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Polymers at an Interface. 2. Interaction between Two Plates Carrying Adsorbed Polymer Layers

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ABSTRACT: We analyze the concentration profiles and the interaction energy for flexible polymer chains, plus a solvent, inside a narrow gap (thickness $2h$) between two weakly adsorbing plates. (1) For complete equilibrium (i.e., when the chains can exchange reversibly with a bulk solution), we prove that the interaction between plates is *always attractive*: this holds in good or bad solvents. (2) A more practical case corresponds to a constrained equilibrium, where the total number of chains between the two plates is fixed. This case is more delicate, and we restrict it here to *good solvents*. (a) The simplest mean field calculation gives an exact cancellation (no force for any h). (b) We have constructed a more sophisticated approach, incorporating the scaling exponents but allowing for precise numerical calculations. The result is a *repulsive* interaction, decreasing like h^{-2} at large h and like $h^{-5/4}$ at small h.

I. Introduction

Colloidal suspensions, where the grains are coated with an adsorbed polymer, are often "protected" or "sterically stabilized".[1-8] Direct measurements of the repulsions between two plates coated with a block copolymer [poly(vinyl acetate) + poly(vinyl alcohol)] have been carried out in Bristol.[9] More recently, the interactions between mica plates covered with adsorbed polystyrene have been studied.[10] Unfortunately, for technical reasons, the choice of solvent was limited, and the data of ref 10 are restricted to a bad solvent (cyclohexane at ~21 °C). They do show forces of range comparable to the coil size, which are in this case repulsive at short distances and attractive at long distances.

On the theoretical side, the situation is somewhat complex.[11-17] Consider, for instance, the more common case where the solvent is good. Each plate is assumed to carry a diffuse adsorption layer of thickness much larger than the monomer size. When we bring the two plates close together, as shown in Figure 1, the two adsorption layers begin to overlap. Because the chains repel each other in good solvent conditions, we can immediately think of a repulsive effect. But we should also keep in mind the fact that each plate attracts the chains: thus an increase in the local monomer concentration near the plates tends to lower the energy; this gives an attractive component to the force.

Thus the overall interaction between plates is the result of a delicate balance between opposite effects. There is a rough qualitative analogy between this situation and the problem of *chemical binding*, where the overlap between electron clouds from two molecules may or may not lower the energy. The analogy is not very deep because the polymer problem does not display any analogue of the Pauli principle. But the relation with quantum effects does exist when we work at the mean field level[18-20] describing the concentration profiles in terms of a field ψ rather than in terms of a monomer concentration $\Phi \sim |\psi|^2$.

We shall show, however, that the mean field approach is *completely inadequate* to discuss the plate–plate interactions in good solvents.[31] Indeed this is one case where a correct scaling description of the concentration profiles is absolutely required to predict even the sign of the forces. In a recent paper[21] (hereafter referred to as I), we constructed the adsorption profile near a single plate, including all scaling exponents. We restricted our attention to *weak coupling*, i.e., to situations where the adsorbing sites are not saturated with polymer. But we pointed out that this weak coupling remains compatible with strong adsorption, i.e., with a free energy of sticking *per chain* which is many times kT. The aim of the present paper is to apply the methods of I to the discussion of interactions between two plates. We are faced with two possible situations:

(1) *Ideal equilibrium*, where the adsorbed layers (in the gap between the two plates) can exchange polymer with an ambient solution of prescribed concentration. Of course, this assumption of complete reversibility is bad for strong adsorption, but we must discuss it first to understand the basic facts (section III).

(2) *Restricted equilibrium*, where we assume that the adsorbed layers have been prepared by contact with a solution (for widely separated plates). Then the solution is washed out and replaced by pure solvent. Each plate keeps an adsorbed layer with a certain number Γ of monomers per cm^2. We then bring the interplate gap down to a prescribed value $2h$ and assume that during this "squeezing" operation no chain leaves the gap region: Γ is fixed. From refractive index measurements, Klein was led to suggest a condition of this sort for his experiments on PS + mica.[10] We further assume that the concentration

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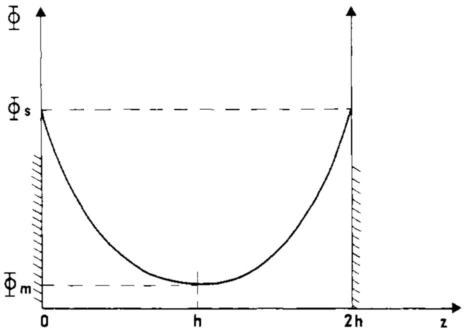

Figure 1. Concentration profile between two adsorbing plates. Φ is a volume fraction ranging between zero and unity. All this paper assumes that the value on the plates Φ_s is smaller than 1.

profile $\Phi(z)$ adjusts during this process and minimizes the free energy for all variations $\delta\Phi$ which leave Γ constant. A similar assumption was introduced in I to predict the effects of a change of solvent quality on the adsorption layer for a single plate.

Our discussion of "restricted equilibrium" breaks into two parts: first, we analyze it in mean field and come out with a very surprising result in good solvents: namely, that the interplate free energy vanishes identically (section III). This is not a very deep result, but it does show the delicate cancellations which can occur between attractive and repulsive forces. To get an improved result, we have to go *beyond mean field*. This is a challenging exercise because it is not sufficient here to estimate the interactions by scaling arguments where all numerical coefficients are ignored! We construct in section III a functional form of the free energy, which was already announced in I; this form includes all scaling exponents but allows for definite numerical calculations of interaction vs. distance. (It may in fact turn out to be useful for many other purposes.) The result for good solvents (derived in section III and discussed in section IV) is a *repulsive* interaction between plates at fixed Γ. This repulsive sign is hardly a surprise: we do know that polymer solutions stabilize many colloidal systems and that they presumably operate in the restricted equilibrium regime. What is new in the present work is the functional form of the repulsion vs. distance between plates.

A final reminder: this paper is concerned only with the *effects of adsorbed polymers*: (a) we do not consider the case of chains grafted at one end to the surface (here, if the chains do not adsorb at other points, the mean field analysis (described, for instance, in ref 16) is probably adequate); (b) we do not incorporate the van der Waals–Lifshitz interactions between the plates (the superposition of these forces with our polymer-induced forces, and the resulting equilibrium distances, barriers, etc., will have to be discussed separately).

II. Reversible Adsorption

Our discussion will start from mean field concepts, which are easier to follow. At the end of the section, we incorporate the correct scaling exponents.

