Interactions between Mica Surfaces in a Polystyrene–Cyclopentane Solution Near the θ-Temperature

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The forces $F(D)$ between smooth mica surfaces immersed in cyclopentane have been measured as a function of their separation D both in the absence and in the presence of polystyrene (of two molar masses, 6×10^5 and 2×10^6) adsorbed onto the mica from the solvent, at a temperature (23 ± 1°C) slightly above the θ-temperature for this system (19.6°C). The interactions between the bare mica surfaces in the cyclopentane were short-ranged ($\leqslant 10$ nm) and attractive. After addition of polymer to the solvent the surfaces were incubated in the solution at small surface separation to limit the rate of polymer adsorption, and interactions were measured following progressively longer incubation periods. The following trends were noted for both molar masses: (i) Following initial adsorption of polymer, a long-ranged attraction between the surfaces was followed by an ultimate repulsion as the surfaces were compressed close together. (ii) At longer incubation times in the solution, the magnitude of the attraction decreased while the range of interaction and the ultimate repulsive regime moved to larger D values. (iii) After overnight incubation at large surface separation the interaction became monotonically repulsive, starting at a surface separation $D \simeq 1.7R_g$ (unperturbed radius of gyration) for both molar masses used. This behavior did not change on further incubation. (iv) When the solution was replaced by pure solvent after overnight incubation, the monotonic repulsion changed to an initial weak *attraction* followed by an ultimate repulsion, very similar to the behavior following partial adsorption. Overall, the results indicate that attraction between the polymer covered mica surfaces is strongly correlated with extent of polymer adsorption, and disappears following full adsorption. The origin of the attraction is probably due to "bridging" effects, while the ultimate repulsion most likely occurs because of the dominance of osmotic interactions.

INTRODUCTION

The forces between two solid surfaces immersed in a liquid medium may be considerably modified by adsorbing polymers onto the surfaces, and this effect is widely used in controlling the stability of disperse systems with high surface-to-volume ratio (such as colloidal dispersions) (1–3). Recently the forces $F(D)$ between two surface-adsorbed polymer layers have been directly studied as a function of distance D between the surfaces (4–7). Thus two mica surfaces bearing adsorbed polystyrene in cyclohexane under poor solvent conditions initially *attract* each other, when the opposing adsorbed layers first come into overlap as the surfaces approach (6). On the other hand, when the surfaces bear adsorbed polyethylene oxide in an aqueous electrolyte, or in toluene, both good solvents, monotonically increasing *repulsion* is observed as the surfaces approach (8). These studies also indicate that adsorption of polymer in both cases is essentially irreversible in the conditions of the experiments. In these circumstances, the origin of the attraction and repulsion in the poor and good solvent conditions, respectively, has been attributed mainly to the osmotic interactions between the adsorbed segments on the opposing sur-

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face-adsorbed polymers as they come into overlap when the surfaces approach.

Very recently the interactions between mica surfaces bearing adsorbed polystyrene in cyclohexane were measured both below the θ-temperature ($T = 24°\mathrm{C} < \theta = 34.5°\mathrm{C}$), as before (6) and also (by heating the system) at slightly *above* the θ-temperature ($T \simeq 37°\mathrm{C}$) (9). The attractive regime observed at $T < \theta$ *persisted* (weakly) even at the higher ($\sim 37°\mathrm{C}$) temperature. In addition, raising the temperature appears to have led to some desorption of the polymer; it was conjectured (7, 9) that this latter effect may have been partly responsible for the attraction at $T \gtrsim \theta$ (due to enhanced "bridging" effects between the surfaces alone), since the osmotic interactions should no longer be attractive above θ (6).

We have measured the interactions between mica surfaces bearing adsorbed polystyrene in cyclopentane at 23 ± 1°C, a little above the θ-temperature of 19.6°C for this system (10). In this way possible complicating effects of temperature variation (such as desorption) used to attain $T \gtrsim \theta$ noted in the earlier study are avoided. In particular, we have been able to observe the effects, on the surface–surface interactions, of *partial adsorbance* of the polymer, and in this way to separate osmotic effects within the gap from purely surface-related effects, such as bridging.

EXPERIMENTAL

The apparatus and experimental procedure have been described in detail previously (6). The method permits the determination of forces $F(D)$ acting between two atomically smooth, curved mica sheets a closest distance D apart, in the convenient range 0–300 nm, with a distance resolution of some ±0.3 nm in this range (6, 11). The main change in the apparatus as used in these experiments compared with the earlier description (6) is a modification to permit the mica surfaces to be moved *laterally* relative to each other, thereby enabling measurements at a number of independent contact points between the same pair of mica sheets.

