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Nonequilibrium Forces between Adsorbed Polymer Layers: The Case of Fixed Surface Contact Density

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ABSTRACT: We studied theoretically the interaction of adsorbed polymer layers, within the Cahn–de Gennes approach, using a model of "doubly restricted equilibrium" (DRE) in which not only the surface coverage but also the surface contact density (i.e., first-layer concentration) are held constant. The latter constraint is unconventional; it provides a paradigm for nonequilibrium interlayer forces, which vanish in the static limit but may become important under conditions of rapid collision between polymer-stabilized colloidal particles. We argue that this model is relevant, for example, to the study of shear-induced flocculation of particles bearing polymers that have a sparse fraction of strongly adsorbing groups. We find that the steric force between particles is much increased in comparison to the usual "restricted equilibrium" (RE) model in which the coverage but not the surface contact density is constrained. Both mean-field and scaling-functional calculations are presented. In the mean-field treatment, the disjoining pressure is finite for the DRE model although it vanishes in the RE case. In the scaling theory, we find that the DRE model can dramatically alter the overall force–distance relationship between sterically stabilized particles subject to attractive van der Waals forces. Our results suggest that there are conditions under which nonequilibrium polymer forces can strongly influence the stability of colloids under shear.

1. Introduction

The interactions between polymer solutions and solid surfaces have been the subject of extensive experimental and theoretical study in recent years.[1–9] Experimental methods are now suitably refined[8–10] to give detailed information about the properties of the solid–solution interface.

Theoretically, a major step forward was made by de Gennes when he applied the Cahn model for interfacial tension and wetting of fluids to describe the effects of homopolymer adsorption from a semidilute solution. The approach enables the polymer density profile and the force between two polymer bearing surfaces to be calculated in terms of a few fundamental parameters. In strict thermodynamic equilibrium, de Gennes found, for a good solvent, that the force is always *attractive*;[3] this is because the polymer can adsorb/desorb, ensuring that the polymer concentration midway between the surfaces always remains small, attractive bridging forces then being dominant. However, under most experimental conditions a polymer is bound to the surface by an energy greatly exceeding k_BT, which, combined with the general slowness of polymer diffusion, leads to effectively irreversible adsorption. The polymer is then under local equilibrium conditions, except that the total amount of adsorbed polymer (surface coverage) is constrained to be a constant. This defines the restricted equilibrium (RE) model. At the level of mean-field theory, the RE model predicts fortuitously an exact cancellation between the excluded-volume repulsion and bridging attraction forces, and hence zero force.[3] However, a more refined version proposed by de Gennes,[2,3] which employs modified exponents appropriate to the semidilute regime, leads to a monatomic repulsive force, consistent with experiments in good solvents.[9] Subsequently, Klein et al.[6] extended the approach to poor solvents, obtaining a repulsive force at small separations and an attractive tail at large separations, again consistent with experiments.[6] More recently, Rossi and Pincus[7] studied the RE model for unsaturated surfaces, obtaining (as in the poor solvent case) an attractive force at large separations. It is thus apparent that the Cahn–de Gennes (CdG) approach does qualitatively describe the problem of interacting polymer surfaces, but the results obtained are very sensitive to the precise assumptions made.

In this paper we propose a simple extension of the CdG approach, in which we assume that surfaces come together under conditions in which the surface contact density, as well as the surface coverage, is constrained to be fixed. We refer to this as the "doubly restricted equilibrium" (DRE) model. This provides an example of a *nonequilibrium interaction force* between polymer layers: a force which vanishes when two layers approach very slowly, but which may be large in the course of a rapid collision, for example between particles in a strongly sheared colloid. The possible importance of such forces has recently been suggested by Lips et al.[11]

In general, such nonequilibrium forces will involve a complex interplay of polymer motion and hydrodynamics. However, in the simplest model of binary collisions,[12] one assumes that stability of colloids under shear is determined by a balance between particle–particle interaction forces and hydrodynamic forces. Nonetheless, the interaction force must depend on the rate of approach between particles, and if this is rapid, it is not necessarily appropriate to calculate the force using equilibrium (or RE) thermodynamics.

Several limiting cases can be considered, depending mainly on the equilibration rates for the loops and tails of the adsorbed chains, and also that for the surface contacts. The DRE model is appropriate if the equilibration of surface contacts is slow compared to both the collision time between particles and the internal relaxation time (Zimm time) of the adsorbed chains. Although the latter inequality seems unlikely for adsorbed homopolymer, such a situation may arise if the adsorbed species is a copolymer containing a relatively sparse fraction of

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groups or blocks that adsorb rather strongly to the surface. As shown by Marques et al.,[13] the adsorption of random copolymer of this type leads to the same equilibrium concentration profile as for homopolymer adsorption, with a renormalized monomer adsorption energy. To obtain a slow equilibration time for surface contacts, however, we require that each adsorption point be attached to the surface with an energy large compared to k_BT, and this is likely only in the copolymer case. (Homopolymer adsorption energies are typically a small fraction of k_BT per monomer.) It seems plausible that, with suitable copolymers, the time scale for surface contact equilibration could be large compared to collision times, which, at high shear rates, can be on the order of milliseconds or less.

In what follows, we consider in detail the DRE model within the usual Cahn–de Gennes framework. We use the language of homopolymer adsorption, although the calculations are more relevant to copolymers, as just described; we assume good solvents throughout. The paper is organized as follows: In section 2 we outline the CdG approach at the mean-field level and calculate the interaction force for the DRE model defined above. In section 3 we reformulate the problem using the de Gennes scaling functional appropriate to semidilute layers and compare our results with those for the standard case of restricted equilibrium.[3] In section 4 we interpret our results in terms of the stability of a sterically stabilized system with attractive van der Waals forces. Concluding remarks are made in section 5.

