$$F_{\mathrm{int}} = \frac{v}{2}\int\phi^2(z)dz \tag{18}$$

and the total number of chains is

$$\mathcal{N} = \int\phi(z)dz/N \tag{19}$$

After some transformations using eqs 3, 8, 17, 13, 11 we rewrite the free energy as

$$F = F_{\mathrm{conf}} + F_s + F_{\mathrm{int}} \tag{20}$$

where F_s is the effective surface energy (Note that F_s includes only part of the true interaction energy, $\int U_s\phi dz$; another part is included in F_{conf}.):

$$F_s = -\frac{1}{b}[\phi(0) + \phi(2h)] \tag{21}$$

and F_{conf} is a redefined conformational energy which now includes also the combinatorial term

$$F_{\mathrm{conf}} = \int\eta'\psi'dz + \mathcal{N}\ln\frac{\mathcal{N}\left(\int\psi^2dz\right)}{e\left(\int\psi dz\right)^2} \tag{22}$$

We have used here the notations $\psi = \psi_0$, and $\eta = \Gamma(\psi_0 + (2r/NK_0))$, the local concentration is thus $\phi = \psi\eta$. The function $\eta(z)$ satisfies an equation similar to eq 13 (with the same boundary conditions as ψ given by eq 6).

$$-\eta'' + (U - E_0)\eta = \frac{2\Gamma}{NK_0}(1 - K_0\psi_0) \tag{23}$$

We now consider the order parameters ψ and η as *unknown* independent functions, and the free energy

F_{conf} as a functional of these order parameters, with the constraint

$$\phi = \psi\eta$$

The total grand canonical free energy of the solution in the slab is,

$$\Omega(\mu_0,h) = F - \mu_0\int\phi\mathrm{d}z + 2h\Pi_0 \tag{24}$$

where $\mu_0 = v\phi_0 + 1/N \ln \phi_0/N$ is the bulk chemical potential and $\Pi_0 = \phi_0/N + v\phi_0^2/2$ is the bulk osmotic pressure. It can also be considered as a functional of the two order parameters ψ and η. An important statement is that $\Omega[\psi, \eta]$ is the relevant thermodynamic potential for the adsorption problem: the equilibium state corresponds to the minimum of Ω with respect to ψ and η. In fact, the minimization of Ω as a functional of ψ and η leads to equations for the order parameters which exactly coincide with eqs 23, 17 with a ground state energy

$$E_0 = \mu_0 + \frac{1}{N}(\ln K_0^2 - \ln N) \tag{25}$$

(the last equation is in agreement with eq 16). The only difference is that the equation obtained for η is slightly more general:

$$-\eta'' + (U - E_0)\eta = 2N\left[\frac{1}{\int\psi\mathrm{d}z} - \frac{\psi}{\int\psi^2\mathrm{d}z}\right] \tag{26}$$

This equation is identical to eq 23 if we impose the normalization condition $\int\psi^2\mathrm{d}z = 1$. It is not, however, necessary to assume any particular normalization of the function $\psi(z)$: eqs 17, 26 imply a family of solutions which can be generated by the transformation

$$\psi \rightarrow \Lambda\psi, \quad \eta \rightarrow \frac{1}{\Lambda}\eta \tag{27}$$

with a real Λ. This transformation does not change any real physical property (in particular neither the concentration profile, nor the free energy). Therefore both $F_{\mathrm{conf}}[\psi, \eta]$ and $\Omega[\psi, \eta]$ are indeed the proper thermodynamic potentials.

This statement is not trivial as the *derivation* of eq 22 ensures that it gives the correct free energy only for the *particular* values of the order parameters ψ and η that satisfy the differential eqs 23, 17, i.e. for the equilibrium values of the order parameters and not in the general case. The conformational free energy could be expressed in a form different from eq 22; for example one could omit $\int\psi^2\mathrm{d}z$ under the logarithm in this equation as this integral is equal to 1 for $\psi = \psi_0$. The grand canonical potential calculated this way would not be a proper thermodynamic potential since its minimization would not lead to the equilibrium values of the order parameters.

In order to obtain the conformational free energy for a *given* monomer concentration profile $\phi(z)$, $F_{\mathrm{conf}}[\psi, \eta]$ must be minimized with the additional constraint $\psi(z)\eta(z) = \phi(z)$. If we omit the second term in eq 22 (which is formally proportional to $1/N$ and is thus representing the end contribution to the free energy), we obtain (up to a trivial transformation of the type 27) $\psi(z) = \eta(z) = (\phi(z))^{1/2}$. We are thus led to the classical "ground state dominance" approximation[18,8,7] with only one order parameter (say ψ):

$$F_{\mathrm{conf}}^{(0)} = \int(\psi')^2\mathrm{d}z, \quad \phi = \psi^2$$

Therefore it is the second term in the rhs of eq 22 that makes a difference between the classical ground state dominance theory and the novel approach presented in ref 10 and in this paper. One can *qualitatively* interpret this term as (minus) the entropy of the chain end points. Indeed, if $\psi(z)$ were constant, this term would be exactly equal to the ideal-gas free energy of the ends, $F_{\mathrm{id}} = N \ln(\rho/e)$ where $\rho \propto \psi$ is the end concentration. However it is dangerous to proceed further with this analogy. In particular, the conformational free energy $F_{\mathrm{conf}}[\psi, \eta]$ given by eq 22 *cannot* be interpreted as the free energy of a polymer system with a given concentration profile $\phi(z) = \psi(z)\eta(z)$ and a given chain end distribution $\psi(z)$.

The functional $\Omega[\psi, \eta]$ is invariant by two families of transformations: those given by eq 27 for any Λ and the translations

$$\psi(z) \rightarrow \psi(z + d), \quad \eta(z) \rightarrow \eta(z + d)$$

If this functional were of the Lagrangian type, these invariances would imply two conservation laws (for the "current" and the "energy"). However $\Omega[\psi, \eta]$ is not of the Lagrangian type because of the nonlocal term (the second term) in the conformational free energy. Still it is possible to define a function $f(z)$ which is analogous to the Lagrangian energy:

$$f(z) = \psi'\eta' - \frac{v}{2}\psi^2\eta^2 + E_0\psi\eta + \rho - N\psi_0^2 - \Pi_0$$

where $\rho(z) = 2N\psi(z)/\int\psi(z)\mathrm{d}z$ is the concentration of chain ends, and $\psi_0(z) = \psi(z)/(\int\psi^2\mathrm{d}z)^{1/2}$. Using eqs 23, 17 one may directly check that $f(z)$ is a constant (it does not depend on the position z), $f(z) = \mathrm{const} = f$. The "energy" f can also be written in the following way:

$$f(z) = \psi'\eta' - \frac{v}{2}(\phi - \phi_0)^2 + \rho - \epsilon_{\mathrm{b}}\phi - N\psi_0^2 - \frac{\phi_0}{N} = f \tag{28}$$

where $\epsilon_{\mathrm{b}} = v\phi_0 - E_0$. Physically, the independence of f on the position z is related to the fact that the normal stress is uniform throughout the polymer solution between the plates.