The present experiments were designed to measure $F(D)$ between the polymer-bearing mica surfaces at *partial* as well as at full absorbance of the polymer. This was achieved by incubating the mica surfaces in the polymer solution under conditions where the rate of arrival (and adsorption) of the polymer molecules at the region of interest (i.e., the points of closest approach between the surfaces, where $F(D)$ is measured) was severely diffusion limited. The detailed experimental procedure is as follows: the air contact position (between the mica surfaces) of the interferometric fringes is first determined; cyclopentane is then introduced into the glass cell, and $F(D)$ measured; following this, the surfaces are taken to a separation $D \simeq 30 \pm 5\ \mu\mathrm{m}$ and polymer introduced into the cell to a concentration of $15\ \mu\mathrm{g\ ml}^{-1}$. Polymer molecules from the bulk solution reaching the region of closest approach between the mica sheets and adsorbing onto the surfaces thus need to diffuse laterally a considerable distance (~ 1 mm) in the narrow gap (30–100 μm) created between the mica surfaces (see Appendix). The rate of arrival and adsorption of polymer molecules at this region of interest (i.e., where $F(D)$ is measured) is thereby severely limited, by this requirement of lateral diffusion, relative to the corresponding adsorption rate from a bulk polymer solution onto a *free* surface (12).

The forces $F(D)$ between the surfaces are measured at various times following introduction of polymer into the cell; during this period (up to about 24 h) the surfaces are generally never further than some 30 μm at their closest point. Following this restricted incubation the surfaces are taken to $D \simeq 0.5$ mm, and left overnight in solution for full adsorption to take place. $F(D)$ is then again determined. This procedure was occasionally slightly varied: any deviations are noted in the Results section. However, the general approach of measuring $F(D)$ as progressively more polymer adsorbs was maintained in all experiments. Finally, the polymer solution is replaced by pure cyclopentane, save for ~ 1 ml remaining between the mica surfaces (6), and the procedure repeated; this results in an approximately 10^4-fold dilution of the original polymer solution. Following this, the surfaces were left for 24 h to equilibrate at this very low polymer concentration, at a large separation, and $F(D)$ was then measured again.

The experimental approach (6, 11) permits the measurement of the mean radius of curvature R ($\simeq$0.5 cm) of the mica surfaces near the region of closest approach; this enables "normalization" of the force–distance profiles as $F(D)/R$, which in the Derjaguin approximation (13) gives the interaction energy $E(D)$ per unit area of two flat parallel plates a distance D apart, obeying the same force–distance law. The force profiles in this paper are normalized in this way to allow comparison of results from different contact points or different pairs of mica sheets, where the local curvature R may differ.

Materials. Anionically polymerized polystyrene of two molecular weights was supplied by Pressure Chemicals and used as received. Its molecular characteristics are given in Table I.

The solvent was spectroscopic grade cyclopentane (Fluka) used as received. All liquids (solvent and solutions) were filtered (0.22 μm Fluoropore) prior to introduction into the force-measurement cell.

The mica used was Muscovite Ruby, best grade FS/GS, supplied by Mica and Micanite LTd. (London).

RESULTS

a. Bare Mica

Prior to introduction of polymer the force profiles $F(D)$ were measured in the pure cyclopentane. Figure 1 shows a typical profile between bare mica surfaces in the polymer-free solvent. There is little interaction at $D \gtrsim 15$ nm, while at lower separations ($D \lesssim 10$ nm) an attraction is observed down to $D \simeq 7 \pm 1$ nm, where the surfaces jump into contact. On separation from contact, the surfaces jump a considerable distance apart, corresponding to an adhesive attraction at contact of order 10^3 μJ m^{-2}. The adhesive energy at contact was to some extent variable (over a factor of 3 or so) probably reflecting the fact that the "contact" separation varied slightly between different experiments. The jumps observed are due to a mechanical instability which occurs (11) whenever $\partial F(D)/\partial D \geqslant k$, the spring constant of the lower leaf-spring in our apparatus (6).

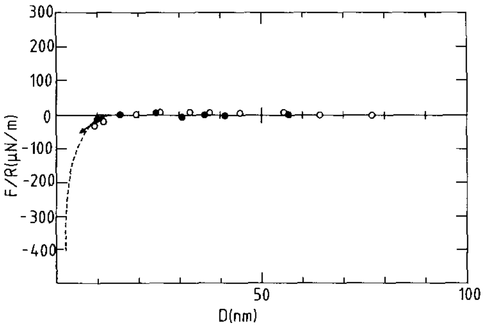

FIG. 1. Force ($F(D)$)–distance (D) profile between two curved mica surfaces (mean radius of curvature $R \simeq 0.5$ cm) immersed in cyclopentane at 23 ± 1°C. The profile is normalized as $[F(D)/R]$ v D, to yield the interaction energy per unit area of flat surfaces a distance D apart, in the Derjaguin approximation. Results from different pairs of mica sheets are shown. The broken curve is the theoretical van der Waals attraction expected between two crossed cylinders of radius R, $F/R = A/(6 \cdot D^2)$ where the Hamaker constant $A = 10^{-20}$ J (estimated for the mica–cyclopentane system (6)).

