Forces between polymer-bearing surfaces: the question of constrained equilibrium

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Abstract. We discuss the nature of the *initial interactions* as two polymer-bearing surfaces in a good solvent approach each other, as measured directly by the mica force apparatus. It is suggested that, while for grafted chains and for adsorbed chains at low surface coverages these initial interactions are probably well described by constrained-equilibrium models, this may not be the case for adsorbed chains at high surface coverages.

1. Introduction

A long-standing problem in the physics of colloidal liquids has been to understand the nature of surface interactions between the colloidal particles in dispersions [1]. The use of polymers to modify surface forces, and hence to control the stability (or, occasionally, to induce instability) in colloidal dispersions, has become increasingly common over the past decades [2]. Surface forces in this case are essentially *entropic* in origin; their understanding is based on the thermodynamics of mixing of polymer chains in solution, the energetics of chain adsorption, and the phenomenon of long-range 'bridging' effects [3]. Bridging occurs whenever an adsorbing chain is quasi-irreversibly adsorbed (see highlighted chain in figure 1) and spans the gap between the two surfaces; one expects such a bridge to lead to attraction [3].

In the past 10 years the forces between two surfaces bearing adsorbed and grafted chains across a liquid medium have been studied directly, using the mica surface force technique (for a review, see [4, 5]). These studies were carried out in sufficiently well defined conditions (atomically smooth surfaces, surface separation known to within a few ångströms, and a known geometry of the mutual zone of closest approach) in order to compare their results with molecular models of surface interactions with adsorbed and grafted chains. The purpose of this paper is to discuss the validity of such comparisons of the theory with the experiments, especially in good solvents (the most common case), and most particularly at the onset of the interactions.

Recent theories of adsorption and of interactions between surfaces bearing adsorbed chains have been developed by de Gennes [6] (and extended by Pincus and co-workers [7, 8]) and by Scheutjens and Fleer [9]. The former models are capable of incorporating scaling results to match the known properties of chains in good solvents, although in the case of poor and θ-solvents both approaches give similar predictions [7]. We shall relate here more to the de Gennes [6] type of approach, which is more easily capable of making
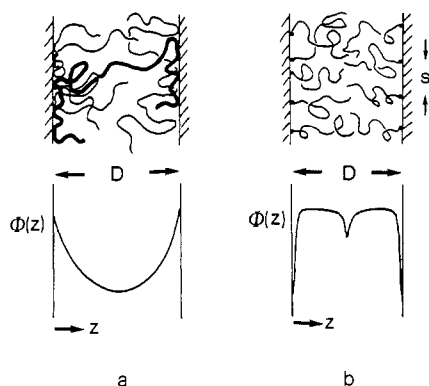
Figure 1. (a) Schematic representation of inter-
action between two surfaces bearing adsorbed
polymer, with the corresponding segment dis-
tribution $\varphi(z)$. Highlighted chain provides a
bridge. (b) As (a) but for grafted chains, assuming
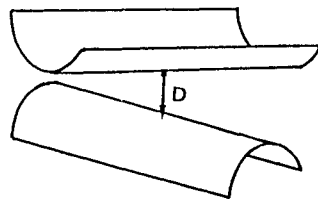little interdigitation.

Figure 2. Configuration of the mica surfaces in the
force experiments. D is the distance of closest
approach.

analytical predictions. The basic idea is illustrated in figure 1; the adsorbed polymer on
two surfaces a distance D apart results in a segment distribution profile $\varphi(z)$ as shown,
and the total excess free energy of the system (relative to pure solvent, i.e. $\varphi(z) = 0$
everywhere) is minimized, at equilibrium, with respect to $\varphi(z)$ in the gap $z = 0 - D$.

An important assumption of all models is that of local or constrained equilibrium,
i.e. the interacting adsorbed layers have sufficient time to adjust $\varphi(z)$ so as to reach the
lowest free-energy state (subject, if appropriate, to irreversible adsorption). For the
case of a good solvent, this approach predicts a repulsive interaction $E(D)$ which varies
as a power law

$$E(D) \propto D^{-\alpha} \qquad (\alpha = 1\text{--}1.25) \tag{1}$$

when the surfaces are strongly compressed (proximal regime), and as

$$E(D) \propto D^{-2} \tag{2}$$

when they are moderately compressed (the central regime), at equilibrium coverage of
the surfaces. At *low* coverages, Rossi and Pincus [8] have predicted that bridging
attraction will dominate the initial stages of the interaction as the surfaces approach,
even for the case of good solvents where high coverage leads to repulsion as in equations
(1) and (2).