C. Interaction Force. We now calculate the interaction force between the two surfaces. The system is symmetric with respect to the middle plane, $z = h$, and we can thus consider only the half-system, $0 < z < h$; all the quantities studied below refer to this half-system.

According to the general rules of statistical physics,[19] the force f between the plates is obtained by taking the derivative of the thermodynamic potential Ω with respect to the distance between the plates:

$$f = -\frac{\partial\Omega}{\partial h} \tag{29}$$

The equilibrium value of the grand canonical potential $\Omega = \Omega(\mu_0, h)$ results from the minimization of the functional $\Omega[\psi, \eta]$ for a given distance h. This extremum property of Ω ensures that we are free to change or not to change both $\psi(z)$ and $\eta(z)$ while taking the derivative. In this respect the situation is exactly the same as with the classical ground state thermodynamic potential analyzed by De Gennes.[3] Let us slightly increase the distance from h to $h + \delta h$. A convenient way to change the order parameters[3] is to keep these functions identical in the region $0 < z \leq h$ and to define them as constants in the region $h \leq z < h + \delta h$. We then get the force as:

$$f = -\frac{v}{2}[\phi(h) - \phi_0]^2 + \rho(h) - \epsilon_b \phi(h) - N\psi_0^2(h) - \frac{\phi_0}{N} \tag{30}$$

Comparing this result to eq 28 we see that the force is exactly equal to the "energy" $f(z) = f$, that is why we use the same notation for the two quantities. The force is thus related to the monomer concentration ϕ and the end-concentration ρ at the midplane between the plates. Note that the force f includes also the osmotic pressure acting on the plates from the bulk solution.

The first contribution to the force is the result obtained from the classical ground state theory;[3] all the other terms are end-corrections. One can check that the term $-N\psi_0^2(h)$ is never important in the regime of strong adsorption ($\epsilon_b N \gg 1$).

The interaction force between the two plates mediated by the polymer solution can now be calculated explicitly. The order parameters are obtained from eqs 23, 17 (the function ψ satisfies the same equation as ψ_0), taking into account the relation 16 between $\Gamma = \int \phi(z) \mathrm{d}z$ and E_0. The force is then obtained by substitution in eq 30.

In most cases it is convenient to normalize the order parameter ψ in such a way that it directly gives the chain end concentration $\psi = \rho$; in this case eq 23 for the other order parameter becomes

$$-\eta'' + (U - E_0)\eta = 1 - K_0\psi_0$$

The last term in this equation, $-K_0\psi_0$, is negligible in all the regimes where the effect of chain ends is important.

In the next sections we give detailed calculations of the interaction force in the various concentration regimes in both cases of reversible and irreversible adsorption.

III. Interaction between Two Plates in Equilibrium with a Bulk Solution

The adsorption of a polymer solution at an interface and the determination of the concentration profiles over the whole range of bulk concentrations were considered in ref 10 using the two order parameter mean-field theory presented in the previous section. In addition to the extrapolation length, b, which measures the strength of the adsorption and the two characteristic length scales of the bulk solution (the Gaussian coil size, $R = N^{1/2}$ and the bulk correlation length, $\xi = 1/(2v\phi_0)^{1/2}$ two other length scales were shown to play an important role: the crossover length z^* between the inner region where the concentration is dominated by monomers belonging to loops and the outer region where it is dominated by monomers belonging to tails,

$$z^* = \begin{cases} \left[Nb \ln \dfrac{N}{b^2}\right]^{1/3}, & 0 < \phi_0 < \phi_1 = \dfrac{1}{v(bN)^{2/3}} \\ Nv\phi_0 b, & \phi_1 < \phi_0 < \phi_2 = \dfrac{1}{vbN^{1/2}} \\ R, & \phi_0 > \phi_2 \end{cases}$$

and the size of the adsorbed layer or cut-off length $\lambda = 1/\epsilon_b{}^{1/2}$,where the effective binding energy per monomer $\epsilon_b = \phi_0 v - E_0$ is determined by eq 16 (For $\phi_0 > \phi_2$ the cut-off length λ only has a formal meaning),

$$\lambda = \begin{cases} R/\left(\ln \dfrac{1}{\phi_0 v b^2}\right)^{1/2}, & 0 < \phi_0 < \phi_1 \\ R/\left(4 \ln \dfrac{\phi_2}{\phi_0}\right)^{1/2}, & \phi_1 < \phi_0 < \phi_2 \\ bv\phi_0 N/4 & \phi_2 < \phi_0 < \dfrac{1}{vb^2} \end{cases}$$

In all this paper we assume that the adsorption is strong enough that the Gaussian size is larger than the extrapolation length, $R \gg b$.

The formalism introduced in the previous section allows the calculation of the concentration profile between two adsorbing surfaces and of the interaction force for any concentration and any distance ($h \ll R$) between the plates, in both cases of reversible and irreversible adsorption. In this section,we only consider the most important asymptotic regimes for two interacting plates, in the case of reversible adsorption. Some of the results have been already reported in a recent letter.[13]

A. Adsorption from a Dilute Bulk Solution. We first consider the case of a very dilute bulk solution, $v\phi_0 \ll 1/N$. The relevant length scales are such that $\xi \sim R \gg \lambda \gg z^* \gg b$. In a dilute solution, the chains do not interact, and the correlation length is of the order of the chain radius.