TABLE I[a]

Polystyrene	M_w	M_w/M_n	R_g (nm)
PS1	5.99×10^5	<1.10	21
PS5	2.05×10^6	<1.03	38.5

[a] Manufacturers data based on light scattering and chromatography. R_g is the unperturbed radius of gyration (14).

b. PS1 ($M_w = 6 \times 10^5$)

Figure 2 shows the force profile between the mica surfaces following addition of PS1 to a concentration of 15 ± 2 μg ml^{-1}, and incubation of the surfaces at a surface separation of 30 μm for 12 ± 2 h, as described. On bringing the surfaces together, little interaction is observed at separations $D \gtrsim 40$ nm,

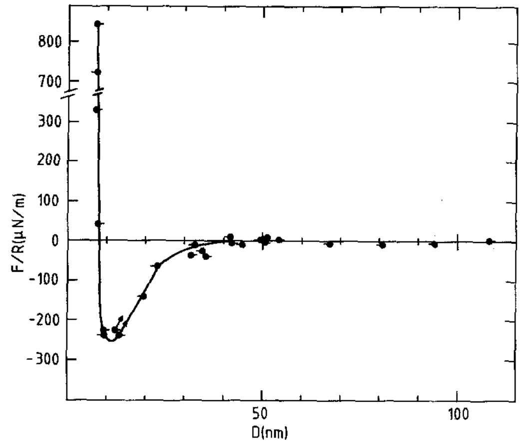

FIG. 2. Force–distance profile between curved mica surfaces in 15 μg ml^{-1} PS1/cyclopentane solution at 23°C, following 12 h incubation in the solution at surface separation of 30 μm. Solid symbols, compression/decompression of surfaces.

while a clear attraction is indicated at $D \leqslant 35$ nm. The attractive well is followed by an ultimate strong repulsion at $D \leqslant 8$ nm, as shown. The force–distance relationship is reversible on decompression of the surfaces, and their separation to $D \geqslant 300$ nm. The profile is reproducible, up to 2 h, while the surfaces are not separated by more than 500 nm or so during this period (to minimize the introduction of additional polymer from the bulk solution into the gap between the surfaces).

Following the incubation of the surfaces at the small separation (~30 μm), they were taken 0.5 mm apart and allowed to stand overnight (16 ± 3 h) in the polymer solution. Figure 3 shows the interaction following this further incubation. No forces are measurable (within the experimental error) as the surfaces are brought together, down to $D \simeq 35$ nm. At smaller separations a monotonically increasing repulsion is observed; The repulsive wall has moved "out"—relative to the partial adsorption profile (Fig. 2)—to $D \simeq 15$ nm (here and in what follows the term "repulsive wall" refers to the regime where $F/R \geqslant 10^3$ μJ m^{-2}). The force–distance profile is reversible on a slow decompression of the surfaces, and does not vary further with time even if the surfaces are taken some way apart and left for further incubation periods.

c. PS5 ($M_w = 2 \times 10^6$)

Figures 4–6 show the changes which occur in the force-distance relationship between mica surfaces immersed in a 15 ± 2 μg ml^{-1} solution of PS5 in cyclopentane (23 ± 1°C), as a function of progressively longer incubation times.

Figure 4 shows the interaction profile following 12 ± 2 h incubation in the PS5 solution at a surface separation of 25 μm. There is little measurable interaction as the surface approach from a large separation down to $D \simeq 50$ nm; at lower D values a strong attraction is observed (leading to a jump, as expected for $\partial F/\partial D \geqslant k$, at $D \simeq 30$ nm) to be followed by an ultimate repulsion at $D \leqslant 7$ nm. The force profile is reversible on slow decompression, and reproducible over a period of some 2 h, as long as the surfaces were not separated by more than about 1 μm over that period.

Figure 5 shows results from a different pair of mica sheets, following overnight incubation (12 h) at a somewhat larger surface separation (~100 μm), curve (a); an additional 2.5 h at a surface separation of 0.5 μm, curve (b); and a further 16 h incubation at 0.25 mm

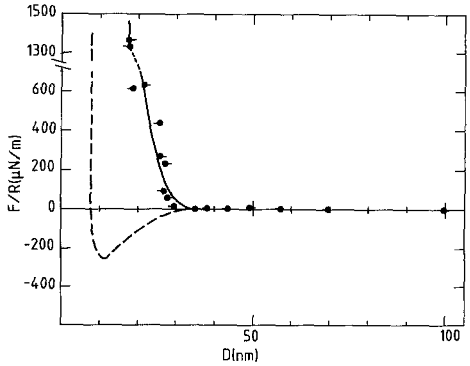

FIG. 3. Force distance profile between mica surfaces in PS1/cyclopentane solution (as Fig. 2), following a further 16 h incubation in the solution at a surface separation of 0.5 mm. Solid symbols, compression/decompression of surfaces. Broken curve: results from Fig. 2 (partial incubation).