(1) Free Energy Functional: Mean Field Approximation. The mean field approach to polymer problems when the concentration is variable in space is due to Edwards.[18] A simplified presentation is given in ref 19 and 20. The basic variable, $\psi(z)$, gives the local concentration $c(z) = |\psi(z)|^2$ or the local volume fraction

$$\Phi(z) = a^{-3}|\psi(z)|^2 \tag{II.1}$$

a^3 being the monomer volume. We shall call $\gamma(h)$ the free energy associated with *half* of the interplate gap (see Figure 1).[32] The basic components of $\gamma(h)$ are the following:

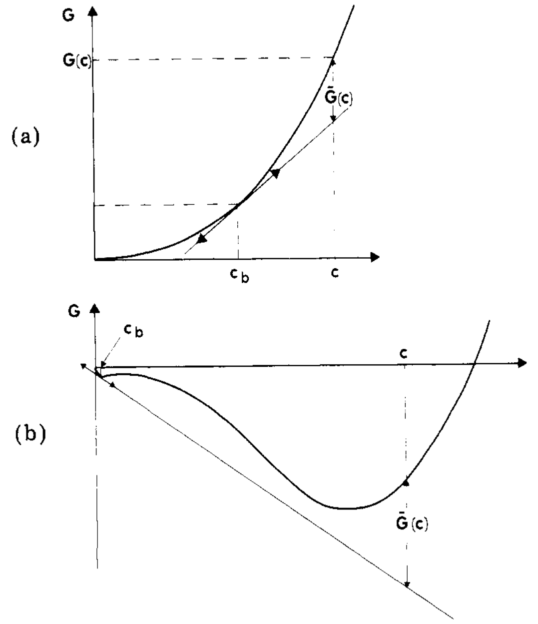

Figure 2. Free energy (per cm^3) $G(c)$ plotted as a function of the concentration c for a polymer solution (a) in good solvents ($G \sim c^2$ in mean field theory) and (b) in bad solvents. In case b, the small negative peak on the left-hand side of the plot is of order $1/N$ (where N is the number of monomers per chain) and can often be replaced by a point at the origin.

(a) *A surface part* describing the direct contact (at $z = 0$) between the solution (local concentration $|\psi_s|^2$) and the plate. Following I, we assume for this contribution the simple form

$$\gamma_d = \gamma_0 + \gamma_1 a^3 |\psi_s|^2 = \gamma_0 - |\gamma_1|\Phi_s \tag{II.2}$$

where γ_1 has the dimensions of surface tension and is here negative to describe an attraction between wall and polymer. Equation II.2 is an expansion in powers of Φ_s. One crucial assumption is that $\Phi_s \ll 1$, i.e., that we are dealing with a weak coupling problem. Quantitatively, as shown in I, this requires

$$|\gamma_1|a^2/kT \ll 1 \tag{II.3}$$

Extensions to the strong coupling case are feasible; they simply require that (II.2) be supplemented by terms which become large and positive for $\Phi_s \rightarrow 1$. However, the essential features, to be described below (for distances z larger than a certain characteristic length D), are the same in strong or in weak coupling.

(b) *A volume contribution*, related to the free energy $G(c)$ for a uniform system of concentration c. The structure of $G(c)$ depends on the quality of the solvent and is shown on Figure 2. What is required for our calculation of $\gamma(h)$ is not simply $G(c)$ but rather the difference $\tilde{G}(c)$ between $G(c)$ and the corresponding tangent at the bulk concentration c_b:

$$\begin{aligned}\tilde{G}(c) &\equiv G(c) - G(c_b) - \frac{\partial G(c_b)}{\partial c_b}(c - c_b) \\ &= G(c) - \mu c + \Pi\end{aligned} \tag{II.4}$$

Here the interplate gap is assumed to be in equilibrium with a macroscopic solution of concentration c_b, chemical potential μ, and osmotic pressure Π:

$$\mu = \partial G(c_b)/\partial c_b$$

Readers who are not familiar with the use of eq II.4 to compute interfacial energies may find a thorough discussion in ref 22. Note that thermodynamic stability imposes that $G(c)$ be a *convex* function of c. This is turn ensures that $\tilde{G}(c)$ is always positive.

(c) *A gradient term*; the practical reason for the use of the variable $\psi(z)$ (rather than $\Phi(z)$) is that (in mean field) it gives a very simple structure to this term:

$$F_{\mathrm{grad}} = kT\frac{a^2}{6}\left(\frac{\mathrm{d}\psi}{\mathrm{d}z}\right)^2 \tag{II.5}$$

Here, we use a as the root-mean-square length of one monomer: the whole scheme is easily visualized in terms of a Flory–Huggins lattice[23] of mesh size a.

(2) Equilibrium Profile. Adding all the contributions (a, b, c), we get the complete structure of the energy $\gamma(h)$:

$$\gamma - \gamma_0 = -|\gamma_1|a^3\psi_s^{\,2} + \int_0^h \mathrm{d}z \left\{G(|\psi(z)|^2) - \mu\psi^2 + \Pi + kT\frac{a^2}{6}\left(\frac{\mathrm{d}\psi}{\mathrm{d}z}\right)^2\right\} \tag{II.6}$$

This must be minimized with respect to $\psi(z)$ at all points.

(a) Boundary Condition at the Surface. Let us first minimize $\gamma(h)$ with respect to the surface value ψ_s. A condition of this sort was first written down by Cahn.[24] As explained in ref 25, the result appears as an equation for the logarithmic derivative of ψ at the wall:

$$-\frac{1}{\psi}\left.\frac{\mathrm{d}\psi}{\mathrm{d}z}\right|_{z=0} = \frac{6|\gamma_1|a}{kT} = \frac{1}{D_{\mathrm{mf}}} \tag{II.7}$$

The length D_{mf} gives the order of magnitude of the thickness of the adsorption layer (in mean field).

(b) First Integral. In ref 24, the minimization problem for integrals such as (II.6) is analyzed in detail. Here we shall only sketch the method. The field $\psi(z)$ obeys a second-order, nonlinear, differential equation, which has a simple first integral:

$$kT\frac{a^2}{6}\left(\frac{\mathrm{d}\psi}{\mathrm{d}z}\right)^2 = \tilde{G}(|\psi|^2) - \tilde{G}(|\psi_{\mathrm{m}}|^2) \tag{II.8}$$

This is the analogue of the energy integral for a particle of coordinate ψ moving during the time z. Equation II.6 is the corresponding action, $-\tilde{G}(\psi)$ is the potential energy, and $kTa^2/3$ is the mass. The integration constant is written as $-\tilde{G}(|\psi_{\mathrm{m}}|^2)$ when $\psi_{\mathrm{m}} \equiv \psi(h)$ is the value of the order parameter at the midpoint between the plates. The reason for this choice is that $\mathrm{d}\psi/\mathrm{d}z$ vanishes for $\psi = \psi_{\mathrm{m}}$.

From eq II.7 it is possible to express $\mathrm{d}z$ as a function of $\mathrm{d}\psi$ (and ψ) and thus to obtain the profile $\psi(z)$ in the implicit form

$$6^{1/2}a^{-1}z = \int_{\psi(z)}^{\psi_s}\mathrm{d}\psi\left[\frac{kT}{\tilde{G}(\psi^2) - \tilde{G}(\psi_{\mathrm{m}}^{\,2})}\right]^{1/2}$$

In particular, choosing $z = h$ gives one relation between ψ_{m} and ψ_s:

$$6^{1/2}\frac{h}{a} = \int_{\psi_{\mathrm{m}}}^{\psi_s}\mathrm{d}\psi\left[\frac{kT}{\tilde{G}(\psi^2) - \tilde{G}(\psi_{\mathrm{m}}^{\,2})}\right]^{1/2} \tag{II.9}$$

Combining this with II.7, one has two equations for the two unknowns ψ_{m} and ψ_s, which fix the solution entirely.[33] One can then proceed to write the energy γ as an integral over ψ.[24] We shall not follow this road here, however, but rather construct a more transparent formula for the *force* between plates. The force per unit area is

$$\Pi_{\mathrm{d}} = -\frac{\partial(2\gamma)}{\partial(2h)} = -\frac{\partial\gamma}{\partial h}$$

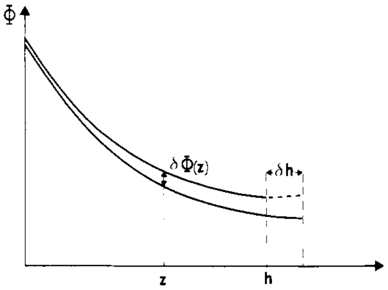

Figure 3. Changing the half-gap thickness from h to $h + \delta h$: (a) changes the domain of definition of the profile; (b) changes the profile by $\delta\Phi(z)$ in the original interval.