When the distance between the plates is small, $h \ll z^*$, the contribution of the chain end sections (tails) is not important, so that the first term in the force between plates given by eq 30 dominates. The force is thus attractive as generally predicted by the classical mean-field theory in the ground state dominance approximation. At very small distances, $h \ll b \ll z^*$, the concentration between the plates is roughly constant and can be determined by balancing the surface (F_s) and the interaction (F_{int}) contributions to the free energy energy. Keeping only these leading terms, we write the grand canonical free energy per unit area as

$$\Omega \simeq \frac{v}{2}\phi^2 h - \frac{\phi}{b}$$

The concentration is obtained by minimization $\phi \simeq 1/vhb$ and the force is $f \simeq -1/2vb^2h^2$ as shown in ref 3. In the loop region, $b \ll h \ll z^*$ three contributions to the free energy, F_{int}, F_s, and the configurational contribution $F_{conf}^{(0)}$, are important. The concentration at the midplane between the adsorbing surfaces can be roughly obtained from the concentration profile close to an isolated surface and scales as $\phi(h) \sim (1/v)(1/h^2)$. The force can thus be written as $f = -C/vh^4$.[3] The numerical prefactor is determined by an explicit calculation of the concentration profile from the classical mean-field free energy with one order parameter (ψ). We obtain $C = (1/2)B(1/4, 1/2)^4 \simeq 5.91^3$ where B(x,y) is the Euler function defined in ref 17. The short distance attraction is due to the formation of many bridges between the surfaces; the bridging attraction overcomes the excluded volume repulsion.

In the outer tail region $z^* < h < \lambda$ the end point pressure is also important, and the dominant contribution to the force is: $f = -(v/2)\phi(h)^2 + \rho(h)$. Using the scaling laws obtained for the concentration profile of a polymer solution adsorbing on a single plate,[10] we find that both contributions scale in the same way $f \simeq 1/h^4$.

As they have opposite signs, the sign of the force can be determined only after finding the order parameter profiles. In this regime the equations for the order parameter can be simplified by neglecting E_0 with respect to U:

$$\begin{aligned} -\psi'' + v\eta\psi^2 &= 0 \\ -\eta'' + v\psi\eta^2 &= 1 \end{aligned} \tag{31}$$

with the effective boundary conditions

$$\psi(0) = \infty,\ \eta(0) = 0,\ \psi'(h) = \eta'(h) = 0 \tag{32}$$

(we choose here the normalization of ψ which leads to $\psi = \rho$). The condition $\eta(0) = 0$ reflects the fact that in the central region the monomer concentration is dominated by monomers belonging to tails (in this region, $\eta(z)$ is approximately equal to $r(z) \simeq \varphi(z)$, where the function $\varphi(z)$ is defined in the Appendix) and that there are no tails close to the wall. These equations can be easily rescaled to a standard form where $h = 1$, $v = 1$ and then solved numerically. The final result for the interaction force is $f \simeq 420/vh^4$; the force is *repulsive*; although f in this regime scales in the same way as for smaller separations, the numerical prefactor for the repulsion is larger by a factor of order 70 than that for the attraction. The repulsion is due to the excluded volume interaction between tails attached to the two surfaces that cannot interpenetrate and thus do not form any bridges.

In the distal region $R > h > \lambda$ the order parameter equations can be rescaled using λ as the unit length (λ is replaced by 1, and $v\psi$ by ψ; the bulk concentration ϕ_0 can also be neglected with respect to $\epsilon_b = 1/\lambda^2$):

$$\begin{aligned} -\psi'' + (\psi\eta + 1)\psi &= 0 \\ -\eta'' + (\psi\eta + 1)\eta &= 1 \end{aligned} \tag{33}$$

Retaining only the dominant terms in eq 30 the interaction force is given by $f = -(v/2)\phi(h)^2 + \rho - \epsilon_b\phi(h) - \phi_0/N$. An analysis of eqs 33 shows that both $\phi(h)$ and $\rho(h)$ are decaying exponentially: $\phi(h) \sim (1/v\lambda^2)e^{-h/\lambda}(1 - \text{const}(h/\lambda)e^{-h/\lambda})$, $\rho(h) \sim (1/v\lambda^4)e^{-h/\lambda}$. At leading order, the second and third term in the force exactly cancel. The next order term gives the interaction force as $f \simeq (\text{const}/v)(1/\lambda^4)(h/\lambda)e^{-2h/\lambda} - \phi_0/N$. The force is repulsive in the region $h \gtrsim \lambda$. However an attraction (which is basically due to the bulk osmotic pressure, $-\Pi_0 = -\phi_0/N$) is recovered for large enough distances. This non monotonic behavior of the force is related to the non monotonic concentration profile of a solution adsorbing onto a single surface. A depletion hole appears due to the depletion of the free nonadsorbed chains repelled by the adsorbed layer. A more detailed description of the force in this attractive region would require a precise description of the concentration profile.

To sum up we find the following dependence of the force f as a function of the distance between the adsorbing surfaces:

$$f \simeq \begin{cases} -\dfrac{1}{2vb^2h^2}, & h \ll b \\ -\dfrac{5.9}{vh^4}, & b \ll h \ll z^* \\ \dfrac{420}{vh^4}, & z^* \ll h \ll \lambda \\ \dfrac{\text{const}}{v}\dfrac{1}{\lambda^4}\dfrac{h}{\lambda}e^{-2h/\lambda} - \dfrac{\phi_0}{N}, & \lambda \ll h \ll R \end{cases} \tag{34}$$

A qualitative plot of the force as a function of distance showing the non monotonic variation is given on Figure 1.

We now consider the (rather narrow, but formally existing) concentration range $1/N \ll v\phi_0 \ll \epsilon_b$. Here $R \gg \xi \gg \lambda \gg z^* \gg b$. At short distances, $h \lesssim \lambda$ the interaction is the same as for the more dilute regime. In the distal range $\lambda \ll h \ll \xi$ the bulk osmotic pressure is dominated by the excluded volume term: $\Pi_0 \simeq v\phi_0^2/2$, so that the force is given by $f = (\text{const}/v)(1/\lambda^4)(h/\lambda)e^{-2h/\lambda} - v\phi_0^2/2$. The force also becomes attractive at large enough distances $h > h^*$, where h^* is approximately defined by the condition $\phi(h) \sim (1/v\lambda^2)e^{-h/\lambda} \sim \phi_0$. In the region $h^* < h < \xi$ the force is attractive and equal to the bulk osmotic pressure. At even larger distances, $h \gtrsim \xi$, the monomer concentration in the middle of the slab is dominated by free chains, so that the theoretical approach developed in this paper cannot be applied. However, the adsorbed layers covering each plate play the role of virtually impenetrable hard walls for the free chains as λ (the decay length of the concentration of adsorbed chains) is much smaller than the bulk correlation length ξ. The interaction in this case is therefore the same as the interaction between two purely repulsive hard walls immersed in the solution. The corresponding force has been calculated in ref 20. The result is

$$f = -32v\phi_0^2e^{-2h/\xi} + 2(1 - \ln 2)^2\frac{1}{vNh^2} \tag{35}$$

for $\xi \ll h \ll R$. Therefore, the force is attractive in the region $h \gtrsim \xi$ and becomes repulsive again for $h \gg \xi$ where the first exponential term can be neglected.