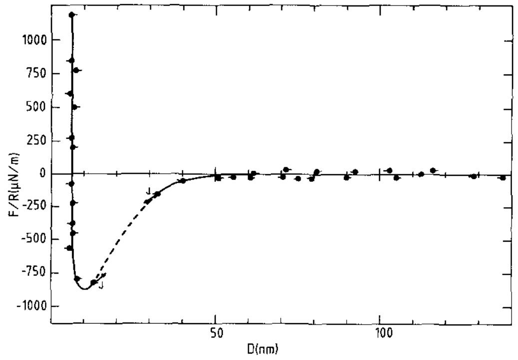

FIG. 4. Force-distance profile between curved mica surfaces in 15 μg ml^{-1} PS5/cyclopentane solution following 12 h incubation in the solution at a surface separation of 30 μm, at 23° ± 1°C (Expt. 34). Solid symbols, compression/decompression; J, "jump" points.

surface separation, curve (c). All profiles are for the same contact point, and clearly reveal the effect of progressively longer incubation times in the solution (with correspondingly greater adsorption) on the nature of the force profiles. The attraction becomes weaker (in the order (a) → (b) → (c), where it disappears altogether) while the ultimate repulsive "wall" moves out: for a repulsive interaction 10^3 μJ m^{-2}, (say), $D \simeq 12$, 18, and 30 nm respectively, for the three profiles (in Fig. 4, where the incubation is even more limited, the attraction is stronger, while the ultimate repulsive wall is closer in—some 7 nm for the same repulsive interaction. The profiles (a)–(c) were reversible on compression/decompression, and reproducible over the measurement periods of some hours in all (during measurements, the surface separation did not exceed about 1 μm). The trend in Fig. 5 illustrates a general observation in these experiments (including PS1): the longer the adsorption time in the solution, the weaker the attractive well eventually becomes, with a corresponding "moving out" of the repulsive regime.

Figure 6 shows force–distance profiles following overnight (16 ± 2 h) incubation of the mica surfaces in the PS5 solution, with a large (0.5 mm) separation between the surfaces. Results from experiments using two different pairs of mica sheets are shown. As for the case of PS1 (Fig. 3), the interaction is monotonically repulsive, commencing at $D \leqslant 65$ nm. There is no evidence (within the scatter) of any attraction prior to the onset of repulsion. The interactions in Fig. 6 are reversible on compression/decompression, and do not change further with time on further incubation in the solution. We again note that the repulsive "wall" (at interaction energies $F/R \gtrsim 10^3$ μJ m^{-2}) has moved out to $D \simeq 30$ nm (compared with 7–18 nm for the same repulsive interaction energy between the partially incubated mica sheets, Figs. 4 and 5).

Following overnight incubation in PS5 solution—which resulted in the profiles shown in Fig. 6—the polymer solution in the cell was replaced by pure cyclopentane, resulting in an approximately 10^4-fold reduction in the concentration of polymer. The surfaces were then left immersed for 24 h in this extremely dilute solution, at a large separation (0.5 mm). Figure 7 shows the resulting force–distance profile. Two features stand out: (a) the monotonically increasing repulsion commencing at $D \leqslant 65$ nm is replaced by a weak

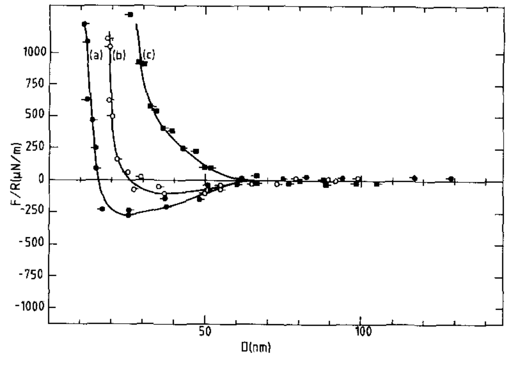

FIG. 5. Force–distance profiles between curved mica surfaces in 15 μg ml^{-1} PS5/cyclopentane solution, following progressively longer incubation periods in the solution (forces measured at the same contact point throughout) at 23°C ± 1°C. Solid circles, compression/decompression following 12 h at ~0.1 mm surface separation; open circles, compression/decompression following a further 2.5 h at 0.5 mm surface separation; open squares, compression/decompression following a further 16 h at 0.25 mm surface separation (Expt. 22).

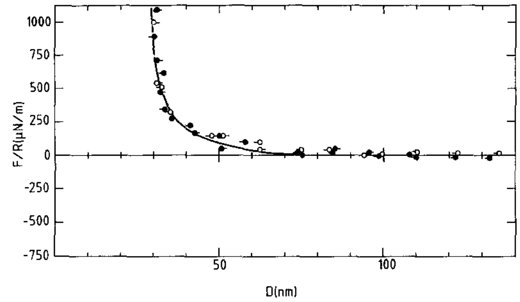

FIG. 6. Force–distance profiles between curved mica surfaces in PS5/cyclopentane solution (as Figs. 4, 5) following 16 h incubation in the solution at a surface separation of 0.5 mm. Results from experiments using different pairs of mica sheets are shown: solid symbols, compression/decompression (Expt. 34); open symbols, compression/decompression (Expt. 21). Temperature: 23 ± 1°C.

attractive regime at 30 nm $\leqslant D \leqslant$ 60 nm, followed by an ultimate repulsion $D \leqslant$ 30 nm; (b) the repulsive "wall"—at interaction energies $F/R \geqslant 10\ \mu\mathrm{J\ m^{-2}}$—has now moved in to D = 20 nm, compared with D = 30 nm prior to replacing the solution by pure solvent (curve (b)). The force–distance profile is reversible on slow decompression, and does not change (over several hours) on further standing of the mica surfaces in the pure solvent.

