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Forces between Surfaces with Weakly End-Adsorbed Polymers

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Abstract. — We study the interaction forces between two plates in a semi-dilute solution of polymers each having one weakly adsorbing end-group. We show that this system exhibits both repulsive and attractive interactions of comparable magnitude and well-separated length scales: when the plate separation is within a range of order the end-to-end distance of the end-adsorbed polymer, repulsion arises with a magnitude of $\epsilon/N_\Phi a^2$ where $\epsilon$ is the end-adsorption energy, $N$ is the degree of polymerization, $a$ is the Kuhn length and $\Phi$ the volume fraction of the polymer. This repulsion is due to desorption of the end-adsorbed chains. At plate separations of order the correlation length of the solution, a depletion attraction sets in with a magnitude that scales with the bulk osmotic pressure.

1. Introduction

The importance of polymeric additives in mediating the interactions between colloidal particles has been understood longer even than has the basic nature of polymers themselves (for instance in the stabilization of ink by addition of polymers) [1]. The action of the polymers depends upon their physical properties and concentration. The contribution of a polymeric additive to interparticle interactions (and hence to colloidal stability) ranges from purely attractive (destabilizing) — for flexible non-adsorbing homopolymers — to repulsive (stabilizing) — for irreversibly adsorbed polymers. In the first case the non-adsorbing chains are depleted near a colloid surface due to configurational entropy loss. This gives rise to an attractive interaction between the particles in which the osmotic pressure of the bulk compresses the gap in order to minimize the free energy cost of the depleted volume [2]. In fact, de Gennes [3] has shown that even the restriction to nonadsorbing chains is unnecessary to establish the sign of the

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interactions between two surfaces: for weakly adsorbing homopolymer chains it can be shown that the interaction is always attractive for systems in full equilibrium with the bulk (an exception to this is discussed later [4]).

Irreversibly end-grafted polymers on the other hand form a hairy shell or corona around the particles which repel similarly coated particles by steric interactions [5]. This is not inconsistent with de Gennes's theorem because irreversibly grafted chains are by definition not in equilibrium with the bulk. In this paper we will show that end-adsorbed chains with finite adsorption energy \( \epsilon \) produce repulsive interactions even in full equilibrium with the bulk [6]. This repulsion can be understood as arising from the loss of adsorption energy when adsorbed chains are squeezed out of the gap. This is a subtle point however, because uniformly adsorbing chains are likewise squeezed out of the gap, yet this leads to attraction rather than repulsion. The end-adsorbed chains are fundamentally different, however, in that they can adopt a preferred orientation with the functional group adsorbed at the wall.

By virtue of their orientation, end-adsorbed chains are distinct from the other chains in the system. The adsorbed chains are distinguished in this respect over their whole length \( R \) (the end-to-end distance), even in a semidilute solution where the chain segments are generally indistinguishable on size scales larger than the correlation length \( \xi \) (also called the mesh size, which is the length scale beyond which intra-chain and inter-chain correlations are no longer distinguishable and is less than \( R \) for semi-dilute solutions [7]). When two such adsorbed layers on opposing walls begin to overlap they will interact. The appropriate length scale for the interaction is thus the end-to-end distance of the adsorbed chain. The resulting repulsive interaction is in contrast with the attraction induced by chains which adsorb uniformly along their whole contour. The sign of the interaction is thus a consequence of the orientation of the chains and is perhaps most clearly understood by analogy with more familiar orientable systems such as magnetic fluids [8]. Magnetic particles can orient their magnetization at a wall. Two such walls will repel one another because of the frustration when the two opposite magnetizations meet in the midplane region, while ordinary surface adsorption of binary liquid mixtures always produces attraction between plates. Similarly, end adsorbed polymers will exhibit an orientation towards the surface, which will induce a repulsion between two such surfaces. This orientation arises from end-adsorption and not from the asymmetry of the molecule. In fact telechelic or randomly functionalized chains can also be oriented this way, and will induce analogous repulsive interactions under certain circumstances. We will have more to say about other chain architectures in the conclusions, but for the sake of clarity will focus primarily on singly end-functionalized chains in the rest of the paper.