We thus find a quite complex behavior of the force in the concentration range $1/N \ll v\phi_0 \ll 1/\lambda^2$. The force is attractive in the loop region $h \lesssim z^*$; it is repulsive in the tail region $z^* \lesssim h \lesssim h^*$. The force is then attractive in a narrow region $h^* < h \lesssim \xi$ and again repulsive for $\xi \ll h \lesssim R$. As was shown in ref 20 at larger separations the force is exponentially decaying over the chain radius, but it also reveals oscillations with a period of order R.

B. Adsorption from a Semidilute Bulk Solution. We now consider more concentrated bulk solutions. In the semidilute tail regime, $\epsilon_b \ll v\phi_0 \ll 1/(z^*)^2 = v\phi_1$, the length scales are such that $R \gg \lambda \gg \xi \gg z^* \gg b$. At short distances $h \ll \xi$, the interaction force follows the laws obtained for the dilute regime given by the first three lines in eq 34 (the 3rd regime corresponding to separations $z^* \ll h \ll \xi$). At intermediate distances, $\xi \ll h \ll \lambda$, the monomer concentration in the middle of the slab is close to ϕ_0; most monomers belong to tails. Actually, the monomer concentration is $\phi = \psi\eta \simeq \phi_0$ everywhere except in narrow zones of thickness $\sim \xi$ near each plate. The interaction force given by eq 30 is dominated by the end point pressure term: $f \simeq \rho(h)$ and is therefore repulsive. The differential equations for the

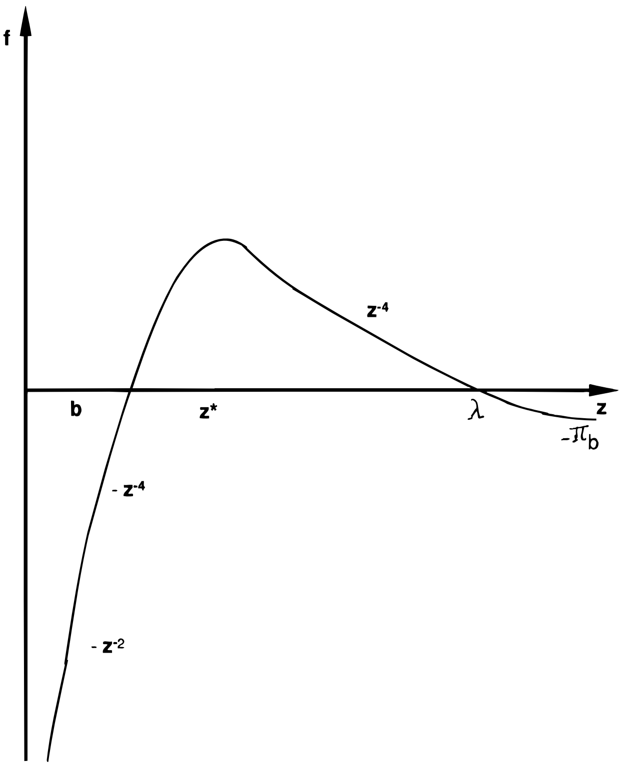

Figure 1. Qualitative sketch of the variation of the force with the distance between plates for equilibrium adsorption from a dilute solution. The various scaling regimes where the force is attractive or repulsive are shown.

order parameters reduce to

$$-\psi'' + u\psi = 0$$
$$-\eta'' + u\eta = 1$$

where the effective potential is $u \simeq v(\psi\eta - \phi_0)$, and it is such that $u \ll v\phi_0$. The boundary condition $\psi(0) = \infty$. As ψ, η, and u are related ($\psi\eta \simeq \phi_0 + u/v$), one can consider ψ and u as two independent unknown functions. The solution of the order parameter equations is

$$\psi \equiv \rho = \frac{\pi^2\phi_0}{h^2}\sin^{-2}\left(\frac{\pi z}{2h}\right)$$

and the force is $f = \pi^2\phi_0/h^2$.

For larger separations, $\lambda \ll h \ll R$, the interaction is governed by free chains which dominate the concentration in the middle of the slab. The force can be obtained from the results of ref 20:

$$f = \frac{\phi_0}{N}\frac{C_0^2}{h^2}$$

where $C_0 = \int_0^h((\phi_f/\phi_0)^{1/2} - \phi_f/\phi_0)\mathrm{d}z$; $\phi_f = \phi_f(z) \simeq \phi_0 - \phi_a(z)$ is the concentration of free chain monomers, and ϕ_a is the concentration of adsorbed chain monomers. The constant C_0 is estimated $C_0 \sim \lambda$, so that the plates repel each other with a force $f \sim \phi_0(\lambda^2/N)(1/h^2)$. We also expect an attraction force for a narrow region of separations, $h \sim \lambda$, quite similarly to the dilute bulk solution case.