The optical method also enables the determination of refractive index $n(D)$ of the medium separating the surfaces (11), and from this the *adsorbance* Γ of the polymer on the mica sheets may be estimated (6). The results are somewhat scattered but suggest that Γ is lower than its value for polystyrene on mica in cyclohexane under poor solvent conditions. Thus the refractive index measurements following equilibrium adsorption correspond to an adsorbance $\Gamma_{\mathrm{eq}} \simeq 2.5 \pm 1.5$ mg m^{-2} of polystyrene (PS1) on the mica, compared with $\Gamma_{\mathrm{eq}} \simeq 5.5 \pm 1$ mg m^{-2} for the same polymer adsorbing onto mica from a poor solvent (6, 7). However, the scatter in the values of $n(D)$ does not enable a systematic correlation of Γ with the extent of incubation.

DISCUSSION

The interaction between the mica surfaces across the cyclopentane in the absence of polymer (Fig. 1) is very similar to that observed between mica sheets in cyclohexane under similar conditions (6). This form of behavior suggests a van der Waals-like attraction between the two crossed mica cylinders across the nonpolar medium with an appropriate Hamaker constant (6), though other effects (such as water-bridging) have also been suggested (15b). We have observed no structural forces in this system, as reported for some other organic solvents (though not cyclopentane) under certain conditions (15); the reasons for this have been previously considered (6). The essential point is that the *range* over which interactions between the bare mica surfaces are important, $0 < D \leqslant 10$ nm, is in general outside the range of interest (8 nm $\leqslant D \leqslant$ 70 nm) after polymer has adsorbed.

Once polymer is introduced into the system, the trend of the results is similar for both PS1 and PS5. To facilitate further discussion we summarize the data (for PS5) in Fig. 8. Following initial adsorption the short-range attraction between the bare mica surfaces (Fig. 1), is replaced by a much longer ranged attractive force (Fig. 8, curve a). As the surfaces are compressed, the attraction passes through a minimum and ultimate

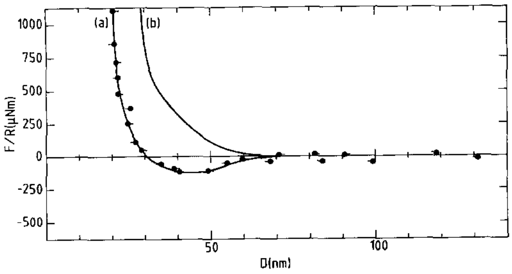

FIG. 7. Force–distance profile between mica surfaces after 16 h standing in PS5/cyclopentane, subsequent replacement of solution by pure cyclopentane, and a further 24 h immersion in the solvent (Expt. 34), all at 23 ± 1°C. Solid symbols, compression/decompression. Curve (b) is the force profile prior to solution/solvent exchange (from Fig. 6).

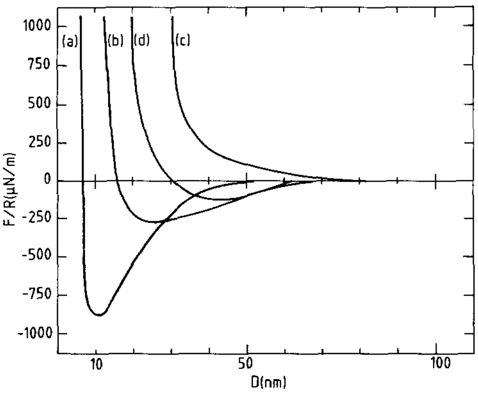

FIG. 8. Smoothed force–distance profiles based on Figs. 4 (curve a), 5 (curves b, c) 6 (curve c), and 7 (curve d), showing the effect of progressively longer incubation (a–c) and subsequent replacement of solvent (d).

repulsion is observed as they are pressed further together.

As the surfaces are left longer to incubate, allowing further adsorption, the range of attraction increases, the magnitude of the attraction decreases, and both the attractive minimum and the repulsive wall move out to larger D values (curve b, Fig. 8. Similar results were observed for PS1). Finally, following overnight equilibration of surfaces with the solution, the attraction disappears altogether, to be replaced by a monotonically increasing long-ranged repulsion, with the repulsive "wall" still further out (curve c, Fig. 8). We recall that the curves in Fig. 8 (based on Figs. 4–7) are reversible on slow decompression.