(3) A Theorem on Forces. The method is sketched in Figure 3. We increase h up to $h + \delta h$, inserting a new slab of solution near the midpoint. The energy $\gamma(h)$ then increases for two reasons: (a) the domain of integration is changed. This gives a contribution

$$\delta\gamma_1 = \tilde{G}(|\psi_{\mathrm{m}}|^2)\delta h \tag{II.10}$$

(b) at all points the profile is modified $\psi(z) \rightarrow \psi(z) + \delta\psi(z)$. However, since the original $\gamma(h)$ was stationary with respect to all variations of ψ, this gives no first-order contribution. We conclude that $\delta\gamma = \delta\gamma_1$, and thus

$$\Pi_{\mathrm{d}} = -\tilde{G}(|\psi_{\mathrm{m}}|^2) \tag{II.11}$$

As mentioned earlier, we know that $\tilde{G}$ must be positive. Thus Π_{d} is *always attractive*. This holds in bad solvents as well as in good solvents.

The above theorem was derived only within a mean field approximation. We expect it, however, to be more general. As will be shown in section III, we can construct a scaling theory based on an explicit free energy functional which retains many qualitative features of eq II.6 and which again contains a positive definite $\tilde{G}$ function: from (II.11), we then predict attraction at thermodynamic equilibrium.

(4) Application to Θ Solvent Conditions. One of the (few) cases where the mean field theory is not far from truth is obtained with a Θ solvent, where the chains are nearly Gaussian.[23] We shall now describe the profiles and the interaction for this case. For simplicity, we consider only the case $c_{\mathrm{b}} \rightarrow 0$ (implying $\mu \rightarrow 0$ and $\Pi_{\mathrm{b}} = 0$).

At $T = \Theta$ the interaction free energy $G(c)$ has no c^2 term but starts with a c^3 contribution. We shall write

$$G(c) = (kT/6)w^2c^3 \tag{II.12}$$

where w has the dimensions (and the order of magnitude) of a monomer volume. Equation II.9 then becomes

$$w(h/a) = \int_{c_{\mathrm{m}}}^{c_s}\mathrm{d}c\ [(c^3 - c_{\mathrm{m}}^{\,3})c]^{-1/2} \tag{II.13}$$

(a) *The limit of large gaps* ($h \gg D_{\mathrm{mf}}$) is particularly simple. In this limit $c_{\mathrm{m}} \ll c_s$ and the integral in (II.13) may be extended up to $c = \infty$. This result is

$$w(h/a) = I/c_{\mathrm{m}}$$

$$I = \int_1^\infty \mathrm{d}u\ (u^4 - u)^{-1/2} \simeq 1.40 \tag{II.14}$$

Note that $c_{\mathrm{m}}(h)$ is independent of the strength of the adsorption (γ_1), provided that γ_1 is large enough (to ensure $D_{\mathrm{mf}} < h$). Also c_{m} is proportional to $1/h$. The force between plates is then (from eq II.11)

$$\Pi_{\mathrm{d}} = -kT\frac{w^2}{6}c_{\mathrm{m}}^{\,3} = -\frac{I^3}{6}\frac{kT}{w}\left(\frac{a}{h}\right)^3 \tag{II.15}$$

and the interaction energy is proportional to kT/h^2:

$$2(\gamma_h - \gamma_\infty) = -\frac{\Gamma^3}{6}\,\frac{kTa^3}{w}\,\frac{1}{h^2} \qquad \text{(II.16)}$$

Note again that (II.15) and (II.16) are independent of γ_1 (or of $D_{\rm mf}$). Of course, all these results hold only when $D_{\rm mf} < h < R_0$ (where $R_0 = N^{1/2}a$ is the unperturbed size of the coils). At $h > R_0$ the interaction drops out very fast, but its detailed form is unknown.

(b) *The limit of small gaps* ($h \ll D_{\rm mf}$) is also simple and can be understood directly from the starting point (eq II.6). Here we have $c_s \sim c_m$. The gradient terms are negligible, and we are left with

$$\begin{aligned}\gamma - \gamma_0 &= -|\gamma_1|c_s a^3 + hkTG(c_s) \\ &= \frac{kT}{6a^2}\left[-c_s\frac{a^4}{D_{\rm mf}} + ha^2w^2c_s^{\,3}\right]\end{aligned} \qquad \text{(II.17)}$$

The optimum c_s is

$$c_s = (a/w)(3D_{\rm mf}h)^{-1/2} \qquad \text{(II.18)}$$

and the corresponding energy is proportional to $h^{-1/2}$:

$$\gamma(h) - \gamma_0 = -3^{-5/2}\frac{kTa^3}{w}(D_{\rm mf}h)^{-1/2} \qquad \text{(II.19)}$$

Thus, even when the chains are very strongly squeezed ($h < D_{\rm mf}$) the plates attract each other. Clearly, this conclusion will become wrong when the adsorption sites on both plates are completely saturated—i.e., when $\Phi_s \equiv c_s a^3$ becomes of order unity. However, looking back at eq II.18, we see that

$$\Phi_s \sim a/(Dh)^{1/2} \qquad \text{(II.20)}$$

Since we have assumed $D \gg a$ and since $h \gg a$ necessarily, we conclude that Φ_s is not too large, and the model makes sense.

(5) Attraction between Plates in Good Solvents. To complete our discussion of thermal equilibrium, we must say a few words about the interactions in good solvents. This can be handled in detail by a suitable free energy functional, going beyond mean field, which will be described in the next section. Here we shall simply give a resume of scaling arguments in good solvents. As explained in I, the thickness D of the adsorption layer in good solvents is not given by eq II.7. We have instead (for $h \to \infty$)

$$D = a\left(\frac{kT}{|\gamma_1|a^2}\right)^{3/2} \qquad \text{(II.21)}$$

For $h \gg D$ (large gaps) the concentration at the midpoint (Φ_m) is comparable (within a coefficient of order 2) to the concentration due to a single plate at the distance h:

$$\Phi_m \sim \Phi_1(h) \sim (a/h)^{4/3} \qquad \text{(II.22)}$$

The interaction free energy $G(c) = G(\Phi a^{-3})$ is known from the des Cloizeaux analysis of semidilute solutions[20,26] and is

$$G \sim (kT/a^3)\Phi^{9/4} \qquad \text{(II.23)}$$

Assuming that a theorem such as (II.11) still holds (as will be justified later), we expect a force

$$\Pi_d = -\tilde{G}(c_m) \qquad \text{(II.24)}$$

Since we assume a *dilute* bulk solution ($\mu \to 0$, $\Pi \to 0$, and $\tilde{G} \to G$), using (II.22) and (II.24), we reach

$$\Pi_d \cong -kT/h^3 \qquad (h \gg D) \qquad \text{(II.25)}$$

i.e., a result for good solvents which is similar to what we found in Θ solvents (eq II.15). The same structure of the force is also found for very different systems: van der Waals interactions between two metallic plates[27] and indirect interactions in a binary mixture at the critical point.[28]

The reason for this common structure is simple: in all cases we are dealing with a fluctuating medium where the size of the relevant fluctuations is *cut off by the gap thickness 2h*. The fluctuations are electromagnetic for the van der Waals problem or are concentration fluctuations for the binary case and for the present polymer problem. In all these cases, the only energy showing is kT, and the only relevant distance is h. Thus the interaction between plates, per cm^2, must be of the form kT/h^2. The fact that this interaction is attractive is also quite general: if one plate wishes to polarize the surrounding medium, the second plate, being identical with the first, lowers its energy by being placed in a polarized region. Some colloid data[34] indicate repulsive interactions at high polymer concentrations in situations which are claimed to be full equilibrium: this disagrees with our viewpoint but may be due in fact to departures from full equilibrium.