The magnitude of the end-adsorption energy \( \epsilon \) will determine which interactions and length scales will be important. For very large \( \epsilon \) the configuration of the system will adjust itself to maximize the number of chain ends attached to the surface. In dense solutions or melts where the polymer density near the wall cannot be significantly increased, the chains are forced to stretch normal to the surface to allow more ends to attach. In more dilute systems this stretching is accompanied by a dramatic increase in the polymer density near the surface. The interactions induced by strongly adsorbing (large \( \epsilon \)) chains will be described briefly at the conclusion of this paper, but our primary focus in this work is weakly end-adsorbing chains.

In the limit of weak end-adsorption (small \( \epsilon \)) in a semi-dilute solution, the overall segment density distribution is not significantly altered by adsorbing end-groups, since these account for only a small portion \((\frac{1}{N})\) of the overall segment density. In this limit the overall segment density will still be depleted within a correlation length \( \xi \) of the wall, and this depletion will give rise to a depletion attraction between the surfaces exactly as in the limit of zero \( \epsilon \). The range of this depletion attraction is \( \xi \). This depletion attraction operates simultaneously with the above mentioned desorption repulsion, but with different ranges. If \( \xi \) is small compared
to $R$ the short range attraction and the long range repulsion will not locally cancel. This separation assures us that there is no threshold value of $\epsilon$ for the repulsive interaction, because any end adsorption will orient some chains, and this causes repulsion at length scale $R$. Thus, in the semi-dilute regime, where $a \ll \xi \ll R$ ($a$ is the Kuhn length), the interaction potential has both a long range ($R$) desorption repulsion and a shorter range ($\xi$) attraction, reminiscent of the DLVO interaction profile, where desorption and depletion are replaced by a long range electrostatic repulsion and a short range van der Waals attraction [9]. Colloids with weakly end-adsorbed polymers thus should show a rich phase behavior, including a transition from flocculation to stabilization as a function of the volume fraction of polymer $\Phi$ and $\epsilon$. Polymers with weak end-adsorption are currently under examination in atomic force studies of polymer surfaces [10].

In this short paper we will approach this problem through three complementary methods. In the next section we construct a phenomenological picture in the small $\epsilon$ regime. By assuming that the overall segment density profile is not significantly altered upon introduction of a moderate adsorption energy at one chain end, a schematic segment density profile for adsorbed and nonadsorbed chains can be constructed. This profile leads to a scaling prediction for the different interaction regimes between two plates and for the relevant length scales for the interaction. The most important omission of the phenomenological treatment is the coupling of the overall segment density near the wall with the adsorption energy $\epsilon$, which will cause some increase in the segment density near the wall in order to increase the number of adsorbed chain ends. This omission is corrected in Section 3 by a more careful thermodynamic treatment of the interaction in the regime $\xi \ll h \ll R$ for moderate $\epsilon$. In that section we also comment upon the factors which limit the application of de Gennes theorem regarding the attractive interplate interactions in the presence of uniformly adsorbing polymers in full equilibrium with the bulk. The thermodynamic analysis confirms the scaling prediction of the phenomenological treatment for the repulsive interaction in that regime. Confirmation of the other features of the phenomenological picture is given by a detailed numerical self-consistent field treatment described in Section 4. We take advantage of the broad range of parameters available to this calculation technique to make a connection between the weakly adsorbed chain limit examined in this paper, and earlier results obtained for larger adsorption energies [11]. Finally, in the last section some rules of thumb are described for determining whether attractive, repulsive, or "DLVO type" interactions are to be expected under a given set of experimental conditions.

2. Phenomenological Description

We consider a semi-dilute solution of polymers of degree of polymerization $N$, with Kuhn length $a$, in a good (athermal) solvent. The volume fraction of polymer is $\Phi$. The chains have a weak end-adsorption energy $\epsilon$, but no other segmental attraction to the surface. For simplicity, we assume that end-groups do not interact significantly with other segments or with one another, that is, we exclude the formation of micelles. For the purpose of simplicity we address the regime in which the adsorption energy $\epsilon$ is not sufficient to cause a significant local excess of monomer density near the surface and can be treated as a small perturbation to the case of nonadsorbing homopolymers near a hard wall; thus we limit our consideration in this section to cases where $\epsilon$ is just a few $kT$.