The results, as summarised in Figs. 8a–c, strongly indicate that the attraction observed is correlated with lower-than-limiting adsorbance of polymer on the surfaces. We may interpret these results as follows: the overall interaction has attractive components associated with adhesion of monomers to the surfaces, which result in the adsorption, and may lead to bridging of the intersurface gap by polymer molecules simultaneously adsorbed on both surfaces; this is generally an *attractive* effect (2). At the same time the segment–segment interactions *within* the gap contribute an effect which depends on the goodness of the solvent. In the slightly-better-than-θ conditions of the present study we would expect a small but positive second virial coefficient (16); however, even in strictly θ conditions a repulsive osmotic interaction is expected at high enough concentrations within the gap (for example, due to effects such as 3-body interactions). Our measurements give the *net overall* force between the surfaces: thus at low adsorbance values the bridging-like component dominates, with net attraction; as progressively more polymer adsorbs the repulsive osmotic segment–segment interactions within the gap become larger, resulting in a decrease of the net attraction and an eventual ultimate monotonic repulsion at the limiting adsorbance (following overnight incubation). The ultimate repulsion observed for the low adsorbance profiles (Figs. 8a, b) at low D values is likewise due to the dominance of the repulsive osmotic interactions when the concentration in the gap become high. In an earlier study (9) on polystyrene in cyclohexane a strong attraction was also observed following partial adsorption, but the poor solvency conditions (which lead to attractive osmotic interactions even between the fully covered surfaces (6)) must play a role in this. In the present system the attraction appears to be a function *only* of the incomplete adsorption. We note that very recently a similar initial attraction on partial adsorption, which disappeared at longer incubation times, was observed (17) for the case of polyethylene oxide on mica surfaces in an aqueous medium under *good solvent* conditions.

The effect of replacing solution by solvent after Γ_{eq} has been attained, and letting the adsorbed layers equilibrate with the (essentially polymer free) solvent, is striking (Fig. 8, curve d); the monotonically increasing repulsion is replaced by a weak (but marked) *attractive* well, and at the same time the ultimate repulsive wall—on further compression—moves *in*. This suggests that the effect of this replacement is to lead to some *de-*

sorption of polymer. The resulting attraction indicates that the attractive bridging forces again dominate the overall interaction on initial overlap, whereas prior to desorption they were weak relative to the repulsive osmotic interactions within the gap, as discussed.

An interesting feature of the present results is that there is no attraction (within error) following overnight equilibration of the surfaces in the polymer solution. In the previous study (9), where mica surfaces equilibrated with polystyrene in cyclohexane under *poor solvent* conditions, some attraction *persisted* on raising the temperature T to $T \geqslant \theta$, together with some desorption. It is thus tempting to correlate the residual attraction as $T \rightarrow \geqslant \theta$ (in the earlier investigation (9) with this desorption, as for curve d, Fig. 8, in the present case, where a similar effect is observed on *dilution* rather than heating. This leads to a paradoxical situation where two surfaces which have equilibrated at $T > \theta$ with a polymer solution repel monotonically on approach (the present study), while if they were equilibrated at $T < \theta$ (albeit in a different solvent) with the same polymer, and then heated to $T \geqslant \theta$, some attraction persists (the earlier study (9)). One possible explanation is that, in the latter case, some desorption occurs on heating (as observed) while the polymer which remains on the surface does not have time to rearrange itself over the course of measurements (several hours); a nonequilibrium situation with many free surface sites and hence attraction could result, but this is a delicate point. The idea could be checked directly—for the polystyrene/cyclohexane/mica system ($\theta = 35°\mathrm{C}$)—by ensuring that the solvent is heated to $T \geqslant \theta$ *prior* to addition of the polymer, so that equilibration takes place under θ conditions. Very recent calculations, however, suggest that there may be a real difference between the two cases at the level of the *third* virial coefficient (J.K., K. Ingersent, P. Pincus, in preparation). Other possibilities have also been proposed for the residual attraction on heating to $T \geqslant \theta$ (9). In any event we note that the long-range monotonically repulsive interaction following overnight adsorption in the present study was observed in several experiments with both polymers (Figs. 5, 6 for PS5 include results from 3 different pairs of mica sheets).

The reversibility of the force–distance profiles suggests in all cases that little desorption occurs on compression of the surfaces, and also that changes in polymer conformation, which do occur on compression, relax rapidly (relative to the time of measurement) on decompression. At the same time the case of the partially adsorbed surfaces (curves a, b, Fig. 8) is clearly one of very local equilibrium, as the force profiles change systematically on allowing further adsorption, till the final quasiequilibrium profile (c) is attained after overnight equilibration with the polymer solution. Following solvent exchange, some desorption appears to result (curve d); it may be that the polymer remaining on the surface is the equilibrium adsorbed amount at the very low final polymer concentration (18) (ca. 10^{-3} ppm). Independent adsorption studies (12) would be necessary to clarify this point, though the reversible and reproducible nature of the final force profile (d, Fig. 8) indicates that it represents the quasiequilibrium relationship in these conditions. We note also that both compression and decompression cycles in these experiments are carried out relatively slowly—around 0.5 h or more per cycle. There was some indication of relaxation effects—similar to earlier reports on a different system (8)—on very rapid decompression, but these were not investigated in detail.

The apparent partial desorption of polystyrene from the mica upon dilution suggests a rather weak or marginal adsorption of polymer in this system. A number of other observations are consistent with this idea: (i) the partial desorption of polymer in the polystyrene/mica/cyclohexane system on increasing the goodness of solvent by raising the temperature (9); (ii) the fact that polystyrene (even of high MW, such as PS5) does not adsorb *at all* on mica from good solvents such as toluene (19); (iii) the lower adsorbance value indicated in a slightly-better-than-θ solvent (cyclopentane, 23°C, i.e., the present study) compared with a poor solvent at the same temperature (6). It would clearly be useful to have direct isotherm studies for the polystyrene/mica/cyclopentane system (using, for example, a microbalance technique (12)) to shed more light on this point. It is of interest that for the case of polystyrene adsorption onto a metallic substrate, chrome, as studied recently by ellipsometry in θ and good solvent conditions at a number of solution concentrations (20, 21), it is found that the adsorbance of the polymer decreases both on lowering the incubation concentration and on increasing the goodness of solvent.