III. Irreversible Adsorption

(1) Sample History. We now consider a set of chains which stick to the plates and assume that the overall coverage Γ remains *fixed* when we vary h.

$$\Gamma = \int_c^h c(z)\,{\rm d}z = \text{constant} \qquad \text{(III.1)}$$

As pointed out in I, we must specify the history of the sample in detail. Here, we shall assume the following three steps: (i) for very large h, the plates are incubated by contact with a very dilute solution; (ii) the solution is washed out and replaced by pure solvent at the same temperature T; (iii) the plates are then brought to the distance $2h$ (always keeping T constant).

To describe the final state, we must optimize a certain free energy $\gamma(h)$ for all variations of the profile which keep Γ constant and equal to the Γ value for distant plates in equilibrium with a dilute solution. We shall carry out this program for *good solvents*, first within the mean field approximation and later with an improved scaling structure.

(2) Mean Field Theory. We must now construct a revised version of eq II.6 adequate for situations of irreversible adsorption. Since there is no exchange with a polymer reservoir, the free energy of interest is now $G(c)$ rather $\tilde{G}(c)$:

$$\gamma - \gamma_0 = -|\gamma_1|a^3\psi_s^{\,2} + \int_0^h {\rm d}z\left\{G(\psi^2) + \frac{kTa^2}{6}\left(\frac{{\rm d}\psi}{{\rm d}z}\right)^2\right\} \qquad \text{(III.2)}$$

We must minimize γ with respect to $\psi(z)$ at constant Γ: this introduces a Lagrange multiplier μ:

$$\delta\gamma = \mu\delta\Gamma \qquad \text{(III.3)}$$

Here μ is *not* an equilibrium chemical potential. We might call it a *pseudopotential*. The boundary condition (II.7) remains valid, but the first integral, replacing (II.8), is

$$kTa^2({\rm d}\psi/{\rm d}z)^2 = G(\psi^2) - G(\psi_m^{\,2}) + \mu(\psi_m^{\,2} - \psi^2) \qquad \text{(III.4)}$$

Equation II.9 becomes

$$6^{1/2}h/a = \int_{\psi_m}^{\psi_s}{\rm d}\psi\left[\frac{kT}{G(\psi^2) - G(\psi_m^{\,2}) + \mu(\psi_m^{\,2} - \psi^2)}\right]^{1/2} \qquad \text{(III.5)}$$

The amount of polymer per cm^2 in the interval $(0,h)$ is

$$\Gamma = 6^{-1/2}a\int_{\psi_m}^{\psi_s}\psi^2\,\mathrm{d}\psi\left[\frac{kT}{G(\psi^2) - G(\psi_m{}^2) + \mu(\psi_m{}^2 - \psi^2)}\right]^{1/2} \tag{III.6}$$

This must remain equal to the value at the end of the incubation period, which is given by a similar formula, with $\psi_m = 0$ (since $h = \infty$):

$$\Gamma \equiv 6^{-1/2}a\int_0^{\psi_{s0}}\psi^2\,\mathrm{d}\psi\left[\frac{kT}{G(\psi^2)}\right]^{1/2} \tag{III.7}$$

where ψ_{s0} is the value at the wall for a single plate in equilibrium with a bulk solution of $c_b \rightarrow 0$: hence μ and Π are set equal to zero in eq III.7.

We shall now specialize our discussion to the case of good solvents using the simplest allowed form for $G(c)$ in semidilute solutions:

$$G(c) = \tfrac{1}{2}kTvc^2 \qquad (ca^3 \ll 1) \tag{III.8}$$

where v is a positive quantity (the "excluded volume parameter"). Solving first the one-plate problem ($\psi_m = \mu = 0$), we find a profile

$$\psi(z) = (3v)^{-1/2}\frac{a}{z + D_{mf}} \qquad (h = \infty) \tag{III.9}$$

and from (III.7) a coverage Γ given by

$$\Gamma = \frac{a^2}{3vD_{mf}} = \frac{2|\gamma_1|a^3}{vkT} \tag{III.10}$$

For finite h, the main problem is to find the correct value of the pseudopotential μ required to maintain the same Γ. The answer turns out to be very simple:

$$\mu = \tfrac{1}{2}kTv\psi_m{}^2 \tag{III.11}$$

Let us first assume that this choice of μ is correct and insert it into the boundary condition, using eq II.7 and III.4. We find

$$\psi_{s0}{}^2 = \psi_s{}^2 - \psi_m{}^2 \tag{III.12}$$

We now turn to eq III.6 for Γ: inserting (III.11), we obtain

$$\begin{aligned}\Gamma &= (3v)^{-1/2}a\int_{\psi_m}^{\psi_s}\psi\,\mathrm{d}\psi\,(\psi^2 - \psi_m{}^2)^{-1/2} \\ &= (3v)^{-1/2}a(\psi_s{}^2 - \psi_m{}^2)^{1/2}\end{aligned} \tag{III.13}$$

Using eq III.12 for ψ_s, we reach

$$\Gamma = (3v)^{-1/2}a\psi_{s0} = a^2/3vD_{mf} \tag{III.14}$$

for all values of h: thus our choice of μ in eq III.11 was correct.

Having obtained the structure of the solution, we can now discuss the resulting force between the plates. The argument is related to, but slightly different from, what we had in section II. We increase h by δh and write again $\delta\gamma = \delta\gamma_1 + \delta\gamma_2$, where $\delta\gamma_1$ is related to the change of the integration domain in (III.2):

$$\delta\gamma_1 = G(\psi_m{}^2)\delta h \tag{III.15}$$

Note that here G (rather than $\tilde{G}$) shows up. Then we turn to the contribution $\delta\gamma_2$ due to changes $\delta\psi(z)$ in the interval $(0,h)$. Here we can use (III.3) and write

$$\delta\gamma_2 = \mu\delta\Gamma_{int} \tag{III.16}$$

where $\delta\Gamma_{int}$ is the variation of monomer content inside the fixed interval $(0,h)$ due to the changes $\delta\psi$. We also know that Γ computed over the total interval $(0, h + \mathrm{d}h)$ is unaltered. Thus

$$\delta\Gamma_{int} + \psi_m{}^2\delta h = 0 \tag{III.17}$$

Combining (III.15), (III.16), and (III.17), we obtain a theorem for irreversible adsorption in mean field:

$$\Pi_d = -[G(\psi_m{}^2) - \mu\psi_m{}^2] \tag{III.18}$$

and inserting the explicit forms (III.8) and (III.11), we conclude that the force Π_d vanishes exactly!

As already pointed out in the Introduction, this conclusion is not very deep: (i) It is restricted to mean field calculations and (ii) even within mean field, the cancellation is not maintained if we add to $G(c)$ higher order terms (proportional to c^3, etc.). However, the result $\Pi_d = 0$ is interesting because it shows the type of delicate cancellations between attractive and repulsive forces which may occur in these systems.