Chains with a weakly adsorbing head group will orient themselves so that chains near the surface will have their end-group attached to the wall. This adsorption should be essentially complete near the surface provided that $\epsilon$ is more than a few $kT$, but will die off gradually for chains farther from the surface with a characteristic length scale of the chain size $R \sim N^{\frac{1}{3}} a \Phi^{-\frac{1}{3}}$ [7]. The upper bound to the weak adsorption regime is defined such that there
Fig. 1. — Schematic segment density profile $\Phi(z)$ for weakly end-adsorbed chains as a function of the distance $z$ from the surface. The solid line is for chains with adsorbed end groups and the dashed line is for non-adsorbed chains.

is no significant anisotropic stretching nor any significant increase in segment density near the surface. For larger $\epsilon$, a large increase in adsorption density leads to stretching normal to the surface which is characteristic of the so-called brush regime. In the brush regime the chains stretch to a length $D$ which scales with $N \epsilon \sigma^{-\frac{3}{8}}$ where $\sigma$ is the dimensionless grafting density and is found by balancing chain stretching with adsorption energy [5,12]. However in the present work we concern ourselves with weak adsorption for which $R$ and $D$ are comparable.

In the weak end-adsorption regime, the concentration of polymer segments is depleted within one correlation length $\xi \sim \frac{a \Phi^{\frac{3}{8}}}{\epsilon}$ of the wall due to the restriction of chain configurations by the wall [7]. Scaling predictions of the profile and interfacial free energy for noninteracting or repulsive polymer chains have been worked out by de Gennes for segment-wall interaction ranging from weakly attractive to repulsive [13]. For a noninteracting wall the free energy of the interface is simply the work done against osmotic pressure II to remove the solute to a distance $\xi$ from the wall.

A schematic representation of the main features of the segment density profile is shown in Figure 1. Numerically obtained profiles are readily calculated using the detailed self-consistent field method discussed in Section 4 below, and are qualitatively consistent with the figure over a broad range of semidilute concentrations and chain lengths. The segment density of adsorbed chains is indicated with a solid line and nonadsorbed chain segment density with a dashed line. The chain density of adsorbed chains becomes significant in the region less than one end-to-end distance $R$ away from the wall. Also there is a depletion of the segment density within a distance $\xi$ from the wall due to the decrease in configurational entropy.

We now consider the interaction between two surfaces of the type described above. Because the system has mirror symmetry it is convenient to describe the plate separation by $h$, the distance between the hard wall and the plane of symmetry. Thus the actual plate separation is $2h$. When the plate separation is many times the chain size $R$ there is no interaction. For half-plate-separation $R > h > \xi$, the proximity leads to the desorption of some chains in order to prevent the chain overlap from causing an increase in chain density (which would cause an increase in the excluded volume interactions). The adsorption energy per unit area is simply the number of adsorbed chains per unit area times $\epsilon$, and can be expressed in terms of the segment density profile of adsorbed chains $\frac{\epsilon \Phi}{N \sigma^3} \int \Phi(z)dz$. For the sample profile in Figure 1 we obtain a force per unit area which is repulsive and is of magnitude $\epsilon \frac{\Phi}{N \sigma^3}$. 

\[
\Phi(z)
\]

\[
\Phi_b
\]

$\xi$, $R$

$z$
Fig. 2. — Schematic force per unit area $\Pi_d$ versus $h$, the half gap separation.

For half-plate separation of less than the correlation length $h < \xi$, the depletion attraction becomes important. Because the chain segment density is depleted near the wall, the bulk solution exerts an osmotic pressure on the depleted region. If the concentration between the plates is depleted, the osmotic pressure leads to an attraction between them. The magnitude of the attractive interaction is given by the osmotic pressure of the bulk solution $\Pi$, although it varies with the extent of depletion.

When the free energy of a single chain between the plates — which consists of the end adsorption energy $\epsilon$ and the cost of confinement between two plates separated by $2h$ — exceeds the bulk chemical potential, $\mu$, of the semidilute solution,

$$- \epsilon + kTN \left( \frac{a}{2h} \right)^{\frac{3}{2}} > \mu \sim kT \frac{N_0^3}{\xi^3} \Phi,$$

the chains will rapidly leave the gap [7]. Thus there will be some threshold spacing $h_c$ at which the interplate chain density becomes vanishingly small (because the polymer concentration in the gap is very low, it is appropriate to use the single chain expression for the confinement cost). Upon using $\xi \sim a \Phi^{-3/4}$, the condition equation (1) becomes

$$2h < \xi \left[ 1 + \frac{\epsilon}{kTN} \left( \frac{\xi}{a} \right)^{\frac{3}{2}} \right] \equiv 2h_c.$$