The semidilute-loop regime $\phi_1 = 1/v(Nb)^{2/3} \ll \phi_0 \ll \phi_2 = 1/vbN^{1/2}$ is characterized by the following hierarchy of scales: $R \gg \lambda \gg z^* \gg \xi \gg b$. At large distances, $R \gg h \gg \lambda$ and $\lambda \gg h \gg z^*$, the interaction is repulsive, and the force is the same as for the previous semidilute-tail regime. At smaller distances, $\xi \ll h \ll z^*$, the monomer concentration is dominated by loops, and the classical ground state concentration profile is recovered

$$\phi(z) \simeq \phi_0\left[1 + \frac{1}{\sin h^2\left(\frac{z+b}{2\xi}\right)} + \frac{1}{\sin h^2\left(\frac{2h+b-z}{2\xi}\right)}\right] \quad (36)$$

In particular ϕ is very close to ϕ_0 in all the central region. The force is dominated by the second term in eq 30 and is equal to the concentration of end points in the middle of the slab, $f = \rho(h)$. The total *number* of ends is roughly constant, and the chain ends are nearly uniformly distributed throughout the layer, so that $\rho(h) \simeq 2N/h = 2\Gamma/Nh$, where the adsorbance is $\Gamma = \int_0^h\phi(z)\mathrm{d}z \simeq 2/vb$. Hence the interaction force is $f \simeq 4/vNbh$; the force is repulsive and is inversely proportional to the distance. For h close to ξ the first (classical) term in eq 30 is of the order of $\rho(h)$, so that the total force is the sum of the "classical" force[3] and $\rho(h)$:

$$f = -32v\phi_0^2e^{-2h/\xi} + \frac{4}{vNbh}$$

The interaction becomes attractive at distances $h/\xi < {}^3/_4 \ln \phi_0/\phi_1$; for $h < \xi$ the classical attraction considered for the dilute regimes is recovered.

Thus we predict the following dependence of $f(h)$ in the regime $\phi_1 < \phi_0 < \phi_2$:

$$f \simeq \begin{cases} -\dfrac{1}{2vb^2}\dfrac{1}{h^2}, & h \ll b \\ \dfrac{-5.9}{vh^4}, & \xi \gg h \gg b \\ +\dfrac{4}{vNbh} - 32v\phi_0^2e^{-2h/\xi}, & z^* \gg h \gg \xi \\ +\dfrac{\pi^2\phi_0}{h^2}, & \lambda \gg h \gg z^* \\ +\dfrac{\text{const}\,\lambda^2}{N}\dfrac{\phi_0}{h^2}, & R \gg h \gg \lambda \end{cases} \quad (37)$$

When the bulk is a concentrated solution, $1/vb^2 > \phi_0 > \phi_2$, the hierarchy of length scales is $z^* \sim R \gg \xi \gg b$, and the adsorption on a single plate[10] can be considered as weak; the binding energy per chain $\epsilon_b N$ is much smaller than 1, and the total one-plate adsorbance, Γ_0, is dominated by long distances $z \sim R \gg b$. The two order parameters formalism is not applicable to the adsorption on a single interface, which was analyzed[10] using another approach described in details in ref 20. The case of the adsorption of a concentrated solution between two plates is slightly different and the description based on two order parameters can always be used whenever $h \ll R$, no matter whether the adsorption is strong ($\epsilon_b N \gg 1$) or weak. The condition of validity of this approach is $\epsilon N \gg 1$, where ϵ is the gap between the ground state "energy" level and the next level; in the case of two adsorbing plates, ϵ_b is not equal to ϵ; $\epsilon_b < \epsilon$.

We can thus still use the general result for the force eq 30 in the concentrated regime (assuming that $h \ll R$). The tail contribution to $\phi(z)$ is never important, so that the classical mean-field theory in the ground state dominance approximation predicts correctly the concentration profile,

$$\phi(z) \propto \psi^2(z) \tag{38}$$

In particular, for $h \gg \xi$ the concentration profile is given by eq 36. The first (classical) term in eq 30 is

$$f_0 \simeq -32 v \phi_0^2 e^{-2h/\xi}$$

The end-corrections to the *force* cannot be neglected if h/ξ is large, when f_0 is exponentially small. A detailed analysis shows that all four nonclassical contributions to the interaction force are important here. These contributions are easily calculated using the results of the classical mean-field theory (for example $\rho(z) = 2N\,(\phi(z))^{1/2}/\int(\phi(z))^{1/2}\mathrm{d}z$, with $N = (1/N)\int\phi(z)\mathrm{d}z$; the effective monomer binding energy ϵ_b can be obtained using eq 16). The total interaction force reads $f = f_0 + f_e$, where

$$f_e = \frac{2\phi_0}{N}\left[\frac{2}{b\phi_0 v h} - \ln\left(1 + \frac{2}{b\phi_0 v h}\right)\right]$$

We obtain two asymptotic regimes corresponding to the strong and weak adsorption limits, respectively:

$$f = \begin{cases} f_0 + \dfrac{4}{vNbh}, & \xi \ll h \ll \xi^2/b \\ \dfrac{4}{Nb^2v^2\phi_0}\dfrac{1}{h^2}, & \xi^2/b \ll h \ll R \end{cases} \tag{39}$$

The interaction is repulsive if $h/\xi > {}^3/_4 \ln \phi_0/\phi_1$. The prediction for the force in the range $\xi^2/b < h < R$ (second line in eq 39) is in agreement with the results[20] obtained from a different quasiperturbative approach. At smaller distances between the plates, $h < \xi$, the interaction is dominated by the classical attraction force, given by the first two lines of eq 37.

IV. Interaction between Irreversibly Adsorbed Polymer Layers

So far we have assumed that the polymer layer between the plates is in equilibrium with a bulk solution. In practice, the time necessary to reach equilibrium may be very long: the relaxation time is infinitely long in the case of infinite plates. A real experimental setup is in general made of curved rather than planar surfaces (e.g. a polymer between two cylindrical or spherical surfaces); in this case the relaxation time is “proportional” to the radius of curvature. It is therefore reasonable to consider the interaction between two plates with a fixed amount of polymer between them. In the most interesting case the plates are first far from each other and are in equilibrium with a dilute solution, the amount of adsorbed polymer per plate (the adsorbance) is $\Gamma = \Gamma^*$. The solution is then washed and replaced by pure solvent, and the plates are brought together before desorption can take place.