What of the configuration of the adsorbed polymer layers in the present study? The earlier work on polystyrene adsorbed on mica in cyclohexane under poor solvent conditions, for a number of polymer molecular weights, indicated an effective extension δ of the adsorbed layers from each surface of some $1.3–1.5R_g$ (6, 9). For polyethylene oxide adsorbed onto mica in *good* solvent conditions, the effective extension δ was in the range $2.5–3R_g$ for several molecular weights (8, 17). In both cases one expects interaction (either attractive or repulsive, for the two cases, respectively) between segments from opposing adsorbed layers as soon as they came into overlap (22, 23). It is reasonable to assume that in the present case (under somewhat-better-than-θ conditions) the extension of polymer layers is also $\delta \simeq 1.5R_g$—one expects an extension from the surface δ comparable with its value in the poor solvent (16, 23). Making this assumption, we find that the distance for onset of interactions—whether attractive, at $\Gamma < \Gamma_{eq}$, (curves a, b, d, Fig. 8) or repulsive, at $\Gamma = \Gamma_{eq}$ (curve c)—is considerably *smaller* than 2δ. For PSl the onset of interactions is at $D \simeq 35$ nm $\simeq 1.7R_g \simeq 1.1\delta$; while for PS5 the onset of interactions is at $D \simeq 65$ nm $\simeq 1.7R_g \simeq 1.1\delta$ (taking $\delta = 1.5R_g$ for both adsorbed polymers). Thus there appears to be a considerable interpenetration or "telescoping" of the opposing adsorbed layers, as the substrate surfaces are compressed together, before interaction is observed. This would certainly be consistent with what one expects of overlapping polymer segments close to θ conditions, where the second virial coefficient (for segment–segment osmotic interactions) is close to zero. In any event, we note that for both polystyrene samples used, the distance for onset of interactions is about $1.7 \pm 0.2R_g$, a value appreciably smaller than in poor solvent conditions for the same polymer/substrate system (6, 9). Figure 9 illustrates this difference for PS1 in the two solvent conditions.

Our results also have implications for the *flocculation* of colloidal dispersions by added polymer (1, 24). On addition of polymer one expects the initial adsorption to result in strong attraction between the particles (as Fig. 8, curves a–b) which would lead to their mutual attraction and aggregation. Once such aggregation takes place, further polymer is prevented from adsorbing at the contact zones, and the attractive forces persist (as Γ

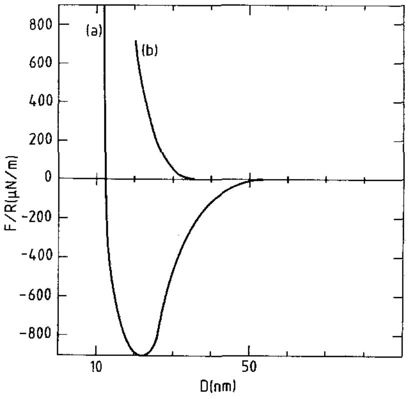

FIG. 9. Comparison of force–distance profiles between mica surfaces following equilibrium adsorption of PS1 from solution, in (a) worse-than-θ conditions, curve (a) (based on ref. (6)), PS1/cyclohexane at 24°C; (b) slightly-better-than-θ conditions, curve (b), (based on Fig. 3), PS1/cyclopentane at 23°C. In both cases the solution concentration is around 10 μg ml^{-1} of polymer.

remains lower than Γ_{eq}). Thus flocculation can occur (as has been observed) (24) even under conditions where *equilibrium* adsorption would lead to *repulsive* rather than attractive forces between the colloidal particles. It is worth remarking on the absolute magnitude of the attractive interactions in the cases of partial adsorption (curves a, b, d, Fig. 8)—the values of $F/R \simeq -(10^2\text{–}10^3)$ μJ m^{-2} at the minimum of the force–distance profiles (for curves d and a, respectively) correspond to attractive interactions of order $10^2\text{–}10^3$ kT acting between two colloidal particles (size ~1 μm) obeying the same force–distance law. Such particles would not readily disperse under their thermal energy (of order kT) once they come together in the energy minimum.