For $h < h_c$, the concentration between the plates becomes vanishingly small and the interaction is simply the bulk osmotic pressure. The length $h_c$ is not a new length scale in the problem, but rather the half-plate separation at which the monomer concentration is completely depleted, a process that began at $h \sim \xi$. Indeed, when $\epsilon = 0$, the threshold separation for all chains leaving the gap $h_c$, is simply $\frac{1}{2} \xi$ from equation (2). The attractive contribution to the interaction begins when the depletion regimes on both surfaces overlap, at plate separation approximately twice the correlation length. Total chain exclusion, on the other hand, arises when the confinement of a single chain between the plates becomes unfavorable, in the limit of small $\epsilon$ this happens at plate separation approximately one correlation length. Thus, the one half prefactor is retained because it arises naturally from the phenomenological picture, as two adsorbed layers give way to one, but should not be taken to indicate that this prediction is correct to a numerical factor.

From this phenomenological description a schematic force profile can be constructed, as is shown in Figure 2. The profile has three principal features. At a distance of $h \sim R$ a repulsive interaction begins with a characteristic magnitude of $\epsilon \Phi_{N_0}$. At $h \sim \xi$ the depletion in polymer...
density decreases the repulsive contribution of the polymer chains and introduces an attractive osmotic term. The attraction grows as \( h \) decreases until, at \( h = h_c \) all of the polymer has left the gap and the interaction is simply the osmotic pressure \( II \).

3. Thermodynamic Analysis for \( \xi \ll h \ll R \)

The prediction of a repulsive interaction between two plates, even in full equilibrium, is unusual and it is appropriate to give it a more careful thermodynamic treatment. We are interested in the disjoining pressure between two plates at separation \( 2h \) where \( \xi \ll h \ll R \) and the solution is in the semidilute regime.

We assume that the segment density \( \Phi \) between the plates is uniform although not necessarily the same as the bulk segment density \( \Phi_b \), and is in the semidilute regime \( \Phi^* \ll \Phi \ll 1 \), where \( \Phi^* \) is the overlap volume fraction (which depends on \( N \) as \( N^{-\frac{3}{2}} \)) \[7\]. The entropic depletion in monomer density at distances less than \( \xi \) from the wall will be described as a surface term. For \( \epsilon > kT \), essentially all of the adsorbing ends should be adsorbed if \( h \ll R \). Under these assumptions, the excess grand potential per unit area is

\[
\Delta \tilde{\omega} = c_1 \frac{kT}{\xi^2} + h \left[ f(\Phi) - \mu_b \Phi \frac{\Phi}{a^3} + \Pi_b \right] - \frac{h}{a^3} \frac{\epsilon}{N} \Phi
\]  

(3)

where \( f(\Phi) \) is the Helmholtz free energy per unit volume of a semi-dilute solution of volume fraction \( \Phi \) given by

\[
f(\Phi) \sim \frac{c_2kT}{a^3} \Phi^\frac{5}{2}
\]

(4)

and \( c_1 \) and \( c_2 \) are numerical constants of order unity. The first term is the cost of the depletion at the surface, the next three represent the contribution to \( \Delta \tilde{\omega} \) from the interior of the gap, and the last term is the adsorption energy. Taking \( \xi = a\Phi^{\frac{3}{4}} \) for the correlation length inside the plates, the grand potential can be expressed entirely in terms of \( \Phi \) and is minimized with respect to \( \Phi \) to yield the relation

\[
\frac{9}{4} c_2 kT \Phi^\frac{5}{4} \left( 1 + \frac{2}{3} \frac{c_1 \xi}{c_2 h} \right) = \mu_b + \frac{\epsilon}{N}
\]

(5)

where

\[
\mu_b \equiv a^3 \frac{\partial f}{\partial \Phi} \bigg|_{\Phi=\Phi_b} = \frac{9}{4} c_2 kT \Phi^\frac{5}{4}
\]

(6)

is the chemical potential per monomer. Finally, the osmotic pressure \( \Pi_b \) of the bulk semi-dilute solution is

\[
\Pi_b \equiv \Phi^2 \frac{\partial (f/\Phi)}{\partial \Phi} \bigg|_{\Phi=\Phi_b} = \frac{5}{4} c_2 kT \Phi^\frac{5}{4}
\]

\[
= \frac{5}{9} \frac{\mu_b \Phi_b}{a^3}.
\]

(7)