The classical mean-field theory[3] predicts an exactly vanishing force at all distances in this case, $f_0 \equiv 0$. One can anticipate that when the end-corrections are taken into account, the force is repulsive. In order to get the force from our new mean-field approach, we need to set formally $\phi_0 = 0$ in all the equations. We also must discard eq 16 which accounts for the equilibrium with the bulk solution and we must replace it by the constraint of constant total coverage, $\Gamma = \Gamma^*$; this constraint determines the ground state energy level, E_0. The equilibrium one-plate coverage Γ^* has been calculated in ref 10:

$$\Gamma^* = \Gamma_0 + \delta\Gamma, \quad \Gamma_0 = \frac{2}{vb}, \quad \delta\,\Gamma \simeq \frac{7.07}{v}\left(Nb \ln \frac{N}{b^2}\right)^{-1/3}$$

where $\Gamma_0 = 2/vb$ is the adsorbance obtained from the classical mean-field theory. The difference between the actual force f and the classical force $f_0 = 0$ is due to (1) the end-corrections to the force given by eq 30, and (2) the correction to the classical force related to the fact that $\Gamma^* > \Gamma_0$. One can check that the second correction is dominant at short distances, $h < z^* = (Nb \ln N/b^2)^{1/3}$. In this regime the (classical) free energy can be written as $F = F_0 + \delta F$ where F_0 is the free energy when the coverage is Γ_0. The correction to the free energy due to the increase in the coverage from Γ_0 to Γ is $\delta F = E_0\delta\Gamma$, where $E_0 = v\phi(h)/2$ is the unperturbed ground state energy level, which coincides with the monomer chemical potential calculated in ref 3. Therefrom, we get the force $f = -\partial F/\partial h$:

$$f = \begin{cases} \dfrac{\delta\Gamma}{bh^2}, & h \ll b \\ \dfrac{\pi^2}{2}\dfrac{\delta\Gamma}{h^3}, & b \ll h \ll z^* \end{cases}$$

In the region $h > z^*$ the correction due to $\delta\Gamma$ is no longer important, and the force is given by the first three terms in eq 30, which have comparable magnitudes: $f = -(v/2)\phi^2(h) + \rho(h) + E_0\phi(h)$. The monomer concentration $\phi = \psi\eta$ is dominated by the contribution of tails in the central region of the gap. The order parameters (using the normalization $\psi = \rho$) satisfy the following equations

$$-\psi'' + (v\psi\eta - E_0)\psi = 0$$
$$-\eta'' + (v\psi\eta - E_0)\eta = 1$$

The effective boundary conditions are the same as for reversible adsorption, eqs 32. The ground state energy level E_0 is determined self-consistently from the condition $\int\phi(z)\mathrm{d}z = \text{const}$ (In order to avoid a formal singularity at $z = 0$ one may take this integral in the limits from ϵ to h with ϵ, independent of h, and $\epsilon \to 0$.).

These equations can be rescaled to a standard form where $h = 1$ and $v = 1$ and lead to the following scaling for the force (for $z^* < h < R$):

$$f = \frac{C}{vh^4}$$

A numerical solution of the order parameter equations gives the constant $C \simeq 1670$. The interaction is more repulsive in the case of irreversible than in the case of reversible adsorption: the force is larger by a factor $\simeq$ 4.

When the adsorbed amount of polymer, Γ^*, is fixed, we thus predict a repulsion at any distance between the plates.

V. Discussion and Conclusions

In this paper, we have presented a generalization of the mean-field theory in the ground state dominance approximation which takes into account explicitly the effect of chain ends (and in particular includes the contribution of the end entropy to the free energy of the polymer solution). The new approach involves two order parameters, $\psi(z)$ and $\eta(z)$, related to the monomer concentration by $\phi = \psi\eta$; ψ is the classical order parameter proportional to the polymer chain end concentration. The order parameters obey two coupled differential equations: the classical eq 17 for ψ, and eq 23 for η. We also have calculated the free energy of the polymer solution by finding a proper generalization of the classical square-gradient conformational free energy in terms of the fields ψ and η. The equilibrium state of the solution is obtained by minimization of this free energy functional with respect to the order parameters. A generalized conservation law which gives a first integral of the differential equations for the order parameters (eq 28) has also been obtained. Although the theory is developed here in one dimension, a further generalization to inhomogeneous solutions in three dimensions is straightforward.

We have shown that the end contribution to the thermodynamic quantities is important at large length scales: for example for a solution in a gap between adsorbing surfaces at large enough distances between the plates the end effect is not only a correction, but it is dominant, and leads to qualitatively new features.

The novel ground state dominance approach has been applied to study the interaction between adsorbing plates in a polymer solution in the marginal solvent regime where the mean-field theory is expected to be accurate. One of our most important results is that the mean-field prediction of an attractive force between two oppositely adsorbed layers kept in equilibrium with a bulk solution) is not valid if the distance between the plates is larger than a length $z^* \propto N^{1/3}$, if the bulk solution is dilute: the plates covered by the adsorbed layers repel each other in this regime.

The critical length scale z^* corresponds to a crossover between regions where the total monomer concentration is dominated by loops ($z < z^*$) and by the tails of the polymer chains ($z > z^*$). In the tail region, an adsorbed layer can be effectively represented as a polydisperse polymer brush consisting of the tails of different lengths. The adsorbed layers are repelling each other, as expected for polymer brushes. The interaction energy can be estimated in a simple way as $F \sim h\phi(h)^2$, where $\phi(h) \sim 1/h^2$ is the concentration at the midplane between the plates. Therefore the interaction force is $f = -\partial F/\partial h \sim h^{-4}$ in agreement with the quantitative result. Although the repulsive force scales with h in the same way as the attractive force at smaller separations, it is remarkable that the numerical prefactor for the repulsion is almost two orders of magnitude higher than for the attraction.

The repulsive force is always due to the end effects. In many cases it can be interpreted as an ideal gas pressure of the chain ends, proportional to the concentration of chain ends, ρ. In fact the structure of the adsorbed layer at scales $z > z^*$ is also determined by the balance between the entropy of the chain ends and the excluded volume interactions: $F_{\mathrm{ent}} \sim F_{\mathrm{int}}$, where $F_{\mathrm{int}} \sim v\phi^2$ is the interaction free energy density and $F_{\mathrm{ent}} \sim \rho$ is the ideal gas of the ends' free energy density. Therefore the interaction (repulsion) force is $f \sim \rho \sim \phi^2 \sim 1/h^4$. Very generally, the interaction force has been expressed as a function of the concentrations at the midplane between the adsorbing plates and includes a contribution that can be interpreted as a pressure of the chain ends. This term can in certain cases be dominant; e.g. in the semidilute regime, $\phi_1 \propto N^{-2/3} < \phi_0 < \phi_2 \propto N^{-1/2}$ if the separation is in between the bulk correlation length ξ and the Gaussian coil size R, $\xi \ll h \ll R$. In this case the force between the plates is nearly exactly equal to the ideal-gas pressure of chain ends (see eq 37).