2. Mean-Field Theory

In this section we formulate the problem in mean-field theory which, despite being known to give qualitatively incorrect results for semidilute layers,[1-3] does provide a useful comparison with the more refined scaling functional approach of section 3. Also, in the limit of small separations, where the polymer concentration is high, we expect mean-field theory to be applicable.

2.1. Saturated Surfaces in the RE Model. In the CdG approach the surface free energy associated with the adsorption of homopolymer can be written as the sum of surface and volume contributions. The surface contribution is written as an expansion in powers of the first-layer volume fraction (the surface contact density). If this is low, as we shall assume, only the linear term is needed.

The volume contribution arises from distortions of the concentration profile and consists of an integral over space of a local free energy functional that depends on concentration and its gradient. It is usual to simplify the functional by use of the order parameter ψ, defined by $\psi^2 = \phi$, where ϕ is the monomer volume fraction. The corresponding free energy per unit area for a single planar surface, in contact with a very dilute bulk reservoir, in units where k_B is unity, is given by[1]

$$\gamma - \gamma_0 = -\gamma_1\psi_s^{\,2} + \frac{T}{a^3}\int_0^\infty\left[\frac{a^2}{6}\left(\frac{d\psi}{dz}\right)^2 + \frac{1}{2}v\psi^4\right]dz \qquad (1)$$

where γ_0 is the surface energy of the pure solvent, γ_1 is the monomeric sticking energy ($\gamma_1 > 0$ for adsorption), T is the temperature, a is the monomer size, ψ_s is the value of ψ on the surface, and $v = 1 - 2\chi$ is a dimensionless excluded-volume parameter (where χ is the Flory parameter).

Minimization of γ with respect to changes in the profile results in the standard Euler–Lagrange equation, which is subject to a condition on the logarithmic derivative at the surface:

$$\frac{a^2}{3v}\left(\frac{d\psi}{dz}\right)^2 - \psi^4 = 0 \qquad (2)$$

$$\left[\frac{1}{\psi}\frac{d\psi}{dz}\right]_s = -k = -\frac{6\gamma_1 a}{T} \qquad (3)$$

The boundary condition of eq 3 introduces a length scale, the "extrapolation length" $D = k^{-1}$, which is a measure of the size of the adsorbed layer.

For a single planar surface the surface coverage (referred to as saturated) is given in the RE model by

$$\Gamma_0 = \frac{1}{a^3}\int_0^\infty \phi\, dz = \frac{1}{a^3}\int_0^\infty \psi^2\, dz \qquad (4)$$

where the subscript o denotes the saturated single-surface value and will be used hereafter to denote all single-surface saturated values. It is simple to solve for the profile in eqs 2 and 3 and substitute the result into eq 4, which yields the coverage as

$$\Gamma_0 = \frac{1}{3vaD} \qquad (5)$$

It should be noted that Γ_0, and other properties of the layer, e.g., γ, are unique functions of the extrapolation length D.

2.2. DRE Model. Let us now consider placing two planar surfaces a distance $2h$ apart and minimize the free energy γ subject to our assumptions of irreversible adsorption *and fixed concentration in the first layer*, i.e., the conditions of "doubly restricted equilibrium". To do so, we introduce as usual a Lagrange multiplier (pseudochemical potential) λ for the surface coverage; there is no need to do likewise for the surface contact density which is (up to a constant) simply the surface concentration denoted by $\phi_s = \psi_s^{\,2}$. This can be constrained by a simple modification of the boundary condition (eq 3), namely that

$$\psi(0) = \psi_{so} \qquad (6)$$

where ψ_{so} is the RE value for a single saturated surface computed as in section 2.1 above. (We leave ψ_{so} as a parameter for the moment.) Hence, in the DRE model we write for each surface

$$\bar{\gamma} = \gamma - \gamma_0 - \lambda\Gamma_0 = -\gamma_1\psi_{so}^{\,2} + \frac{T}{a^3}\int_0^h\left[\frac{a^2}{6}\left(\frac{d\psi}{dz}\right)^2 + \frac{1}{2}v\psi^4 - \lambda'\psi^2\right]dz \qquad (7)$$

where $\lambda = T\lambda'$. Minimizing $\bar{\gamma}$ with respect to changes in the profile subject to the boundary condition (eq 6) yields

$$\frac{a^2}{6}\left(\frac{d\psi}{dz}\right)^2 = \frac{v}{2}(\psi^4 - \psi_m^{\,4}) - \lambda'(\psi^2 - \psi_m^{\,2}) \qquad (8)$$

where ψ_m denotes the value of ψ at the midpoint where, by symmetry, $d\psi/dz$ vanishes. Having solved eq 8 to find the profile, the free energy γ for a given coverage Γ_0 is found from $\bar{\gamma}$ by inverting the Legendre transform.