(3) Free Energy Functional with Scaling Exponents. The construction of a local free energy for situations beyond mean field has been described briefly in the last section of I. We repeat the discussion here, using as our variable the volume fraction $\Phi(z) = a^3c(z)$ rather than $c(z)$ itself. The basic idea is to introduce at each point a local correlation length $\xi(\Phi)$. For our problem, in very good (athermal) solvents, we may set[20,30]

$$\xi(\Phi) = a\Phi^{-3/4} \tag{III.19}$$

(a) For situations where Φ is *constant in space*, we know that the interaction free energy has the structure[20,26]

$$G(\Phi) = \alpha kT/\xi^3(\Phi) \tag{III.20}$$

where α is a numerical constant which we can relate to the experimental osmotic pressure of semidilute solutions:

$$\Pi = -\frac{\partial(G/\Phi)}{\partial(1/\Phi)} = \frac{5}{4}\alpha kT\xi^{-3}(\Phi) = \frac{5\alpha}{4}\frac{kT}{a^3}\Phi^{9/4} \tag{III.21}$$

(b) we must supplement $G(\Phi)$ by suitable gradient terms. Our simplifying assumption here is to consider only terms proportional to $(\mathrm{d}\Phi/\mathrm{d}z)^2$. The coefficient of this term is not constant but will depend on Φ. It must be compatible with scaling in terms of the local correlation length $\xi(\Phi)$. This imposes a structure of the form

$$\begin{aligned}&\gamma - \gamma_0 = \\ &\quad -|\gamma_1|\Phi_s + \alpha kT\int_0^h\mathrm{d}z\;\xi^{-3}(\Phi)\left[1 + \left(\frac{m_0\xi(\Phi)\;\mathrm{d}\Phi}{\mathrm{d}z}\right)^2\right]\end{aligned} \tag{III.22}$$

where m_0 is a numerical constant. (It is possible to relate m_0 to experimental data on the coherent scattering by semidilute solutions. This is discussed on the Appendix). The merit of eq III.22 is to permit precise calculations of the profile. For irreversible adsorption, the steps are very similar to what has been described in eq III.2 to III.18. We sketch them briefly below.

(4) Scaling Profiles for Irreversible Adsorption. (a) Self-Consistent Equations. It is often convenient to shift from the variable $\Phi(z)$ to another variable $f(z)$ such that the gradient term in (II.22) becomes $(\mathrm{const})(\mathrm{d}f/\mathrm{d}z)^2$. This is obtained with $f = \Phi^{3/8}$, yielding

$$\begin{aligned}&\gamma - \mu\Gamma = \gamma_0 - |\gamma_1|f_s{}^{8/3} + \\ &\quad \frac{\alpha kT}{a^3}\int_0^h\left[f^6 - \mu/(\alpha kT)f^{8/3} + \left(\frac{m\,\mathrm{d}f}{\mathrm{d}z}\right)^2\right]\mathrm{d}z\end{aligned} \tag{III.23}$$

where

$$m = 8m_0a/3 \tag{III.24}$$

As before we call f_s the value of f at the plate and f_m the value of f at the midpoint. We also find it convenient to express the pseudopotential in terms of a dimensionless constant $g(h)$ by

$$\mu = \alpha kT f_{\mathrm{m}}^{10/3} g(h) \qquad \text{(III.25)}$$

The first integral—replacing eq III.4—is then

$$\left(\frac{m\,\mathrm{d}f}{\mathrm{d}z}\right)^2 = f^6 \Delta^2(x) \qquad \text{(III.26)}$$

$$\Delta^2(x) = 1 - gx^{-5} + (g-1)x^{-9} \qquad \text{(III.27)}$$

where x is another convenient variable, related to f through

$$f = f_{\mathrm{m}} x^{3/2} \qquad \text{(III.28)}$$

All the final integrals are conveniently expressed in terms of x. First the condition on the gap thickness—replacing eq III.5—is

$$\frac{2h}{3m} = \Phi_{\mathrm{m}}^{-3/4} \int_1^{x_{\mathrm{s}}} \mathrm{d}x\; x^{-4}\Delta^{-1}(x) \qquad \text{(III.29)}$$

The condition on the amount of monomer per unit area is

$$\frac{2\Gamma a^3}{3m} = \Phi_{\mathrm{m}}^{1/4} \int_1^{x_{\mathrm{s}}} \mathrm{d}x\; \Delta^{-1}(x) = \text{constant} \qquad \text{(III.30)}$$

and

$$\Pi_{\mathrm{d}} = -\frac{\delta\gamma}{\delta h} = \frac{4}{5}\Pi(\Phi_{\mathrm{m}})(g-1) \qquad \text{(III.31)}$$

where $\Pi(\Phi)$ is the osmotic pressure displayed in eq III.21 and calculated here at the midpoint. Finally, the boundary condition at the wall is

$$-\frac{2m^2}{a^3}\left.\frac{\mathrm{d}f}{\mathrm{d}z}\right|_0 = \frac{8}{3} f_{\mathrm{s}}^{5/3} \frac{|\gamma_1|}{\alpha kT} \qquad \text{(III.32)}$$

We shall stick to the notation of I and write this condition in the form

$$-\frac{1}{\Phi}\left.\frac{\mathrm{d}\Phi}{\mathrm{d}z}\right|_0 = -\frac{8}{3}\frac{1}{f}\left.\frac{\mathrm{d}f}{\mathrm{d}z}\right|_0 = \left(\frac{f_{\mathrm{s}}}{f_{\mathrm{s}0}}\right)^{2/3} \frac{1}{D} \qquad \text{(III.33)}$$

where $f_{\mathrm{s}0}$ is the surface value of f for the single-plate problem (with $\mu = 0$) and D^{-1} is the logarithmic slope of Φ for the same reference situation:

$$D = \frac{2\alpha kT}{|\gamma_1| a^3} f_{\mathrm{s}0} \left(\frac{3m}{8}\right)^2 \sim \frac{kT}{\gamma_1 a} f_{\mathrm{s}0}^{-2/3} \qquad \text{(III.34)}$$

As shown in I, we have $f_{\mathrm{s}0} \sim (a/D)^{1/2}$ and (since $m \sim a$)

$$\frac{D}{a} \sim \left(\frac{kT}{\gamma_1 a^2}\right)^{3/2} \qquad \text{(III.35)}$$

We can now insert the boundary condition (III.33) into the first integral (III.26) and obtain

$$-\frac{1}{f}\left.\frac{m\,\mathrm{d}f}{\mathrm{d}z}\right|_0 = f_{\mathrm{s}}^2 \Delta(x_{\mathrm{s}}) = \frac{3m}{8D}\left(\frac{f_{\mathrm{s}}}{f_{\mathrm{s}0}}\right)^{2/3} \qquad \text{(III.36)}$$

Setting $3m/8D = u$, we find

$$u = \Phi_{\mathrm{s}0}^{1/4} \Phi_{\mathrm{m}}^{1/2} x_{\mathrm{s}}^2 \Delta(x_{\mathrm{s}}) \qquad \text{(III.37)}$$

Using this first in the limit $h \to \infty$ ($\Phi_{\mathrm{m}} x_{\mathrm{s}}^4 = \Phi_{\mathrm{s}} \to \Phi_{\mathrm{s}0}$, $x_{\mathrm{s}} \to \infty$, and $\Delta(x_{\mathrm{s}}) \to 1$), we note that $u = \Phi_{\mathrm{s}0}^{3/4}$. Thus, we reach the final form of the boundary condition:

$$\Phi_{\mathrm{s}0}/\Phi_{\mathrm{m}} = x_{\mathrm{s}}^4 \Delta^2(x_{\mathrm{s}}) \qquad \text{(III.38)}$$