The repulsion due to the end effects also plays a major role in the interaction between two irreversibly adsorbed layers when the adsorbed amount Γ^* is obtained by saturation of each plate with the polymer. In this case we find a repulsion at all distances, in contrast with the classical mean-field result that the force vanishes identically.

We have not discussed in detail bridging by chains connecting two adsorbing surfaces. These chains create an additional attraction between the plates. Although these chains are not explicitly considered in this paper, their effect is implicitly taken into account both in the general expression of the free energy and of the force. The concentration profile of monomers belonging to the bridges can be explicitly calculated using a method similar to that used in the Appendix, where general expressions for the concentration contributions of loops/bridges and of tails are obtained.

Finally one should keep in mind that all our results have been obtained within the framework of a mean-field theory and thus neglect concentration fluctuations which are known to be important for a polymer solution in a good solvent. Scaling laws can be constructed for polymers in a good solvent to describe polymer adsorption, but for several of the problems discussed here they are not sufficient to obtain the sign of the force. A naive guess is that the mean-field theory presented in this paper qualitatively gives good results and can be combined with the scaling laws to obtain predictions for polymer adsorption in a good solvent. A precise calculation of the interaction force between adsorbed polymer layers in a good solvent is, however, not available to our knowledge.

Acknowledgment. This work was performed during the stay of one of the authors (A.N.S.) at Strasbourg University (Institut Charles Sadron). A.N.S. would like to thank the University and the Ministry of Higher Education of France for the opportunity to stay in Strasbourg. This work was also supported in part by NATO's Scientific Affairs Division in the framework of the Science for Stability Programme.

Appendix A: Concentration Due To Loops vs Concentration Due To Tails

For a polymer inside a slab between two plates one can define (1) loop chain sections between contacts with the same plate; (2) bridge sections between two contacts with different plates; (3) tail sections between a chain end and a first contact with one of the plates. There might be also free chains which do not touch any plate at all, but their amount is negligible if $h \ll R$. The formalism described in section 2 does not make any distinction between loops, bridges, and tails: only the *total* monomer density profile, $\phi(z)$, is considered. This is *sufficient* to calculate the interaction between the plates. Therefore it is *not necessary* to read this Appendix in order to understand the results presented in this paper. However, as the tail contribution constitutes an important physical aspect of the novel approach, we show below how to discriminate between loops/bridges and tails.

Let us consider an n-chain with one end fixed at position z. We call the chain free if it does not have any contact with the surfaces, and adsorbed otherwise. Following ref 10 let us split the partition function of the chain into two parts corresponding to the adsorbed and free states: $Z(n, z) = Z_a(n, z) + Z_f(n, z)$. Once Z_a and Z_f are known, the concentration of monomers belonging to loops/bridges, ϕ_l, and tails, ϕ_t, can be calculated[10] using standard expressions similar to eq 2. In particular, $\phi_l(z)$ is defined by eq 2 with Z replaced by Z_a, and

$$\phi_t(z) = \frac{2\Gamma}{NZ(N)}\int_0^N Z_a(N-n, z)Z_f(n, z)\mathrm{d}n \qquad \text{(A1)}$$

The last integral is dominated by the region $n \ll N$. In this region $Z_a(N - n, z) = Z(N - n, z) = K_0\psi_0(z)e^{-(N-n)E_0}$ up to a correction which is exponentially small if $h \ll R$. The free-chain partition function, Z_f, can be represented as an expansion in eigenstates analogous to eq 5, but with different eigenfunctions ψ_{fs}, and eigenvalues E_{fs} corresponding to the true hard wall boundary conditions $\psi_{fs}(0) = \psi_{fs}(2h) = 0$. For $n \gg 1/\epsilon \sim h^2$ the function Z_f is dominated by its ground state: $Z_f(n, z) \propto e^{-nE_{0f}}$, so that $Z_a(N - n, z)Z_f(n, z) \propto e^{-NE_0}e^{-n(E_{f0}-E_0)}$. The ground state "energy" for the free chain problem, E_{f0}, is higher than E_0. The difference $\epsilon_f = E_{f0} - E_0$ is of order of $\epsilon \gtrsim 1/h^2$ (in the one-plate case both E_1 and E_{f0} correspond to the bottom of the continuous spectrum, $E_1 = E_{f0} = U(\infty)$, so that ϵ and ϵ_f are exactly equal). In fact in the regime which is being considered in this paper ($N\epsilon \gg 1$) ϵ_f always nearly coincides with ϵ. Even more generally the first (even) state ψ_1 nearly coincides with the ground state ψ_{f0} for free chains. As we do not use these stronger statements here, we do not have to comment more on them. Therefore the integral in eq A1 is exponentially converging in the region $n \sim n_0 \sim h^2$ where $n \ll N$, so that this equation transforms to

$$\phi_t(z) = \frac{2\Gamma}{NK_0}\psi_0(z)\varphi(z), \qquad \text{(A2)}$$

where the function $\varphi(z)$ is

$$\varphi(z) = \int_0^\infty Z_f(n, z)e^{E_0 n}\mathrm{d}n$$

This function obeys the following equations:

$$-\varphi'' + (U - E_0)\varphi'' = 1, \quad \varphi\ (0) = \varphi(2h) = 0 \qquad \text{(A3)}$$

This is the same equation as derived for the order parameter φ in ref 10 for the adsorption on a single surface.

The easiest way to obtain the loop contribution to the concentration is just to subtract ϕ_t from the total concentration given by eq 11:

$$\phi_l(z) = \phi(z) - \phi_t(z) = \Gamma_l\psi_0^2(z) + \delta\phi_l(z) \qquad \text{(A4)}$$

where

$$\Gamma_l = \Gamma - \Gamma_t = \Gamma\left[1 - \frac{2}{NK_0}\int_0^{2h}\varphi(z)\psi_0(z)\mathrm{d}z\right]$$

is the contribution to the total adsorbance due to loops/bridges, and

$$\delta\phi_l(z) = -\frac{2\Gamma}{NK_0}\psi_0(z)[\vartheta(z) - \psi_0(z)\int_0^{2h}\psi_0(z)\vartheta(z)\mathrm{d}z]$$

Here $\vartheta(z)$ is the new order parameter defined by equations:

$$-\vartheta'' + (U - E_0)\vartheta = K_0\psi_0, \quad \vartheta\ (0) = \vartheta(2h) = 0 \qquad \text{(A5)}$$

Using eqs 17, A5 it is straightforward to show that $\vartheta'(0) = (1/2)(K_0/\psi_0(0))$.