2.3. Reduced Variables. It is now convenient to normalize ψ by the midpoint value ψ_m, introducing $y = \psi/\psi_m$, and to measure all lengths in units of the extrapolation length D, e.g., $z = D\tilde{z}$. Writing $\lambda' = v\mu\psi_m^{\,2}/2$ enables eq 8 to be expressed in reduced units as

$$\left(\frac{dy}{d\tilde{z}}\right)^2 = \frac{1}{y_{so}^{\,2}}[(y^4 - 1) - \mu(y^2 - 1)] \qquad (9a)$$

with boundary condition

$$y(0) = y_{so} \tag{9b}$$

From eq 9 it is possible to express $d\tilde{z}/dy$ as a function of y, thus obtaining the profile $y(\tilde{z})$ in the implicit form

$$\tilde{z} = y_{so}\int_{y(\tilde{z})}^{y_{so}} \frac{1}{[y^4 - 1 - \mu(y^2 - 1)]^{1/2}}\, dy \tag{10}$$

Choosing $\tilde{z} = \tilde{h}$ gives one relation between y_{so} and μ:

$$\tilde{h} = y_{so}\int_{1}^{y_{so}} \frac{1}{[y^4 - 1 - \mu(y^2 - 1)]^{1/2}}\, dy \tag{11}$$

To write eq 11, it has been assumed that $y_{so} > 1$. However, in the DRE model y_{so} can be less than unity and indeed must be so for small surface separations if the constraint of constant surface coverage is to be maintained. [Recall that $y_{so}^2 = \psi_{so}^2/\psi_m^2$ represents the ratio of concentrations in the first layer and at the midplane.] This is in contrast to the RE model[3] where, for all surface separations, the logarithmic boundary condition ensures that the surface concentration exceeds the midpoint value: $\psi_s > \psi_m$. From now on, all integrals containing y_{so} in the limits will be written for the case $y_{so} > 1$, it being understood that y_{so} can also be less than unity, in which case the limits on the integrals in eqs 10 and 11 must be reversed.

The surface coverage per unit area, in the reduced units, is given by

$$\Gamma = \frac{\Gamma_0}{y_{so}}\int_{1}^{y_{so}} \frac{y^2}{[y^4 - 1 - \mu(y^2 - 1)]^{1/2}}\, dy \tag{12}$$

Since we are constraining $\Gamma = \Gamma_0$, eq 12 reduces to

$$y_{so} = \int_{1}^{y_{so}} \frac{y^2}{[y^4 - 1 - \mu(y^2 - 1)]^{1/2}}\, dy \tag{13}$$

Equations 11 and 13 are enough to completely determine y_{so} and μ for a particular surface separation $2\tilde{h}$; substitution of these values into eq 10 then ables the volume profile $\phi(\tilde{z}) = \phi_m y^2(\tilde{z})$ to be calculated. From this, it is possible to find the free energy γ, but it is perhaps more enlightening to calculate instead the force between the surfaces.

2.4. Calculation of the Force. The force per unit area or "disjoining pressure" between the two planar surfaces bearing adsorbed polymer is given by[3]

$$\Pi_d = -\frac{\partial(2\gamma)}{\partial(2h)}\bigg|_{\Gamma_0,\psi_{so}} = -\frac{\partial\bar{\gamma}}{\partial\tilde{h}}\bigg|_{\mu,\psi_{so}} \tag{14}$$

which, in reduced units, becomes

$$\Pi_d = \frac{Tv{\phi_{so}}^2}{2a^3}\left[\frac{\mu - 1}{{y_{so}}^4}\right] \equiv \Pi_d{}^*\left[\frac{\mu - 1}{{y_{so}}^4}\right] \tag{15}$$

where the second equality defines a characteristic scale of disjoining pressure, $\Pi_d{}^*$. Positive (negative) Π_d corresponds to repulsive (attractive) forces. Again, using the values of y_{so} and μ from eqs 11 and 13 enables Π_d to be calculated as a function of $\tilde{h}$. For the RE model[3] it is straightforward to show that (in our units) $\mu = 1$, and thus the pressure Π_d vanishes for all values of the separation $2h$. For the DRE model it is not possible, in general, to find an analytic solution; before turning to numerical methods, we present asymptotic results for some limiting cases.

2.4.a. Large Separations: $\tilde{h} \to \infty$. For $h \gg D$, we expect the extra constraint of fixed surface concentration to have little effect, and the pseudochemical potential will tend to the RE value $\mu = 1$ as $y_{so} \to \infty$. Expanding eq 13 in terms of the small parameters $\mu - 1$ and $1/y_{so}$ and changing variables to $1/y$ enable the integrand to be written as a simple power series. Integration then gives (ignoring all numerical prefactors)

$$y_{so} \sim \frac{1}{\mu - 1} \tag{16a}$$

Equation 11 can be evaluated in a similar manner, giving

$$\tilde{h} \sim y_{so} \tag{16b}$$

Combining these results with eq 15, we find the disjoining pressure obeys

$$\Pi_d \sim \frac{\Pi_d{}^*}{\tilde{h}^5} \tag{16c}$$

In practice, h can be no larger than R_F (the Flory radius of a chain), and thus the validity of eq 16c is limited to the regime $D \ll h < R_F$.

2.4.b. Small Separations: $\tilde{h} \to 0$. For $h \ll D$, $\mu \to \infty$ and $y_{so} \to 0$, since to satisfy the constraint of constant surface coverage, the concentration at the midpoint must exceed that at the surface by a large factor. As for the large separation limit, a suitable expansion in terms of y and y_{so} (assuming large μ) simplifies the integrals of eqs 11 and 13, giving

$$y_{so} \sim \tilde{h}^{1/2} \qquad \mu \sim \frac{1}{\tilde{h}} \tag{17a}$$

Substitution into eq 15 gives the disjoining pressure as

$$\Pi_d \sim \frac{\Pi_d{}^*}{\tilde{h}^3} \tag{17b}$$

This scaling is dominated by the entropy loss of confining each chain between the plates and therefore coincides with the disjoining pressure for trapped nonadsorbing polymer[14] or end-adsorbed polymers at high compression.[15]

2.4.c. General Case. The effects of the DRE model, within mean field, is to give a repulsive force at all surface separations (as would be expected), the pressure varying $1/\tilde{h}^5$ at large separations and $1/\tilde{h}^3$ at small separations. We remark again that, within the mean-field description, this disjoining pressure would vanish identically for the RE model as opposed to the DRE case studied here.