For the case of *grafted* chains in a good solvent an early scaling attempt by Alexander
[10] has proved very fruitful. This is illustrated in figure 1(b). The basic idea is that non-
adsorbing chains are anchored at one end only, a mean distance s apart, dangling into
solution as shown. Two effects are balanced: chains tend to stretch normal to the surface
to minimize their net mutual repulsion in the good solvent, but stretching also increases
the free energy owing to reduction in configurational entropy. The equilibrium layer
thickness L_0 is that which minimizes the overall energy. An assumption by Alexander
of a *uniform* density profile (figure 1(b)) predicts that $L_0 = \text{constant} \times s(R_F/s)^{5/3}$ (for
$s \ll R_F$) where R_F is the swollen radius of the free chains in the good solvent, and the
constant is undetermined (as for all scaling approaches) but is of order unity. The
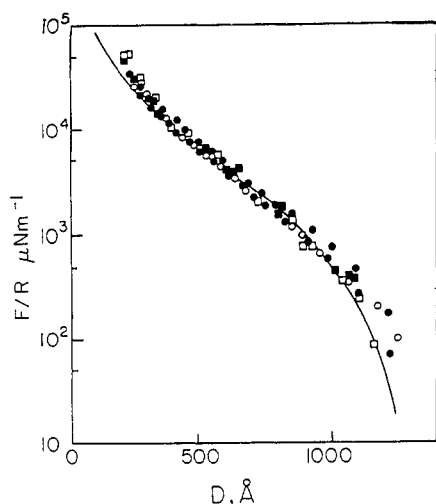
Figure 3. Force–distance profile, for mica sheet bearing *end-anchored* polystyrene chains ($M = 140 \times 10^3$) immersed in the good solvent toluene. The full curve is based on equation (3). R is the mean radius of curvature of the surfaces. (From [5].)

Alexander picture was extended by de Gennes [3] to the case of two interacting grafted layers (figure 1(b)) where the forces (normalized per unit area of two parallel plates a distance D apart) are given by

$$f(D) = \text{constant} \times (kT/s^3)[(2L_0/D)^{9/4} - (D/2L_0)^{3/4}] \qquad D < 2L_0. \qquad (3)$$

The two terms on the RHS of equation (3) represent the increasing osmotic repulsion and the approach to a less 'stretched' (and hence lower-energy) configuration, respectively, as the separation D decreases. Implicit in equation (3) is the assumption that the two layers do not interdigitate but merely compress (figure 1(b)). The force $f(D)$ per unit area is directly related to the interaction energy $E(D)$ per unit area [7, 11] (the quantity actually obtained from the experiment).

2. Experimental situation and discussion

The mica experiments measure the force $F(D)$ as a function of separation between two curved mica surfaces (mean radius of curvature R) in a crossed-cylinder configuration a closest distance D apart (figure 2) [12]. Here the measured $R \simeq 1$ cm while D varies but is typically of order 1000 Å. In the Derjaguin approximation, for $R \gg D$ (as in these experiments), $E(D) = F(D)/2\pi R$ gives the interaction energy $E(D)$ per unit area of flat parallel plates a distance D apart obeying the same force law $F(D)$. The experiments thus yield directly the quantities predicted by the models, equation (1), (2) or (3).

Of the large body of data that has accumulated [4, 5], we focus on two characteristic systems:

   (i) interaction between two surfaces bearing *adsorbed* polymer and
   (ii) between surfaces bearing *grafted* chains.

Both of these interactions are in good solvent conditions. Figure 3 shows the interaction between mica sheets, immersed in toluene, bearing polystyrene chains anchored to each surface by a highly polar end group [5]. It is known from independent studies that polystyrene which has not been end functionalized in this way does *not* adsorb to mica
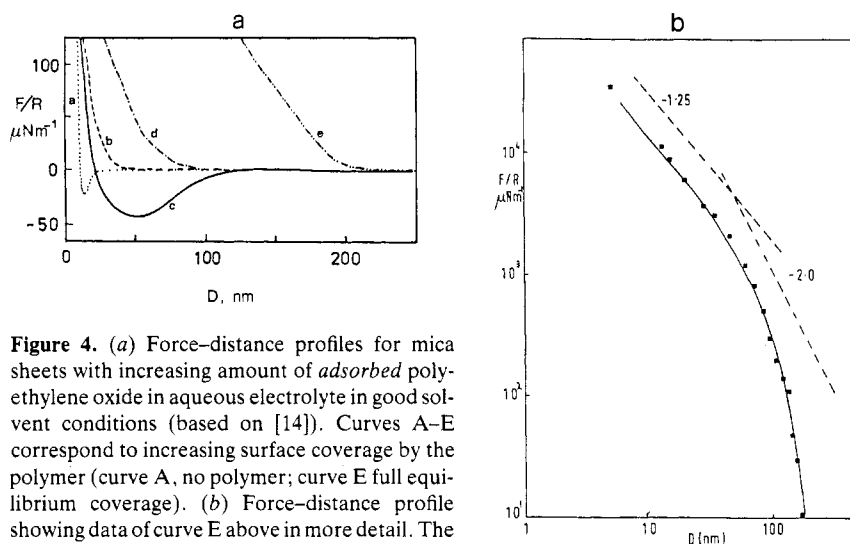
Figure 4. (a) Force–distance profiles for mica sheets with increasing amount of *adsorbed* polyethylene oxide in aqueous electrolyte in good solvent conditions (based on [14]). Curves A–E correspond to increasing surface coverage by the polymer (curve A, no polymer; curve E full equilibrium coverage). (b) Force–distance profile showing data of curve E above in more detail. The broken lines correspond to equations (1) and (2), while the full curve corresponds to equation (3).

