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Effects of Time and Compression on the Interactions of Adsorbed Polystyrene Layers in a Near-Θ Solvent

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ABSTRACT: We have investigated the effects of molecular weight, adsorption time, force-measuring rate, and repeated compression−decompression cycles (previous history) on the interactions between high molecular weight polystyrenes adsorbed on mica from dilute cyclopentane solutions under near-Θ solvent conditions. On the first slow approach, a long-range bridging attraction, which needs several minutes to fully develop for each incremental movement of the surfaces, is found at separations below $6R_g$. The interaction becomes a steep hard-wall repulsion at separations below $0.5R_g$. With increasing molecular weight the thickness of the adsorbed layers increases, and the attractive bridging force on approach and adhesion on separation decreases. Self-consistent field theory underestimates the onset location and depth of the attractive minima but accurately predicts the location of the hard-wall repulsion. For shorter (nonequilibrium) adsorption times, the bridging attraction and adhesion are stronger and occur at smaller separations, consistent with incomplete coverage. If the first approach and compression are done slowly, the layers become “irreversibly” compressed and no long-range bridging attraction is observed on subsequent approaches, even after allowing the polymer layers to relax for several days.

Introduction

Polymers adsorb on solid surfaces if the attraction of the polymer for the surface outweighs the polymer’s loss of configurational entropy upon adsorption. The initial stages of the adsorption process are relatively fast[1] and, for practical applications, irreversible, due to the small probability of complete desorption of a chain attached to several surface sites.[2] These features make adsorbed polymer useful for both steric stabilization and polymer-induced flocculation of colloidal dispersions.

Recent reports[1,3] have reviewed efforts to quantify the kinetics of polymer adsorption and desorption. Experimental studies have sought to discriminate among various steps in the adsorption process, including polymer convection and diffusion through solution toward the surface, initial attachment, and equilibration within the adsorbed layer. The mass transfer and attachment steps have been thoroughly studied.[1,3] However, there have been no systematic studies of the kinetics of equilibration of polymers within adsorbed layers undergoing interactions.

Theoretical models have attempted to predict polymeric interaction forces for two limiting cases. Under full equilibrium conditions, the polymer freely redistributes between the adsorbed layers and solution during an interaction. Constrained (or restricted) equilibrium conditions imply that the adsorbed amount of polymer remains constant during an interaction. In both cases, the interaction rearranges the distribution of polymer segments among trains, loops, tails, and bridges, but the set of polymer configurations within the adsorbed layers remains an equilibrium distribution.

Changes in the polymer distribution have direct consequences for the forces between the interacting surfaces. For the full equilibrium situation, earlier analyses[4,5] presumed that the differential surface tension is the appropriate work potential for polymeric interactions. These models predict a monotonic attraction between polymer layers. More recent models,[6,7] based on the fundamental postulates of mass, energy, and linear momentum conservation, have shown that the product of stress and differential strain is the appropriate work potential. The result is that the disjoining pressure (force/area) between two interacting polymer layers equals the excess osmotic pressure evaluated at the centerline between the surfaces. The predicted monotonic repulsion (at full equilibrium) is entirely analogous to the monotonic repulsion predicted for electrostatic interactions between like-charged surfaces in electrolyte solutions. In physical terms, compression of an adsorbed polymer layer decreases the entropy of the polymer; some molecules leave the gap, but some remain adsorbed because they form additional surface contacts with sites vacated by the departing molecules. The average number of polymer−surface contacts per molecule increases with further compression, so the polymer never completely leaves the gap. The centerline polymer concentration, the centerline osmotic pressure, and the disjoining pressure all rise monotonically with increasing compression.

For the interactions under constrained equilibrium conditions, the work potential contains an additional contribution due to the constraint of constant adsorbed amount.[6,7] Upon compression, the disjoining pressure may go through an attractive minimum before becoming steeply repulsive. Minimizing the free energy might occasionally favor additional polymer adsorption as two surfaces approach: the energy gained by bridging molecules outweighs the entropy loss. However, the constant adsorbed amount constraint prevents increases as well as decreases in the adsorbed amount. Thus the polymer that is in the gap redistributes to form bridges, the centerline osmotic pressure decreases, and the

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disjoining pressure becomes attractive. Model predictions indicate that further compression ultimately leads to steep hard-wall repulsion.

An alternative model for the interactions at constrained equilibrium has been suggested by Ingersent et al.,[8] using a mean-field model based on a Cahn–de Gennes approach. The differences in the predictions of the model in ref 8 and our model,[7,9] described further below, will be discussed together with our experimental results.

Experimental results have been obtained with a surface forces apparatus on attractive interactions between adsorbed polymer layers that can be rationalized by the bridging mechanism.[10–14] For polymer adsorption below the equilibrium level, incomplete surface coverage facilitates bridge formation and leads to relatively deep attractive minima.[11,12] At adsorption equilibrium, coverage increases with polymer molecular weight, and consequently, bridging decreases; the corresponding force–distance curves display weaker attractive minima that disappear at high polymer molecular weight. The bridging attraction is generally long-ranged (several R_g) and can be stronger than van der Waals and depletion forces at similar surface separations. The force invariably becomes repulsive at small surface separations. The ultimate layer thickness, denoted as the compressed layer thickness, is always smaller than R_g per surface.[4] In principle, the compressed layer thickness should be approximately equal to the adsorbed amount divided by the bulk polymer density, assuming that most of the solvent has left the gap.