For general values of $\tilde{h}$ it is necessary to turn to numerical methods to solve eqs 11 and 13. Two numerically calculated volume fraction profiles are shown in parts a and b of Figure 1 for $\tilde{h} = 14.9$ and 0.105, respectively. The numerically calculated disjoining pressure as a function of the dimensionless intersurface separation distance $2\tilde{h}$ is shown in Figure 2, along with the analytic asymptotes. We defer further discussion of these results until after the next section, which concerns the scaling approach to the DRE model.

3. Scaling Theory

The mean-field theory of polymer adsorption often gives good qualitative results, but it does not take into account correctly the correlations induced by the excluded-volume interaction. It was shown by de Gennes[2] that an adsorption functional could be made to give the correct scaling results, so long as it is assumed that the polymer concentration profile is regular in the proximal region; in fact, this assumption is not quite correct, although the existence of a proximal singularity[4] has little effect in the regime of strong adsorption, which is of most interest here. The de Gennes functional for adsorption on a single planar surface

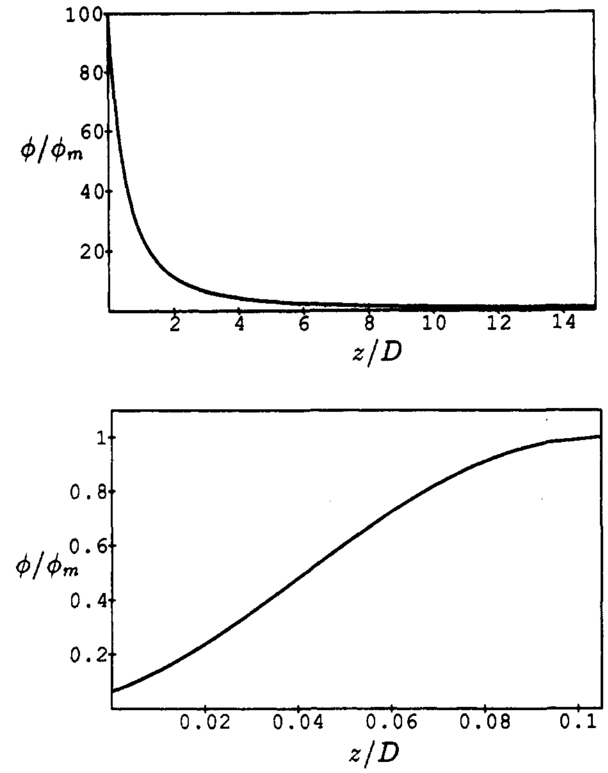

Figure 1. Normalized volume fraction profiles ϕ/ϕ_m for DRE, calculated using mean-field theory: (a, top) for an intersurface separation distance of $2h/D = 29.8$; (b, bottom) for an intersurface separation distance of $2h/D = 0.21$.

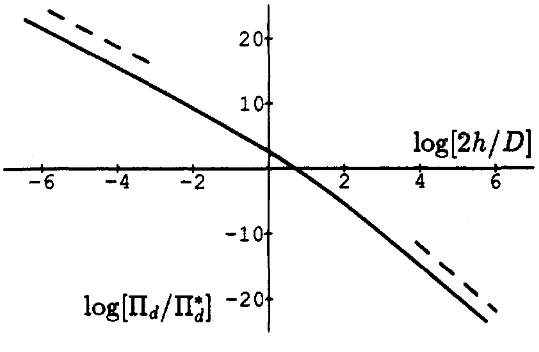

Figure 2. Variation of disjoining pressure Π_d/Π_d^* with intersurface separation distance $2h/D$ for DRE, calculated using mean-field theory (solid curve). Dashed curves are asymptotes for small and large intersurface separations.

from a very dilute bulk (in units where k_B is unity) takes the form[3]

$$\gamma - \gamma_0 = -\gamma_1\phi_s + \frac{\beta T}{a^3}\int_0^\infty \left[\frac{1}{\phi^{5/4}}\left(m_0\frac{d\phi}{dz}\right)^2 + \phi^{9/4}\right] dz \qquad (18)$$

where the variables are the same as previously defined in section 2, ϕ is the polymer volume fraction, and β and m_0/a are constants. Within the scaling theory, these are expected to be universal (independent of chemical microstructure), a fact used in section 4. We have as usual approximated the polymer size exponent $\nu = 0.588$ by the Flory estimate $^3/_5$.

3.1. Reduced Variables. It is useful now to introduce the reduced variable f, defined by $f = \phi^{3/8}$, rewriting eq 18 as

$$\gamma - \gamma_0 = -\gamma_1 f_s^{8/3} + \frac{\beta T}{a^3}\int_0^\infty \left[\left(m\frac{df}{dz}\right)^2 + f^6\right] dz \qquad (19)$$

where $m = 8m_0/3$. Minimizing eq 19 gives the profile equation and boundary condition at the surface as

$$\left(\frac{m d\psi}{dz}\right)^2 - f^6 = 0 \text{ with } \frac{8}{3}\left(\frac{f_{so}}{f_s}\right)^{2/3}\left[\frac{1}{f}\frac{df}{dz}\right]_s = -\frac{1}{D} = -\frac{32\gamma_1 a^3 f_{so}{}^{2/3}}{9\beta T m^2} \qquad (20)$$

where D is the scaling extrapolation length, defined by $[(1/\phi)(d\phi/dz)]_s = -1/D$, and f_{so} is the saturated surface value of f. Solving eq 20 results in the standard scaling law[2] $\phi \sim z^{-4/3}$ for the saturated volume fraction profile at a single surface. The equilibrium surface coverage, given by $\Gamma_0 = (1/a^3)\int_0^\infty \phi \, dz$, is then found to be

$$\Gamma_0 = \frac{4D\phi_{so}}{a^3} \text{ where } \phi_{so} = \left(\frac{3m}{8D}\right)^{4/3} \qquad (21)$$

As in the mean-field calculation, Γ_0 and ϕ_{so} are unique functions of the extrapolation length D.