from the good solvent toluene. The full curve in figure 3 is the variation predicted by equations (3) and (4) (recalling that $E(D)$ is related to $F(D)$). The absolute agreement is within a factor of 1.5 of the scaling prediction with a prefactor of unity in equation (4). (Similarly close fits [5] are obtained over a wide range of end-grafted chain dimensions and s-values.)

The main implication of this fit of the models [3, 10, 11] to the data [13, 14] is that we appear to have a reasonable quantitative picture of interactions between surfaces with *grafted* chains. However, this fit by itself does not tell us whether these experimental results for grafted chains are the equilibrium ones. This is suggested rather by the following experimental observations.

(i) In our experiments [5] there appears to be little evidence for hysteresis in the forces even after high compressions and at rapid decompression rates (in contrast to adsorbed chains [13, 14]; see later).

(ii) We know that the polystyrene chains do not undergo adsorption [5], where time scales can be long.

(iii) Interdigitation and/or entanglement of the compressed chains may occur—although there is no evidence that it does so in our studies—but for the *initial interactions* as the opposing layers meet (the focus of this discussion) this is not likely to play a role.

(iv) Finally, very recent experiments [15] on the shear of grafted chains suggest relaxation times (over the range of experimental parameters studied) that are very much shorter than the time for measurement of each datum point of $F(D)$ in figure 3.

These considerations strongly suggest that the measured interactions at the onset of the repulsion do represent the equilibrium force law.

The situation with *adsorbed* chains (figure 4) may be different. Figure 4(a) shows schematically how the interactions vary with surface excess for the case of two surfaces bearing an adsorbed polymer (polyethylene oxide) in a good solvent (0.1 M KNO_3). The marked attractive well in curve C of figure 4(a) is due to bridging; it disappears on higher adsorbance as the bridging attraction is swamped by the osmotic repulsions. What

is especially noteworthy is that, over the times of our measurements (the time for each data point on which curve C is based is of order 30 s, and around 15 min for the full profile), the attraction occurs on *approach* as well as on separation; it appears that the chains have the opportunity to bridge the gap (tunnelling through the opposite adsorbed layer [3]), the effect underlying this attraction. This suggests that the interactions in the *low-adsorbance* regime are close to equilibrium. If the attraction was manifested only on *separation* of the surfaces, this might indicate a disentanglement effect, i.e. a kinetic rather than equilibrium phenomenon.

Figure 4(*b*) shows the high-adsorbance limit, curve (E) of figure 4(*a*), in more detail, on a log–log plot. The broken lines have slopes corresponding to the predicted variation of de Gennes' [6] model for the respective regimes. What is remarkable here, as very recently pointed out in [14] is how closely the predicted variation (equation (3)) of the Alexander–de Gennes model for *grafted* chains (full curve) fits the data in figure 4(*b*), which is for adsorbed chains. The absolute value of $F(D)/R$ also corresponds (within a factor of order unity) to equation (4), where s is estimated from the experimentally known adsorbance and the assumption of two tails per adsorbed chain.

This fit, taken together with the consistency of the data with the 'constrained-equilibrium' prediction for the central and proximal regions (broken curves in figure 4(*b*)), suggests the following picture [14]. The adsorbed layers consist of a relatively compact layer at and near the surface, consisting of trains and loops, which anchor the 'tails' (i.e. ends) of each adsorbing chain. The tails extend out into the solution and are the first to interact as the adsorbed layers overlap. These initial interactions (for high surface coverages) may not be in full equilibrium with respect to the near-surface layers. In other words, the *overall* segment density profile (which included the highly entangled near-surface segments) may not have had time to 'react' to the initial compression of the dangling tails, in order to minimize the excess surface energy. In this case the initial mutual interaction resembles that of permanently end-grafted chains as in figure 3. This picture of some inequilibrium over the times of measurement at the *onset* of interaction is consistent also with the known slow relaxation behaviour of adsorbed layers in a good solvent, when highly compressed and rapidly decompressed. A tentative conclusion is that at *high adsorbances*, the initial interaction between adsorbed layers, at least as measured over the time scales of the surface force apparatus, may be better understood in terms of the compression of tails (independently of the underlying near-surface layer) rather than by models that assume constrained equilibrium which requires the whole of the density profile to respond to the changes in free energy induced by this initial compression.

Acknowledgments

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