We have constructed three equations (eq III.29, III.30, and III.38) for three unknowns (g, x_{s}, and Φ_{m}). It is convenient to eliminate Φ_{m} between (III.38) and (III.29), obtaining

$$u\frac{2h}{3m} \equiv \frac{h}{4D} = x_{\mathrm{s}}^3 \Delta^{3/2}(x_{\mathrm{s}}) \int_1^{x_{\mathrm{s}}} \mathrm{d}x\; x^{-4}\Delta^{-1}(x) \qquad \text{(III.39)}$$

We can then return to eq III.30 for Γ. Considering first the limit $h \to \infty$, we find (for $\Phi_{\mathrm{m}} \to 0$, $x_{\mathrm{s}} \to \infty$)

$$\frac{2\Gamma a^3}{3m} \to \Phi_{\mathrm{m}}^{1/4} x_{\mathrm{s}} \to \Phi_{\mathrm{s}0}^{1/4} = u^{1/3} \qquad \text{(III.40)}$$

Inserting this value of Γ in (III.30) and eliminating Φ_{m} through (III.38), we find

$$x_{\mathrm{s}} \Delta^{1/2}(x_{\mathrm{s}}) = \int_1^{x_{\mathrm{s}}} \mathrm{d}x/\Delta(x) \qquad \text{(III.41)}$$

The problem is now reduced to two coupled equations, eq III.39 and III.41. Numerically, one starts by choosing a value of g and then deduces one (or more) roots x_{s} from (III.41). Then returning to (III.39), one obtains the associated thickness. This has been carried out on an IBM34 computer. The results appear in Figures 4–6. We shall now describe specifically some simple limiting cases.

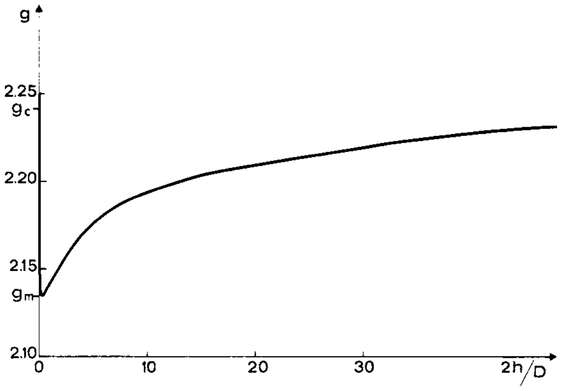

Figure 4. Reduced pseudopotential g as a function of reduced gap thickness ($2h/D$) for irreversible adsorption in a good solvent.

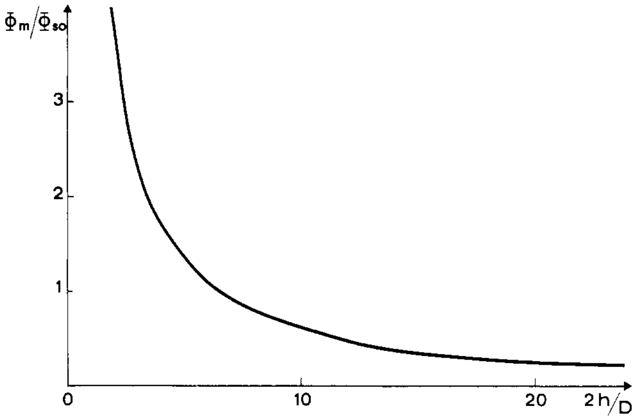

Figure 5. Concentration at midpoint Φ_{m} normalized by concentration on the surface of a single plate ($\Phi_{\mathrm{s}}(h \to \infty) \equiv \Phi_{\mathrm{s}0}$) for irreversible adsorption in good solvent.

(b) Narrow Gap Limit ($h < D$). This case is particularly simple. Here $\Phi_{\mathrm{m}} \sim \Phi_{\mathrm{s}} \sim \Gamma/h$, and (returning to eq III.22) we can check that both the gradient terms and the surface term ($\gamma_1\Phi_{\mathrm{s}}$) become negligible in this limit. This means that we are back to a homogeneous solution between two pistons. The force per unit area is then exactly equal to the osmotic pressure:

$$\Pi_{\mathrm{d}} = \Pi(\Phi_{\mathrm{m}}) = \Pi(\Gamma/h) = (5\alpha/4)kTa^{-3}(\Gamma a^3/h)^{9/4} \qquad (h < D) \quad \text{(III.42)}$$

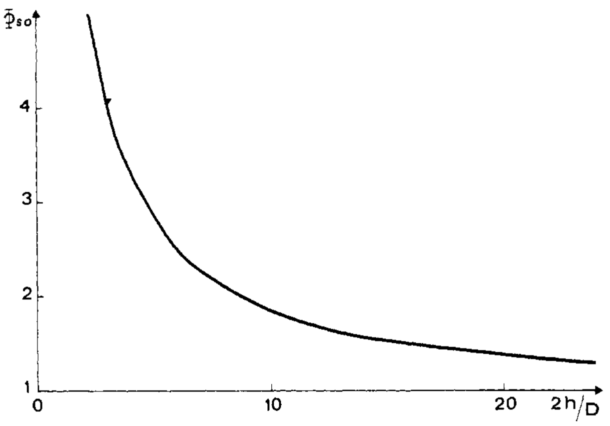

Figure 6. Shift in the concentration at the surface of one plate Φ_s induced by the presence of the second plate at a distance $2h$. Note the large effects predicted, even when $2h \sim 10D$.

The interaction *energy* is then proportional to $h^{-5/4}$. This result deserves some remarks:

(i) Since Π_d is exactly $\Pi(\Phi_m)$, this implies, by comparison with (III.31), that $g(h) \rightarrow {}^9/_4$ for $h \ll D$. The value ${}^9/_4$ is in fact an upper limit for g.

(ii) Our reader may wonder why a similar property did not hold for the mean field calculation, giving a short-range interaction which would be dominated by the osmotic pressure and, thus, repulsive. In actual fact, we know that the mean field interaction vanishes. Why? Answer: When the interaction free energy is quadratic in Φ (as it is in mean field), it is never possible to neglect the surface term $\gamma_1\Phi_s$ in comparison with the osmotic term: in fact, these two terms cancel out exactly. (This compensation occurs only when $G(\Phi) \sim \Phi^2$.)

(c) Large Gap Limit ($h \gg D$). Of course, this large h limit can be discussed with our self-consistent equations only if the two adsorption layers have a certain overlap. As explained in section II, we expect that the largest polymer loops extend up to a distance comparable to the coil size $R_F = N^{3/5}a$. Thus, we must have $h < R_F$, and the existence of the "large gap" regime requires $R_F \gg D$. This will often be realized in practice.