The above discussion of the main findings of our experiments has been essentially qualitative. When we come to compare our results with current theoretical models (22, 23, 25) there are two difficulties. First, models where full equilibrium is assumed as the polymer-bearing surfaces approach each other, result in a force which is *attractive* at all D values, even in a good solvent (22, 25); the underlying reason for this is that polymer is free to *desorb* as the surfaces are compressed. In the present case (as in previous studies (6, 8)) the adsorption is essentially irreversible on a compression/decompression cycle, so that an assumption of full equilibrium is not correct. In the model proposed by De Gennes (22) and extended by Pincus and one of us (23), it is possible to impose a *fixed adsorbance* condition, and this has been done in detail in the case of good (22) and of poor (23) solvents, but not in θ conditions. The second difficulty concerns the partial-surface-coverage situation (Fig. 8, curves a, b); present models (22, 23) generally assume a surface coverage resulting from (irreversible) adsorption to completion from the incubating solution, and so again it is not appropriate to compare predictions with experiment. Detailed calculations, based on the generalized van der Waals approach used in the earlier models (22, 23) with boundary conditions corresponding to (a) partial surface coverage, (b) full irreversible adsorption from solution, and (c) to partial desorption on dilution of the solution, all in θ conditions, are currently under way (J. Klein, K. Ingersent, and P. Pincus, in preparation).

To summarize: the attractive, short-ranged ($D \leqslant 10$ nm) interaction between bare mica surfaces immersed in cyclopentane is strongly modified when polystyrene is added to the system, at slightly-better-than-θ conditions.

(i) Following some adsorption of the polymer from the solution, a long-range attraction is observed as the surfaces approach, to be replaced by an ultimately repulsive regime as they are further compressed. The forces are reversible and reproducible for a given extent of adsorption.

(ii) As the surfaces are incubated for longer times, the magnitude of the attractive forces decreases, while at the same time the onset of the ultimate repulsive regime moves out to larger D values. When the surfaces have finally equilibrated with the solution, no further attraction is observed, and a monotonically increasing long-ranged, reversible repulsion sets on, as the surfaces are compressed, at a surface separation $D = 1.7 \pm 0.2R_g$ (for the two molecular weights studied).

(iii) Extreme dilution of the polymer solution by exchange with pure solvent (after equilibration in the former) again leads to an initial attraction on approach and the ultimate repulsive regime moves to lower D values, much as in the partially incubated case in the solution.

The origin of the attraction between the partially incubated surfaces appears to be a bridging of the intersurface gap by adsorbed polymer (though other explanations are possible), and the attractive interaction is correlated with the extent of polymer adsorption; the attraction is strongest at the lower incubation times, and disappears altogether once equilibrium adsorption from solution has taken place. The ultimate repulsion between the surfaces is probably mainly due to an osmotic repulsion at the higher polymer concentrations in the gap resulting from compression of the irreversibly adsorbed layers.

APPENDIX

The experimental configuration of two crossed cylindrical surfaces, mean radius R, a closest distance D apart ($D \ll R$), has a relative geometry closely resembling that of a sphere (radius R) on a flat (13). Figure 10 shows approximately to scale a section through the point of closest approach O between a sphere (radius $R \simeq 5$ mm) and a flat surface at a separation D_0 ($\simeq 30$ μm). To estimate the time required for full adsorbance (to a value $\Gamma = \Gamma_{eq}$) of polymer on the surface near O we proceed as follows.

For a polymer concentration C/unit volume, and in the absence of stirring, the gap between the surfaces about O will be depleted of polymer when an amount

$$\Gamma \simeq \tfrac{1}{2}CD_0 \text{ per unit area}$$

has adsorbed on each surface, for adsorption rapid relative to the time required by polymer from the bulk to diffuse to O. At surface separations

$$h > h_0 = \frac{2\Gamma_{eq}}{C}$$

we thus expect the adsorbance to rapidly reach its limiting value Γ_{eq}; if $x(h)$ is the radial distance from O to the point of surface separation h, regions at $x > x(h_0)$ can act as reservoirs of polymer to re-supply the depleted gap at $x < x(h_0)$. The characteristic time τ for the surfaces at O to attain the limiting adsorbance Γ_{eq} will then be of order $[x^2(h_0)]/\Delta$, where Δ is the diffusion coefficient of the free polymer in solution (as long as h, $D_0 \gg R_g$). From the geometry,

$$x^2(h) \simeq 2R(h - D_0) \quad \text{for} \quad h, D_0 \ll R$$

putting in values for the present system

$$\Gamma_{eq} \simeq 2 \text{ mg m}^{-2}, \quad C = 10\ \mu\text{g ml}^{-1},$$

$$D = 30\ \mu\text{m}, \quad \text{and} \quad \Delta \simeq 10^{-7}\ \text{cm}^2\ \text{s}^{-1}$$

(for PS of MW = 10^6) gives $\tau \simeq 0$ (5×10^5 s) (some days).

In practice, any compression/decompression of the surfaces, and in particular withdrawal of the surfaces from near contact (where forces are being measured) to a separation $D_0 \simeq 30$ μm (for additional incubation), leads to some agitation of the solution about O, and is equivalent to stirring: this must have the effect of reducing τ.

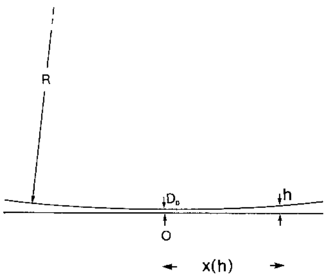

FIG. 10. Section through the point of closest approach O between a sphere and a flat surface at a separation D_0.

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