In the limit \( h \gg \xi \), equation (5) gives

\[
\frac{9}{4} c_2 kT \Phi^\frac{5}{4} \approx \mu_b + \frac{\epsilon}{N}.
\]

(8)

Substituting in the calculated expression for \( \mu_b \) from equation (6) leads to a monomer density \( \Phi \) between the plates which is always greater than or equal to the reservoir segment density:

\[
\Phi^\frac{5}{4} = \Phi^\frac{5}{4}_b + \frac{4}{9c_2kT} \frac{\epsilon}{N} = \Phi^\frac{5}{4}_b \left( 1 + \frac{\epsilon}{\mu_b N} \right)
\]

(9)
Inserting equation (8) in equation (3) we obtain an expression for the disjoining pressure $\Pi_d$, which is the negative derivative of $\Delta\bar{w}$ with respect to $h$,

$$
\Pi_d = -\frac{d\Delta\bar{w}}{dh} = -\frac{\partial\Delta\bar{w}}{\partial h} = \frac{1}{a^3} \left( -c_2 kT\Phi^\frac{4}{3} + \mu_b\Phi - \Pi_b a^3 + \frac{\epsilon}{N} \Phi \right)
$$

(10)

which, using equation (8), leads to

$$
\Pi_d = \frac{1}{a^3} \left[ \frac{5}{9} N \Phi + \frac{5}{9} \mu_b \Phi - \Pi_b a^3 \right]
$$

(11)

where we have used equation (8).

Because $\Phi \geq \Phi_b$ it is clear that the disjoining pressure is repulsive ($\Pi_d \geq 0$). Moreover, when the bulk chemical potential (on a per segment basis) is far greater than the adsorption energy per segment

$$
\mu_b \left( = \frac{9}{4} kT\Phi^\frac{4}{3} \right) \gg \frac{\epsilon}{N}
$$

(12)

and therefore

$$
\frac{\epsilon}{\mu_b N} \ll 1,
$$

(13)

then the expression for $\Phi$ in equation (9) can be expanded about $\Phi_b$

$$
\Phi = \Phi_b \left( 1 + \frac{4}{5} \frac{\epsilon}{\mu_b N} + O \left[ \left( \frac{\epsilon}{\mu_b N} \right)^2 \right] \right).
$$

(14)

Substituting this into equation (11) we obtain, to leading order,

$$
\Pi_d \approx \frac{1}{a^3} \left[ \frac{5}{9} N \Phi + \frac{4}{9} \Phi_b \right] \approx \frac{1}{a^3} \frac{\epsilon}{N} \Phi_b
$$

(15)

which is the result predicted on the basis of the phenomenological model.

At first sight the prediction of a repulsive interaction between the plates appears to contradict the theorem of de Gennes. However, this is not the case. In his treatment, de Gennes assumes that the same functional form of the free energy density $f(\Phi)$ describes both the free energy within the gap and in the bulk, and the effect of polymer-wall interaction amounts to a boundary condition [3]. This, together with the concavity of $f(\Phi)$ immediately leads to $\Delta W > 0$ and $\Pi_d < 0$. In the case of end-adsorbed polymers however, the free energy density in the gap has a different form than the free energy density in the bulk, $f(\Phi) = -\frac{\epsilon}{N^2} \Phi + f_p(\Phi)$ where $f_p(\Phi)$ has the same functional form as the bulk. The difference in the functional form of the Helmholtz free energy density leads to the difference in interactions. In fact, a repulsive disjoining pressure can be shown to arise whenever there is a favorable energy contribution per particle in the gap.

4. Numerical Results

We now approach the problem with a detailed self-consistent field method, which gives us full configurational and thermodynamic information (at the mean-field level) for any adsorption energy $\epsilon$ and for polymer volume fractions $\Phi$ from the semi-dilute all the way up to the
melt. In this approach \[14,15\] the many-body problem is reduced to a one-body problem in a mean field which accounts for the effect of inter-chain and intra-chain interactions and polymer-solvent interactions. The one chain problem is solved exactly by enumerating all configurations on a lattice using a recursion relation. The field is obtained self-consistently by an incompressibility constraint which requires that the total chain and solvent volume fractions add up to unity. The Helmholtz free energy \( F \) is obtained from the partition function \( Q \)

\[
F = -kT \ln Q(n_p, n_s)
\]