In the large gap regime, we have $\Phi_m \ll \Phi_s$ or $x_s \gg 1$. Returning to eq III.41, we can write $\Delta^{1/2}(x_s) \rightarrow 1 - (9/4)x_s^{-5}$. The integral on the right-hand side can be transformed as follows:

$$\int_1^{x_s} \mathrm{d}x\, \frac{1}{\Delta(x)} = J(g) + x_s - \int_{x_s}^{\infty} \mathrm{d}x \left(\frac{1}{\Delta(x)} - 1\right) \qquad \text{(III.43)}$$

where

$$J(g) = -1 + \int_1^{\infty} \mathrm{d}x \left(\frac{1}{\Delta(x)} - 1\right) \qquad \text{(III.44)}$$

The last term in eq III.44 may be calculated explicitly using the asymptotic form of $\Delta(x)$ at large x. Ultimately, eq III.41 becomes

$$J(g) + {}^1\!/_8 g x_s^{-4} = 0 \qquad x_s \gg 1 \qquad \text{(III.45)}$$

Thus in the large gap limit ($x_s \rightarrow \infty$) we must have $J(g) = 0$. This defines an asymptotic value of g, which we call g_c:

$$J(g_c) = 0$$

The numerical calculation gives $g_c \cong 2.234$. The essential property is that g_c is *larger than unity*. Then if we return to the formula for the force Φ (eq III.31), we see that $\Phi > 0$: the interaction at large distances is *repulsive*.

Knowing g_c, we can construct Φ_s and Φ_m. First, using eq III.30, we see that Φ_s is only weakly different from the single-plate value Φ_{s0}. Second, from eq III.29, we find

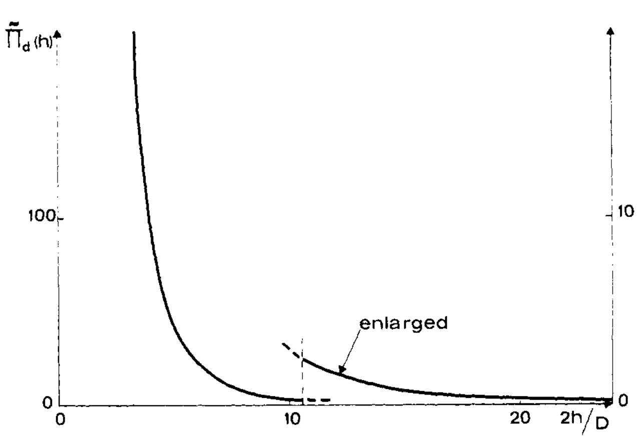

Figure 7. Reduced force $\tilde{\Pi}_d(h)$ between the two plates (as defined in eq III.51) vs. reduced distance ($2h/D$), for irreversible adsorption in a good solvent.

$$\frac{2h}{3m} \rightarrow Q(g_c)\Phi_m^{-3/4} \qquad \text{(III.46)}$$

$$Q(g) = \int_1^{\infty} \mathrm{d}x\, x^{-4}\Delta^{-1}(x)$$

$$Q(g_c) \cong 4 \qquad \text{(III.47)}$$

and thus Φ_m is of order $(a/h)^{4/3}$ as expected. Inserting (III.46) into (III.31), we arrive at a force

$$\Pi_d = \alpha kT(g_c - 1)\left(\frac{3mQ(g_c)}{2ha}\right)^3 \sim \frac{kT}{h^3} \qquad \text{(III.48)}$$

Thus the long-range repulsive energy is proportional to kT/h^2.

(d) Remarks on the Intermediate Regime ($h \sim D$). The most striking feature is that the parameter

$$g(h) = \mu/(\alpha kT\Phi_m^{6/5}) \qquad \text{(III.49)}$$

is nearly constant. For $h \rightarrow 0$, g : 2.25. For $h \rightarrow \infty$, $g \rightarrow g_c \cong 2.24$. It must be observed, however, that $g(h)$ is *not* monotonously decreasing; in fact, g reaches a minimum $g_m \cong 2.135$ at $h/D \cong 0.4$ as is shown in Figure 4. The existence of a minimum is clear on eq III.45. Since $J(g_c) = 0$, we must have a large x_s

$$\left.\frac{\mathrm{d}J}{\mathrm{d}g}\right|_{g_c} (g - g_c) = -(g_c/8)x_s^{-4} \qquad \text{(III.50)}$$

The derivative $\mathrm{d}J/\mathrm{d}g$ is easily seen to be positive, and this implies that g is slightly below g_c at large x_s, while we know that $g = 2.25$ is larger than g_c at small x_s: thus there must be a minimum in the plot of $g(x_s)$ or $g(h)$.

The main conclusion is that $g_{\min} > 1$, ensuring that the interaction is repulsive at all distances. (The small variations of $g(h)$ displayed in Figure 4 might in fact result from the approximate form of our free energy functional: the exact $g(h)$ could be strictly constant.)

In Figure 5 we show the predicted variation of the concentration Φ_m at the midpoint as a function of the gap thickness $2h$. In Figure 6 we display the concentration at the wall Φ_s: note that Φ_s is significantly increased as soon as $2h/D \lesssim 20$, i.e., for rather large gaps (always assuming $h < R_F$).

Finally, in Figure 7 we give the result for the force $\Pi_d(h)$ in terms of a reduced function $\tilde{\Pi}_d(h/D)$, setting

$$\Pi_d(h) = \alpha kT(u/a)^3\tilde{\Pi}_d(h/D) \qquad \text{(III.51)}$$

IV. Conclusions

It appears possible to construct a self-consistent description of two adsorption layers in interaction, at least in the limit of good overlap, i.e., when the gap half-thickness h is smaller than the size R of the largest loops ($R = R_F = N^{3/5}$ in good solvents). The main conclusions are the following:

(1) The sign of the interplate forces depends critically on the physical conditions: the forces are always attractive in the case of an ideal exchange between adsorpted and free chains. But if we deal with the more realistic case of zero desorption, the situation is very different. We must, in such a case, specify carefully the sample history. For the simplest case (where the plates have been incubated in a dilute solution with a good solvent and then brought into contact at the same temperature) we predict *a repulsion at all distances h smaller than R.* This is roughly what the Bristol group observed[9] but their situation with block copolymers is more complex than what we describe here.

(2) Our analysis was restricted by one assumption (already introduced in ref 25 and in I, namely, that $\gamma_1 a^2 < kT$ or, more concretely, that the monomers do not fill all the available sites at the plate surface ($\Phi_s \ll 1$). This ensures that $D \gg a$ and allowed for a discussion of the interesting limit $a < h < D$. What happens if we set $\gamma_1 a^2 \sim kT$ or $D \sim a$? As explained in section II, we must then add extra terms in the contact energy $\gamma_d(\Phi_s)$. When this is done, we find no spectacular change: all the profiles described above for $z \gg D$ remain valid, and the interaction formulas in the large gap limit ($D < h$) remain unaltered.

(3) From an experimental standpoint, measurements of forces between plates will probably become more current in the next few years. Unfortunately, our present predictions on the forces are limited to good solvents and good overlap ($h < R$). For *poor solvents* the general scheme of sections II and III is easily written down but is numerically complex. We can, however, mention two remarks bearing on the poor solvent case:

(a) At short distances ($h < D_{mf}$) a simplified discussion (omitting the gradient terms in the free energy as in section III.4.b) suggests a *repulsion* decreasing like h^{-2}.

(b) It may be that the attraction observed by Klein[10] does not correspond to the good overlap regime considered here ($h < R$) but rather to the onset of overlap ($h \sim R$), i.e., when the chains of plate 1 begin to touch the outer loops from plate 2 (which attracts them at low c and $T < \Theta$) but do not yet feel the inner part of the adsorption layer (2) which is denser and repulsive.

(4) Apart from direct force measurements, a number of other experimental approaches can be considered for the future.