Using eqs 13, A3, A5, we relate the new order parameter to the rest function r and the free chain partition function φ by

$$r(z) = \varphi(z) - \vartheta(z) - \psi_0(z)\int_0^{2h}[\varphi(z) - \vartheta(z)]\psi_0(z)\mathrm{d}z \qquad \text{(A6)}$$

The first term in eq A4 was obtained in ref 10. The second term (which was not taken into account before) is actually a small correction: one may directly check that this term is subdominant in all the regimes of strong adsorption considered in ref 10 (for $z < D = 2N\epsilon^{1/2}$). In fact, the solution of eq A5 scales as

$$\vartheta(z) \sim K_0\psi_0(z)(z + b)^2 \qquad \text{(A7)}$$

for $z < h$ if $h > z^*$. One can use the single-plate results for the purpose of an order of magnitude estimate. In particular for one plate in equilibrium with a dilute solution we get:[10]

$$U(z) - E_0 \sim \frac{1}{(z+b)^2};$$

$$K_0\psi_0(z) \sim \begin{cases} \dfrac{b}{z+b}, & z < z^* \\ \dfrac{b}{z^*}\left(\dfrac{z}{z^*}\right)^{-4}, \quad h > & z > z^* \end{cases}$$

A scaling analysis of eq A5 with the above equations then gives rise to the estimate, eq A7. Therefore the ratio of the second term, $\delta\phi_l \sim (\Gamma/NK_0)\psi_0(z)\vartheta(z)$, to the first term $\simeq \Gamma\psi_0^2(z)$, is of order of $z^2/N \lesssim h^2/N \ll 1$. Thus the second correction term in eq A4 can be neglected in a first approximation.

In order to illustrate the physical meaning of the correction, $\delta\phi_l$, which was obtained above in a rather formal way, let us consider a particular example: a polymer between two plates in equilibrium with a very dilute solution, assuming that the distance $2h$ is larger than the crossover length $z^* \sim (bN)^{1/3}$ separating the regions of loops and tails dominance: $N^{1/2} > 2h > z^*$. Due to an obvious symmetry, we can consider only the half system, $z < h$. As was suggested in ref 10 we anticipate that $Z_a(n, z)$ can be approximately factorized as $C(n)\psi_0(z)$ and we estimate the accuracy of this approximation.

An adsorbed chain consists of a tail fragment (between the fixed end and the first contact) of m links and the rest part of $n - m$ links, so that the corresponding partition function can be represented as

$$Z_a(n, z) = \int_0^n Z(n - m, 0)Z_{\text{tail}}(m, z)dm \qquad \text{(A8)}$$

Without any loss of generality we can assume here that $E_0 = 0$. In the limit $n \to \infty$, $Z_a(n, z) = Z(n, z) = K_0\psi_0(z)$ (see eq 9). Taking this limit in eq A8 we get

$$\int_0^\infty Z_{\text{tail}}(m, z)dm = \psi_0(z)/\psi_0(0)$$

Obviously $Z_{\text{tail}}(m, z)$ must vanish in both limits $m \ll z^2$ and $m \gg z^2$. Using the results of refs 9 and 10, it is possible to show that in the region $m \gg m_0 = z^2$ the tail function decays according to a power law:

$$Z_{\mathrm{tail}}(m, z) \sim Z_{\mathrm{tail}}(m_0, z)\left(\frac{m}{m_0}\right)^{-\alpha}$$

where $\alpha = 2.5$.

The function $Z(n, 0)$ reaches its asymptotic limit, $K_0\psi_0(0)$, in the region $m \gg 1/\epsilon$. In the region $m < 1/\epsilon$ it smoothly depends on n, so that $\partial Z(n, 0)/\partial n \sim Z(n, 0)/n$. Using the expansion $Z(n - m, 0) \simeq Z(n, 0) - m(\partial Z(n, 0)/\partial n)$ which is valid if $m \ll n$ we can rewrite eq A8 as

$$Z_a(n, z) \simeq Z(n, 0)\int_0^n Z_{\mathrm{tail}}(m, z)dm - \frac{\partial Z(n, 0)}{\partial n}\int_0^n m Z_{\mathrm{tail}}(m, z)dm$$

The second integral in the last equation can be estimated as m_0 times the first integral. Thus using the above equations we get (Note that by changing the upper boundaries in the integrals from n to ∞ we introduce a subdominant correction which is smaller than $O(z^2/n)$ if $\alpha > 2$.)

$$Z_a(n, z) = Z(n, 0)\frac{\psi_0(z)}{\psi_0(0)}\left[1 - O\left(\frac{z^2}{n}\right)\right] \qquad \text{(A9)}$$

The relative correction $\sim z^2/n$ is qualitatively due to the fact that a chain with the end position z can hardly be absorbed if the number of links in the chain $n \ll z^2$, as it would have to stretch on many its Gaussian sizes in order to reach the (nearest) plate.

Using eqs 9, A9 and taking into account that $N\epsilon \gg 1$ as before, we get

$$\phi_l(z) = \Gamma\left[1 + \frac{2r(0)}{NK_0\psi_0(0)}\right]\psi_0^2(z)\left[1 - O\left(\frac{z^2}{N}\right)\right] \qquad \text{(A10)}$$

The negative correction of order z^2/N is due to the fact that very end parts of chain of length smaller than $m_0 \sim z^2$ can hardly be involved in a loop of size z.

The loop concentration can also be obtained directly from eq A4. With the help of eq A6 we obtain

$$\phi_l(z) = \Gamma\psi_0^2(z) + \frac{2r(0)}{NK_0\psi_0(0)}\Gamma\psi_0^2(z) - \frac{2\Gamma}{NK_0}\psi_0(z)\vartheta(z) \qquad \text{(A11)}$$

Obviously eq A10 agrees with eq A11: the last term in eq A11 is a correction of relative order z^2/N (see eq A7). Note that the correction to the loop surface excess $\int\phi_l(z)dz$ due to the second term in eq A11 is of order $\Gamma/N^{1/3}$, whereas the third term leads to a subdominant correction $\sim \Gamma/N^{2/3}$.

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MA961263+