3.2. DRE Scaling Model. We now consider two planar surfaces a distance $2h$ apart and minimize the free energy γ subject to our assumption of doubly restricted equilibrium. Again we implement the constraint of fixed surface coverage by introducing a Lagrange multiplier λ and minimizing $\gamma - \gamma_0 - \lambda\Gamma_0$. For each surface

$$\bar{\gamma} = \gamma - \gamma_0 - \lambda\Gamma_0 = -\gamma_1 f_s^{8/3} + \frac{\beta T}{a^3}\int_0^h \left[\left(m\frac{df}{dz}\right)^2 + f^6 - \lambda' f^{8/3}\right] dz \qquad (22)$$

where $\lambda = \beta T\lambda'$. Minimizing $\bar{\gamma}$ with respect to changes in the profile and holding f_{so} fixed yields

$$\left(m\frac{df}{dz}\right)^2 = (f^6 - f_m{}^6) - \lambda'(f^{8/3} - f_m{}^{8/3}) \qquad (23)$$

with the boundary condition $f(0) = f_{so}$ and where f_m is the value of f at the midpoint between the surfaces.

As before, it is convenient to introduce a reduced variable y such that $y = (f/f_m)^{2/3}$ and measure all lengths in units of the scaling extrapolation length D, e.g., $z = D\tilde{z}$. Equation 23 now becomes

$$\left(\frac{dy}{d\tilde{z}}\right)^2 = \frac{1}{16 y y_{so}{}^6}[(y^9 - 1) - \mu(y^4 - 1)] \qquad (24)$$

with the boundary condition $y(0) = y_{so}$ and where μ is a reduced pseudochemical potential given by $\mu = \lambda' f_m{}^{-10/3}$. From eq 24 the reduced profile $y(\tilde{z})$ has the implicit form

$$\tilde{z} = 4y_{so}{}^3\int_{y(\tilde{z})}^{y_{so}} \frac{y^{1/2}}{[y^9 - 1 - \mu(y^4 - 1)]^{1/2}}\, dy \qquad (25)$$

Again, as in mean field, the values of y_{so} and μ for given values of $\tilde{h}$ are determined using the relations

$$\tilde{h} = 4y_{so}{}^3\int_1^{y_{so}} \frac{y^{1/2}}{[y^9 - 1 - \mu(y^4 - 1)]^{1/2}}\, dy \qquad (26)$$

$$\frac{\Gamma}{\Gamma_0} = 1 = \frac{1}{y_{so}}\int_1^{y_{so}} \frac{y^{9/2}}{[y^9 - 1 - \mu(y^4 - 1)]^{1/2}}\, dy \qquad (27)$$

3.3. Disjoining Pressure. Substituting the results from eqs 26 and 27 into eq 25 enables the volume fraction profile $\phi(\tilde{z}) = \phi_m y^4(\tilde{z})$ to be calculated. Finally, the disjoining pressure between the two planar surfaces is given by

$$\Pi_d = -\left.\frac{\partial\bar{\gamma}}{\partial h}\right|_{\mu,\phi_{so}} = \Pi_d^*\left[\frac{\mu-1}{{y_{so}}^9}\right] \tag{28}$$

where $\Pi_d^* = \beta T {\phi_{so}}^{9/4}/a^3$. As with the mean-field approach, analytic results can be given only in the limits of large and small intersurface separations.

3.3.a. Large Separations: $\tilde{h} \to \infty$. As before, we expect that the constraint of fixed surface concentration will have little effect and that the pseudochemical potential will tend to the RE value, as $y_{so} \to \infty$. It was shown by de Gennes[3] that in this large $\tilde{h}$ limit the RE value is $\mu \simeq 2.2$. Regarding μ as a constant (greater than unity) results in the integral of eq 26 being also a constant; hence y_{so}, to lowest order, must scale as

$$y_{so} \sim \tilde{h}^{1/3} \tag{29a}$$

Substitution into eq 28, regarding $\mu - 1$ as independent of $\tilde{h}$, gives

$$\Pi_d \sim \frac{\Pi_d^*}{\tilde{h}^3} \tag{29b}$$

The result is, as would be expected to lowest order in $1/\tilde{h}$, the same as that of the RE result.[3] [Note that the analogous argument does *not* apply in mean field due to the fortuitous cancellation, in that case, of the leading (RE) term in the force law.]