where \( n_p \) and \( n_s \) are the number of polymers and solvent molecules in the system and the excess grand potential \( \Delta W \) is in turn obtained from the Helmholtz free energy \( F \). which, for an incompressible system, is given by

\[
\Delta W = F - n_p \mu_p - n_s \mu_s
\]

where \( \mu_p \) and \( \mu_s \) are the chemical potentials of the polymers and solvent molecules respectively. Because the system is incompressible, \( n_s a^3 + n_p N a^3 = V \) where we have set both the monomer volume and the solvent molecule volume equal to \( a^3 \). Substituting \( n_s = V/a^3 - n_p N \) into equation (17) we obtain

\[
\Delta W = F - n_p N \left( \frac{\mu_p}{N} - \mu_s \right) - V' a^3 \mu_s
\]

which can be expressed in the same form as equation (3) in Section 3:

\[
\Delta W = F - n_p N \mu_b + V \Pi_b
\]

where \( \mu_b \) is the exchange chemical potential per monomer of the polymer in the bulk

\[
\mu_b = \frac{\mu_p}{N} - \mu_s = a^3 \frac{\partial f_b}{\partial \Phi}
\]

and the osmotic pressure is related to the solvent chemical potential

\[
\Pi_b = -\frac{\mu_s}{a^3} = \Phi^2 \left( \frac{\partial f_b}{\partial \Phi} \right)
\]

and \( V f_b \equiv F_b \) is the Helmholtz free energy in the bulk. The force is simply the negative derivative of the grand potential with respect to \( h \).

\[
\text{force} = -\left. \frac{\partial \Delta W}{\partial h} \right|_{\mu_b, \Pi_b}
\]

Because of the mean-field nature of the calculation, results will scale with mean-field exponents. However, because this method enforces the incompressibility condition explicitly (as opposed to a second virial approach) it can consistently examine any value of \( \epsilon \) as well as a wide range of \( \Phi \) without any of the difficulties encountered in analytical treatments.

In Figure 3 the force profile is shown for a system of \( N = 2000 \), \( \Phi = 0.005 \) and \( \epsilon = 10 \). The osmotic pressure \( \Pi \), polymer size \( R \), correlation length \( \xi \) and total chain exclusion threshold \( h_c \) are shown, as is a scaling estimate of the magnitude of the repulsive force \( (h_c) \) was obtained from Eq. (2) using appropriate prefactors and mean-field exponents for consistency with the calculation). All of the features predicted by the phenomenological model are observed. Similar agreement with the schematic density and force profiles and more generally with the phenomenological description of the system is found for a large range of \( N \) and \( \Phi \) in
the semidilute regime. The preceding section demonstrated that \( \frac{\text{c}}{N_{\text{A}}^{1/3}} \Phi \) is the correct scaling for the repulsive interaction in the range \( \xi \ll h \ll R \), while for the attractive interactions the osmotic pressure \( \Pi_b \) gives the appropriate scale. In all cases, the depletion induced attraction obtained numerically indeed reaches a maximum magnitude of exactly the osmotic pressure \( \Pi_b \) while the repulsive force reaches a maximum of magnitude \( \epsilon \frac{c}{N_{\text{A}}^{1/3}} \). The numerical prefactor for the repulsive force is about 0.6 independent of \( \Phi \) in the range \( 0.005 \leq \Phi \leq 0.2 \) for \( \epsilon = 10 \) and \( N = 2000 \). For smaller \( \epsilon \) the assumption that all chain ends near the surface are adsorbed apparently breaks down and the numerical constant gets smaller and becomes dependent on \( \Phi \). For larger \( \epsilon \) chain stretching becomes important and the polymer brush picture is more appropriate [11].

5. Conclusions

In this paper we have shown that weakly end-adsorbed polymers induce complex interactions between interfaces which have implications for understanding the stability of colloidal suspensions. In contrast to homogeneously adsorbing chains — which, according to the theorem of Gennes, always induce attractive interactions between surfaces when they are in complete equilibrium [3] — end adsorbed chains induce repulsion at separations comparable to \( R \) and attraction at separations comparable to \( \xi \). The end-adsorption energy \( \epsilon \) plays a crucial role in the restoration of the length scale \( R \) by orienting the polymers near the wall. In fact, even a uniformly adsorbed chain will have some orientation of nonadsorbed chain ends or “tails,” and this has recently been shown by Semenov et al. to lead to a weak repulsive interaction for uniformly adsorbed polymers in full equilibrium [4]. This repulsion arises from considering the difference between the loops and tails, and is beyond the level of the theorem of de Gennes.