(a) Local probes on plate 1 can detect the changes in the surface concentration Φ_s when plate 2 is brought in. In the notation of section III

$$\Phi_s(h)/\Phi_s(\infty) = \Delta^{-2}(x_s) \qquad \text{(IV.1)}$$

This function is plotted in Figure 5.

For large h/D eq IV.1 gives

$$[\Phi_s(h) - \Phi_s(\infty)]/\Phi_s(\infty) \rightarrow g x_s^{-5} = (\text{const})(D/h)^{5/3} \qquad \text{(IV.2)}$$

In practice, we might try to measure Φ_s by fluorescence techniques or by sensitive spectroscopic techniques (EPR, optical or IR).

(b) Hydrodynamic measurements may be of interest. For instance, if we impose a pressure gradient $\partial p/\partial x$ parallel to the plates, we can measure the resulting solvent flux J (integrated over the gap width $2h$):

$$J_x = \delta\left(-\frac{\partial p}{\partial x}\right) \qquad \text{(IV.3)}$$

For $D < h < R$, an analysis based on the ideas of Appendix B in I suggests that δ has the same scaling structure which we would find for pure solvent flow in a clean slit (no adsorption), namely, $\delta \sim h^3/\eta_s$, where η_s is the solvent viscosity. But the coefficient should be strongly reduced by the adsorbed chains. Similar conclusions are expected for flow inside a narrow pore covered with an adsorbed layer (h is then the pore radius).

(5) A final remark: we concluded that two *flat plates* carrying irreversibly adsorbed polymer sheets, in good solvents, repel each other. However, if we turn to the case of two *spherical grains*, in similar conditions, the problem is much more delicate: even the sign of the intergrain interaction is not obvious! This can be understood as follows: (a) When two flat plates can exchange polymer with a reservoir, they attract each other. (b) Consider two grains and assume that the chains are not allowed to leave the grain vicinity but are allowed to creep along the grain surface: then the "gap region" between the grains may adjust its local Γ, the "outer caps" of each grain playing the role of a reservoir. Thus, with this rule of the game, the intergrain interaction might become very weakly repulsive, or even attractive.

This situation, with creep allowed along the adsorbing surface, could prevail when the "grains" are *liquid* droplets. On the other hand, if the grains are *solid*, it may often happen that creep is not allowed during the relevant time intervals (the "time of collision" of grains moving by Brownian motion). Then a different calculation, with Γ fixed at all points on each grain, is required. In this case, the interaction is probably repulsive. Thus the two-grain problem appears extremely sensitive to the detailed dynamical properties of the adsorbed chains.

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Appendix. Relation between the Coefficient m_0 and Scaling Data on Semidilute Solutions

Starting from the free energy functional (III.22), we can return to the (relatively) simple case of a bulk solution and investigate the small fluctuations $\delta\Phi = \Phi - \Phi_b$. The coherent scattering intensity at a scattering wave vector $\mathbf{q}$ is proportional to the thermal average:

$$S(\mathbf{q}) = \langle |\delta\Phi_q|^2 \rangle \qquad \text{(A.1)}$$

where $\delta\Phi_q$ is a Fourier component. From (III.22) we can express the free energy in term of all $\delta\Phi_q$'s:

$$F = \sum_q |\delta\Phi_q|^2 \alpha kT \left[\frac{1}{2} \frac{\partial^2}{\partial\Phi^2}(\Phi^{9/4})|_{\Phi_b} + {\Phi_b}^{1/4}(m_0 q \xi_b)^2 \right] \qquad \text{(A.2)}$$

Applying the equipartition theorem, we require that each q gives an average contribution $kT/2$. This gives

$$\langle |\partial\Phi_q|^2 \rangle = \alpha^{-1}{\Phi_b}^{-1/4}\left[\frac{45}{16} + 2(m_0 q \xi_b)^2 \right]^{-1} \qquad \text{(A.3)}$$

$$= (\text{const})(q^2 + {q_c}^2)^{-1} \qquad \text{(A.4)}$$

where

$$q_c = (m_0 \xi_b)^{-1}\left(\frac{45}{2}\right)^{1/2}\frac{1}{4} \qquad \text{(A.5)}$$

Our definition of ξ_b (for athermal solvents) was $\xi_b = a{\Phi_b}^{-3/4}$.

Thus if the scattering is reasonably described by eq A.4, we can derive m_0 from q_c using (A.5).

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(31) This observation destroys our confidence in most of the earlier theoretical work which was carried out at the mean field level.
(32) This notation ensures that $\gamma(h \rightarrow \infty)$ is the interfacial tension for *one* plate.
(33) One of our referees pointed out the structural analogy between these equations and the classical DLVO theory for overlapping double layers.
(34) Cowell et al. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 337. I am indebted to a referee for mentioning this reference.

Measurement of an Equilibrium Density Gradient of a Solvent Mixture in an Ultracentrifuge

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ABSTRACT: The equilibrium density gradient of a solvent mixture in an ultracentrifuge was analyzed from the thermodynamic viewpoint, including the effects of pressure. Several techniques of the measurement of the gradient were discussed. The technique using a marker polymer and several equilibrium runs, each run sequentially equilibrated at several rotor velocities, was tested experimentally. A sample of polystyrene was used as a marker for the isorefractive mixture of cyclohexane and 1,2-dibromo-1-chloro-1,2,2-trifluoroethane. The rather plausible result for this mixture is believed to be the first detailed density profile measured experimentally in the ultracentrifuge.

Sedimentation equilibrium of polymer samples in a density gradient potentially provides a wealth of information about chemical heterogeneity of the sample, its molecular weight, polydispersity, impurities, etc. However, for a proper analysis, the density profile in the cell must be known with a good precision. As far as we know, a satisfactory evaluation of the density gradient (considered as a constant throughout the cell) was achieved only for aqueous solutions of several salts (e.g., CsCl).[1-3] These solutions were used as a density gradient forming media for the study of nucleic acids. The evaluation was based on a detailed knowledge of the activity coefficients of the salts from auxiliary measurements. For a study of most synthetic polymers, mixtures of organic solvents are needed. Some of the solvents are unusual and thermodynamic parameters of the mixtures are unknown. We have shown in a previous paper[4] that even for more common mixtures, the extraction of the necessary data from the literature is rather difficult. A direct evaluation of these thermodynamic parameters requires tedious research with rather sophisticated equilibrium distillation stills and precision calorimetry.

Under these circumstances, it is desirable to develop a method for the measurement of the density gradient using the ultracentrifuge itself. In this paper, we will first discuss the usefulness of the schlieren photographs and ultraviolet scans of the density gradient for its direct measurement and will show that these techniques do not yield information of sufficient quality. In a later part we will analyze the density gradient in detail from the thermodynamic point of view. Using this analysis as a basis, we will then develop a technique that employs a polymer sample as a probe for the evaluation of the density gradient. The technique requires a preparation of several solutions of the same polymer sample in mixtures of the two solvent components with different mass ratios. Each solution is then sequentially brought to an equilibrium at several rotor velocities. The density profile is evaluated from the polymer band positions at all the equilibrium conditions. The method has been applied to a mixture of cyclohexane and 1,2-dibromo-1-chloro-1,2,2-trifluoroethane. This solvent mixture is very convenient for studying samples of polystyrene.

Direct Measurement of a Density Profile

The Spinco Model E ultracentrifuges are equipped with ultraviolet absorption optics with a scanner and with two optical systems based on the refractive index: schlieren and interference. If the two solvents forming a density gradient have rather different UV spectra, then the UV

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