3.3.b. Small Separations: $\tilde{h} \to 0$. In this limit, $y_s \to 0$ and $\mu \to \infty$. A suitable expansion in terms of y and y_{so}, assuming $\mu \gg 1$ (see section 2.4.b), simplifies eq 26 and 27, giving

$$y_{so} \sim \tilde{h}^{1/4} \qquad \mu \sim \tilde{h}^{-1/2} \tag{30a}$$

The resulting disjoining pressure is thus

$$\Pi_d \sim \frac{\Pi_d^*}{\tilde{h}^{11/4}} \tag{30b}$$

This contrasts with the RE value of $\Pi_d \sim \Pi_d^*/\tilde{h}^{9/4}$.[3] It should be noted that, despite the DRE system under high compression behaving like trapped nonadsorbing or end-attached polymer (see section 2.4.b), the result of eq 30b does not exactly coincide with scaling "blob" arguments, which give $\Pi_d \sim h^{-8/3}$.[1] The discrepancy is however not surprising and arises from the free energy functional (eq 18) not accurately describing the DRE system for $h \ll D$. The gradient and osmotic term in the functional expression are constructed by considering the stretching and excluded-volume interaction energy of correlation blobs,[3] where the local correlation length is given by the three-dimensional value $\xi = a\phi^{-3/4}$.[1] The functional is then valid providing the correlation blob size is always smaller than the intersurface separation, which is the case for the high-compression limit of the RE model where the scaling functional and scaling blob arguments are in agreement.[3] In contrast, in the DRE system (under high compression) the size of the correlation blobs are governed not by the single three-dimensional correlation length but now by two length scales: the intersurface separation and a two-dimensional correlation length in the plane of the surfaces. The stretching and osmotic energies of this two-dimensional correlation blob are not accurately described by the terms in the de Gennes functional (eq 18). It may be possible to amend the functional to describe the DRE system under these high compressions, but since we are mainly interested in the limit $h \geq D$ (see section 4), we use the standard functional and discuss the discrepancy no further.

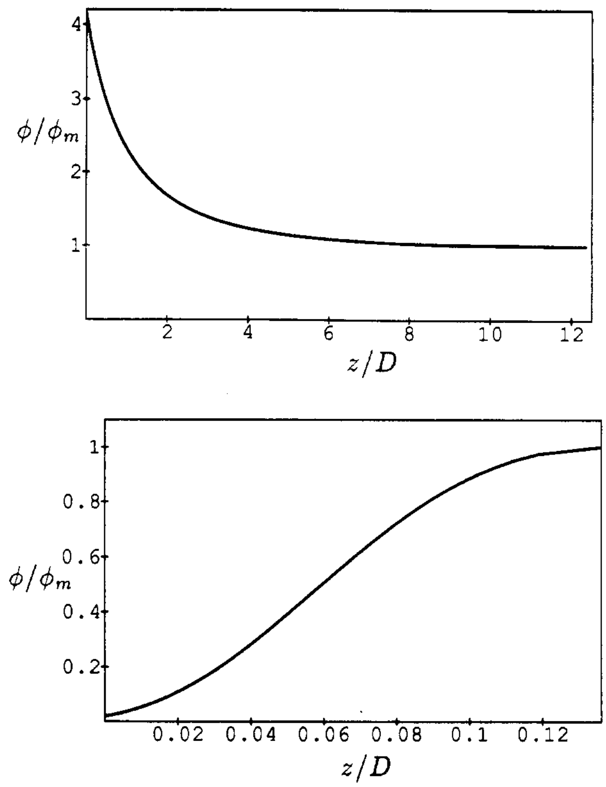

Figure 3. Normalized volume fraction profiles ϕ/ϕ_m for DRE, calculated using scaling theory: (a, top) for an intersurface separation distance of $2h/D = 24.8$; (b, bottom) for an intersurface separation distance of $2h/D = 0.28$.

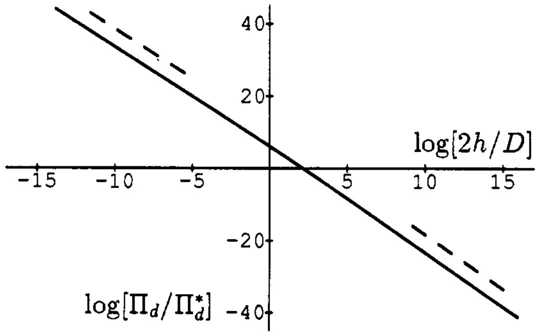

Figure 4. Variation of disjoining pressure Π_d/Π_d^* with intersurface separation distance $2h/D$ for DRE, calculated using scaling theory (solid curve). Dashed curves are asymptotes for small and large intersurface separations.

3.3.c. General Case. The effects of DRE, within the scaling functional approach, is to give a repulsive force at all surface separations, the pressure varying like $1/\tilde{h}^3$ for large surface separations and $1/\tilde{h}^{11/4}$ for small separations.

As in the mean-field case, numerical calculations were performed for general values of $\tilde{h}$. Two numerically calculated volume fraction profiles are shown in parts a and b of Figure 3 for $\tilde{h} = 12.4$ and 0.14, respectively. The numerically calculated disjoining pressure as a function of the intersurface separation distance $2\tilde{h}$ is shown in Figure 4, along with the analytic asymptotes.

It is useful, in the scaling approach, to make a direct comparison between the disjoining pressure calculated in the RE and DRE models, since in section 4 we wish to consider the relative effects of the two types of equilibrium upon a sterically stabilized colloidal dispersion. We have therefore recalculated de Gennes' data for the RE

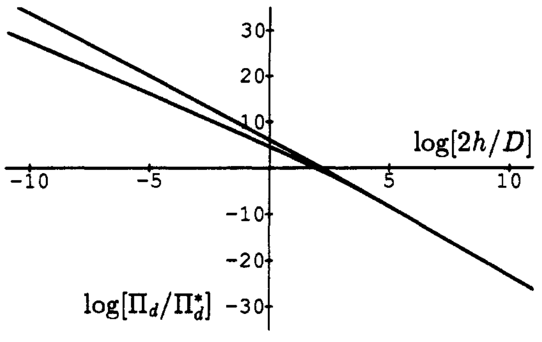

Figure 5. Disjoining pressure Π_d/Π_d^* for DRE (upper curve) and RE (lower curve) models, calculated using scaling theory.