Let us review scaling estimates for the magnitude of the forces and length scales relevant to the problem. These estimates provide rules of thumb, with which the importance of the attractive and repulsive interactions can readily be gauged, and a conclusion can be reached as to whether the brush, non-adsorbing or crossover description is most appropriate in a particular system.

The interesting force profile described in this paper arises from the fact that two length scales are simultaneously active, \( \xi \sim a \Phi^{-\nu/(3\nu-1)} \sim a \Phi^{-\frac{1}{3}} \) and \( R \sim (N a^3 / \Phi \xi)^{1/2} \sim N^{1/2} a \Phi^{-\frac{1}{6}} \). This occurs only in semi-dilute solution and for relatively weak end-adsorption (given by the criterion equation (13). The magnitude of the depletion attraction in this regime is given by

\[
\epsilon \Phi / N_{\text{A}}^{1/3}
\]

Fig. 3. — Force per unit area \( \Pi_d \) versus \( h \), the half gap separation for \( N = 2000 \), \( \Phi = 0.005 \) and \( \epsilon = 10 \).
the bulk osmotic pressure of the system, $\Pi \sim kT\xi^{-3} \sim kT\Phi^{2/3}a^{-3}$ \cite{7} and the magnitude of the repulsive interaction is $\epsilon_{\frac{\Phi}{N_0a}}$.

Although the treatment in Sections 2 and 3 assumes weak end-adsorption in the semi-dilute regime, the prediction that the repulsive interaction scales as $\epsilon_{\frac{\Phi}{N_0a}}$ is more robust, and is not limited by these assumptions. In dense solutions or melts, the correlation length tends towards the segment length, which causes the attractive portion of the interaction profile to disappear. However, the repulsive interaction will remain with a magnitude $\epsilon_{\frac{\Phi}{N_0a}}$, even as $\Phi$ tends toward one. In this high concentration regime the local segment density at the wall cannot be significantly modified by either end-adsorption or the overlap of opposing adsorbed layers on surfaces at separations of less than $2R$. Thus bringing the plates within $2R$ of one another will result in desorption and therefore repulsion of the same type described in Section 2. Similarly, for strong adsorption, even in dilute and semi-dilute solutions, the segment density at the wall will be quite high, characteristic of the brush regime with excluded volume interactions and stretching balancing the adsorption energy. As two brushes overlap from opposing plates, chains will desorb to avoid overcrowding. This leads to a repulsive interaction of magnitude $\epsilon_{\frac{\Phi}{N_0a}}$, where $\Phi$ is the local segment density within the brush. Because the segment density in the brush is higher than in the bulk solution, there is no depletion attraction on length scales much larger than the segment length. Thus in either the melt or the strongly adsorbing cases, the repulsive interaction is given by $\epsilon_{\frac{\Phi}{N_0a}}$ where $\Phi$ is the local segment density. These conclusions have been confirmed by self-consistent field methods as described in Section 4, the semi-dilute in previously published work \cite{11} and the melt in unpublished results.

The general picture developed in this paper is also applicable to amphiphilic molecules of more complex architectures than the singly end-functionalized chains discussed in this paper. The minimum necessary condition to observe an equilibrium repulsive interaction is that all (or at least most) of the adsorbing species in a region larger than the correlation length are localized at the surface. In this case, the overlap of the adsorbed layers leads to a decrease in the adsorption density in order to maintain the local density of the rest of the chain segments. The decrease in adsorption density has an associated energy cost which leads to the repulsive interaction. This could equally well-occur with telechelic chains with adsorbing groups at both ends, or even randomly functionalized chains, provided that the number of functional groups was small enough that most of them could be localized at the surface while still having the unfunctionalized portions of the chain extend into the solution a distance greater than the correlation length. However, these different chain architectures also introduce other complexities, including bridging of a single chain adsorbed on both plates \cite{16}. This bridging can lead to an attractive interaction which is entropic in origin, and will act for the most part independently of the repulsive interaction caused by the removal of adsorbed chains. Thus more complex interaction profiles with multiple attractive and repulsive regions are possible.

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References

[6] This paper is concerned solely with the case of full equilibrium. In colloidal stabilization the system may not reach equilibrium during a Brownian collision, in which case a “restricted equilibrium” treatment such as is discussed in reference [14] may be more appropriate.