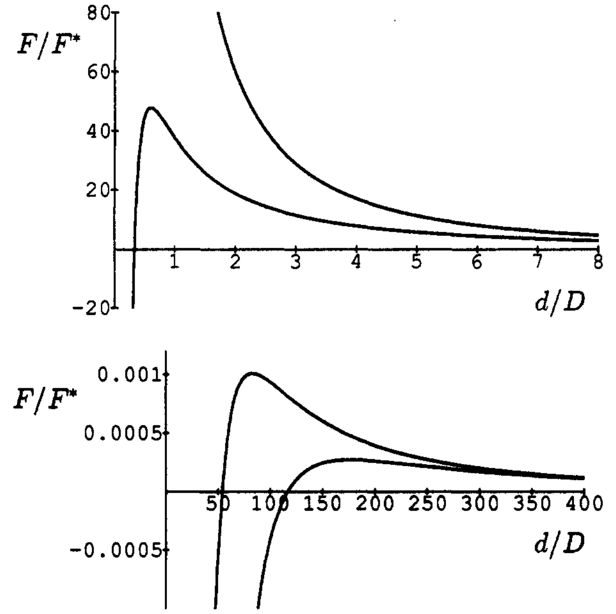

Figure 6. Variation of interparticle force F/F^* with interparticle distance d/D for sterically stabilized particles, calculated using scaling theory: (a, top) for a reduced Hamaker constant of $\sigma = 35$; (b, bottom) for a reduced Hamaker constant of $\sigma = 400$. The upper curve is for the polymer subject to DRE and the lower curve for RE.

model. For a given $\tilde{h}$ one must now find y_s, the value of y on the surface (which can now vary subject to the boundary condition of eq 20), and μ. The relations for y_s and μ can be written in convenient form as[3]

$$\tilde{h} = 4y_s^3\Delta^{3/2}(y_s)\int_1^{y_s} y^{-4}\Delta^{-1}(y)\,\mathrm{d}y \qquad (31a)$$

$$y_s\Delta^{1/2}(y_s) = \int_1^{y_s}\Delta^{-1}(y)\,\mathrm{d}y \qquad (31b)$$

where $\Delta(y) = y^{-9/2}[y^9 - 1 - \mu(y^4 - 1)]^{1/2}$. The disjoining pressure is then given by

$$\Pi_d = \Pi_d^*\left[\frac{\mu - 1}{y_s^9\Delta^{9/2}(y_s)}\right] \qquad (32)$$

As in the DRE model we have calculated the disjoining pressure numerically, and Figure 5 shows the pressure as a function of the intersurface separation distance $2\tilde{h}$ for both the RE and DRE models. The increase in the pressure using DRE, in comparison with RE, is dramatic for small values of $2\tilde{h}$, while at large $2\tilde{h}$ the two pressure curves almost coincide. For these large values of $2\tilde{h}$ the DRE pressure is only slightly greater than that of the RE model but, as will be seen in section 4, this can still have a marked effect on the interparticle force between colloidal particles.

4. Colloidal Stability

Colloidal dispersions with attractive van der Waals are often protected against aggregation by steric stabilization with adsorbed polymer, the stability being readily understood in terms of the restricted equilibrium model.[12,16] The resulting interparticle potential is the sum of the attractive van der Waals and a repulsive polymer contribution (the shape of the potential is very similar to that of the DLVO theory); at very small particle separations there exists a deep negative primary minimum and at an intermediate separation there is a positive primary maximum, while at larger separations (depending on whether the surface coverage is below saturation or the solvent is bad) there is a negative secondary minimum.[12] In balancing steric and van der Waals forces within a scaling or mean-field approach, it is found that the latter always dominate at short enough distances giving a deep primary minimum. In what follows we are interested in the barrier preventing flocculation, which in this language is the primary maximum. However, it should be borne in mind that neither the mean-field nor the scaling model gives reliable predictions at extremely high compressions (where the polymer segment density is high); if one takes into account the much stronger steric forces that can arise at high segment densities, the primary minimum may entirely disappear and the colloidal could become absolutely stable. We ignore this complication in the following discussion.

Suppose we have a dispersion of spherical particles coated with a saturated polymer layer, having a slow surface contact equilibration time (for example a copolymer layer as discussed in the Introduction). If the particles are undergoing ordinary Brownian motion, then the interparticle potential (potential of mean force) is precisely as determined by equilibrium thermodynamics, subject to the usual proviso of the RE model, namely a fixed coverage on each particle. We therefore do not expect our results for the DRE model to be relevant in the Brownian flocculation regime. On the other hand, it is known that some sterically stabilized dispersion can be made unstable by shearing, and even in gentle shear, particles experience a local Stokes force greatly in excess of thermal forces. For sufficiently high shear rates, where a collision between particles is rapid compared to the surface contact equilibration time, we might expect the DRE model to be relevant in describing the polymeric contribution to the interparticle force.

We therefore calculate in the DRE model the force between two spherical particles with a van der Waals attraction that are sterically stabilized. [We choose to work with the interparticle force, instead of the potential, since this has more relevance in determining the stability under shear.[12]] As usual, the results for flat surface geometry can be converted to curved surfaces via the Derjaguin approximation, in which the interparticle force is given by[10]

$$F(d) = -\frac{AR}{12d^2} + \pi R W(d) \qquad (33)$$

where the first term represents the van der Waals attraction (the nonretarded, additive form being used for simplicity), A is the Hamaker constant, R is the colloidal particle radius, and d is the separation distance between particles. The second term is the polymer contribution, $W(d)$ being the energy of interaction per unit area for the two planar surfaces a distance d apart, which is simply the integral of the disjoining pressure:

$$W(d) = \int_d^{\infty} \Pi_d(d')\, d(d') \qquad (34)$$

It should be noted that eq 33 is strictly valid only for $R \gg d$ due to the use of the Derjaguin approximation.

To proceed further, we use the results of the scaling theory of section 3 to calculate $W(d)$, and hence $F(d)$, for both the RE and DRE models. [The use of scaling theory is justified if the layers are not in strong compression, this being true near the primary maxima of the force curves if these occur at distances $d > D$.] Equation 33 can be reexpressed in terms of the reduced length $\tilde{d} = d/D$ and a dimensionless quantity $\tilde{W}(\tilde{d})$ where

$$W(\tilde{d}) = \frac{\beta T {\phi_{\rm so}}^{9/4} D}{a^3} \tilde{W}(\tilde{d}) \equiv \left(\frac{m_0}{a}\right)^3 \frac{\beta T}{D^2} \tilde{W}(\tilde{d}) \qquad (35)$$

This enables $F(\tilde{d})$ to be written as

$$F(\tilde{d}) = F^* \left[-\frac{\sigma}{\tilde{d}^2} + \tilde{W}(\tilde{d}) \right] \qquad (36)$$

where $F^* = \pi R (m_0/a)^3 \beta T / D^2$ and σ is a reduced Hamaker constant, depending upon the bare Hamaker constant A, temperature T, and the polymer constants m_0/a and β, according to

$$\sigma = \frac{A}{12\pi\beta T}\left(\frac{a}{m_0}\right)^3 \qquad (37)$$

Equation 36 is interesting; for each value of σ there is only one master curve which can be scaled to correspond to any chosen values of D and R. This is a result of the scaling theory, in which the polymeric interaction energy varies as $1/D^2$ which enables the steric force to be written as a unique function of $\tilde{d}$. [As mentioned above, this is really only applicable for $d > D$, with nonscaling osmotic forces coming into play at smaller separations; no master curve exists in this high-compression regime.] Moreover, it is possible to determine the value of the universal constant $12\pi\beta(m_0/a)^3$ appearing in the expression for the reduced Hamaker constant (eq 37) from theoretical and experimental work on semidilute solutions;[3,17] the best theoretical estimate is 0.57, while the value determined from experimental measurements is 0.91. We choose to work with the former for definiteness.

From the numerical results of section 3 we have calculated $\tilde{W}(\tilde{d})$, using eq 34, for both the RE and DRE models. Figure 6a shows the interparticle force curves, as given by eq 36, for the two cases, with $\sigma = 35$ which implies a value for the Hamaker constant of $A \simeq 20T$. In this case, the effect of DRE is to dramatically increase the height of the primary maximum in comparison to the RE case (the attractive part of the DRE force curve lies very close to $d/D = 0$ and is thus imperceptible in Figure 6a). Figure 6b shows the interparticle force curves for an increased value of the reduced Hamaker constant, $\sigma = 400$ ($A \simeq 220T$). This is a somewhat unphysical value for the Hamaker constant, but as would be expected the very much increased van der Waals attraction shifts the polymer dominated part of the curve to large values of $\tilde{d}$, where, as calculated in section 3, the interaction energy of the two models tends to coincide. Conversely, for $\sigma < 35$ the difference between the RE and DRE force curves becomes even more pronounced, though as already stated neither mean-field nor the scaling model gives reliable predictions at these extremely high compressions.

As discussed above, for a dispersion undergoing shear, a rough criterion for stability is given by balancing the maximum viscous force with the maximum interparticle force.[12] We therefore expect that if, for a high enough shear rate, the polymer layer becomes governed by the DRE model, a noticeable increase in the stability of the dispersion to shear will arise.[11] Much higher shear rates would be necessary to flocculate the dispersion than would be predicted using the normal RE model. In some cases, it is possible that when nonscaling contributions to the steric force (at small separations) are taken into account, a primary minimum that is present in the RE model (appropriate to Brownian conditions) could entirely disappear in the DRE case (appropriate under shear). This is likely whenever the primary minimum in the DRE case is shifted from a relatively large separation to one that is small compared to the extrapolation length D.

5. Conclusions

The CdG framework has provided some interesting results for the effects of constraining surface contact density on the interactions of adsorbed polymer layers. The use of mean-field and scaling theory enabled us to calculate the variation of the disjoining pressure with intersurface separation distance for adsorbed layers on two planar surfaces, using a simple model of "doubly restricted equilibrium". Although it is dangerous to draw very general conclusions from such a simple model, it does appear that nonequilibrium polymer forces, as exemplified by the DRE model, could play a major role in the behavior of sterically stabilized colloids under high shear. Recent experimental work by Chang et al.[18] has considered the effects of shear on the stability of latex dispersions stabilized with adsorbed homopolymer. Adopting similar techniques for adsorbing copolymer might enable the existence of any DRE regime to be probed. Although the DRE model also gives predictions for the variation of the disjoining pressure with intersurface separation, it seems unlikely that standard force-balance experimental methods could be used to verify these results, unless a polymer could be found with extremely long-lived surface contacts compared even to those expected in a copolymer. (Such experiments take minutes or hours to perform.) However, there is some evidence for "relaxation" or nonequilibrium force effects in the experiments of Klein and Luckham.[9]

All our results for the DRE model were calculated assuming that the adsorbing surfaces were at saturated coverage and that the solvent was good. Both of these assumptions could be relaxed in principle. Rossi and Pincus[7] and Klein et al.[6] have considered the effects of low coverage and poor solvent, respectively, for the restricted equilibrium case, both finding an attractive force replacing the good solvent/saturated repulsion at large distances. It seems clear that the effect of poor solvents and low coverages would be a reduction in the long-range repulsions found in the present work.

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