Experimentally measured attractive interactions between adsorbed polymer layers in poor solvents have been attributed to a combination of bridging and polymer–polymer attraction.[10,11] The individual contributions of these components to the net force cannot, however, be easily distinguished. Compared to interactions in good or near-Θ solvents, force–distance curves obtained in poor solvents show a shorter-ranged, but stronger, attraction due to the segment–segment attractions. Because the adsorbed amount is higher in poor solvents, the compressed layer thickness is greater than that for good or near-Θ solvents.[11,14]

We have studied the complete interactions (on approach and separation) of two surfaces covered with physisorbed layers of high molecular weight homopolymer, polystyrene, adsorbed from dilute cyclopentane solution under near-Θ solvent conditions (23 °C). The structure of the adsorbed layers, and thus the range and magnitude of the interactions, should be determined by the adsorbed amount of polymer, if the surface energy and polymer–solvent interaction conditions are kept constant.[4] The adsorbed amount of polymer is generally not strongly dependent on the bulk solution concentration of a very dilute solution.[4]

The polystyrene–cyclopentane system and also polystyrene in cyclohexane, have been extensively studied, especially the effects of molecular weight, solvent purity, and temperature. Experiments have been performed both in solvents containing trace amounts of water or other components[10–13] and in dry solvents.[11,14] The presence of minor components can have a significant effect on the quantitative details of the interaction forces at small surface separations. On the basis of previous investigations of this system[14] and on related work on the kinetics of polymer adsorption,[1] we suspect that the chain relaxation processes within the adsorbed layers in this system are slow, especially for higher molecular weights. Possible effects of adsorption time, the presence of solute contamination altering the solvent quality, and the time allowed for equilibration in confined geometries have been discussed, perhaps most extensively by Hu and Granick[14] but also by Almog and Klein.[12] These experimental parameters have not been optimized in the same experiment, nor have the effects of nonequilibrium conditions, different approach and separation rates, and previous history on the interactions been systematically investigated.

The interactions in the polystyrene–cyclopentane system under Θ conditions have been modeled previously by Ingersent et al.,[8] who obtained qualitatively similar force–distance curves to those in the experimental results in ref 12. However, the model in ref 8 was found to underestimate the extension of the attractive bridging force and the thickness of the adsorbed layer at the “hard-wall” by a factor of 4 and the magnitude of the interaction forces by a factor of 2.5.

We have studied the effects of molecular weight, adsorption time, force-measuring rate, and number of compressions on this system at constant temperature and quantified the suspected effects of the adsorption and equilibration times during a measurement. In addition, we have found a number of interesting features, not expected or fully appreciated earlier. It will be apparent that the interactions in this system are not only strongly time-dependent but also dependent on the previous history of the interacting surfaces. The experimental results will also be compared to results on interaction forces and adsorbed amount of polymer obtained from a recent model based on self-consistent field theory.[7,9]

Experimental Section

The interactions were studied using a Mark III surface forces apparatus. The technique has been described in detail elsewhere.[15,16] Interactions are measured by monitoring the actual change in separation of two surfaces, one mounted on a rigid support and the other suspended on a weak force-measuring spring, whose deflection during an interaction is also measured. The separation between the surfaces can be controlled to about 1 Å and independently measured with the same accuracy by a multiple beam interference technique. The spring constant, k, used in these experiments was chosen to be in the range $k = 5 \times 10^4$ to 2×10^5 mN/m. One advantage of the distance control in the Mark III model is the relatively short mechanical path between the two surfaces, which reduces thermal drift to a minimum (less than 1 Å/min if the temperature is controlled to within 0.1 °C).[16] Since only a small volume (about 73 mL) of solution is needed to fill the chamber of the instrument, the system can also reach thermal equilibrium rapidly with the surroundings.

The mica sheets were glued onto cylindrical silica disks. The glue chosen[17] was a 1:1 mixture of dextrose (Fisher) and D-(+)-galactose (Sigma, purified grade), which does not dissolve in cyclopentane. The molten sugar mixture does not spread on the surface of the disk, but when a sheet of mica is placed on a small drop of the melt, it rapidly spreads in the narrow gap between the mica and the disk, forming a very smooth adhesive layer between them.

Cyclopentane (Fluka, for UV-spectroscopy, purity >99%) was distilled (bp 49 °C) under nitrogen in a clean and dry glass apparatus before use. The Θ temperature for polystyrene in cyclopentane is 19.5 °C.[18] In this study, all experiments were carried out at 23.0 ± 0.5 °C.

The polystyrene was obtained from Polysciences, Inc. and was used as received. When not in use, the polymer was stored in an evacuated desiccator to ensure dryness. Stock solutions of polystyrene in pure, freshly distilled cyclopentane were prepared in advance of each experiment.

The contact between two clean mica sheets in dry nitrogen gas, which represents the “zero” distance ($D = 0$) between the surfaces, was determined before solvent was added as follows: The chamber of the instrument was filled by injecting pure, dry cyclopentane through a previously flush-cleaned Millipore Acrodisc CR PTFE filter (pore size 0.2 μm). During filling, the instrument, which is attached to its base plate by hinges, was tilted to an upright position so that the two surfaces face each other in a vertical plane. When the surfaces are close together, the capillary force will cause the surface of the rising liquid to pass very rapidly through the narrow gap between the surfaces, and this minimizes deposition of possible surface active contaminants. The surfaces were allowed to equilibrate in pure cyclopentane for several hours before starting the first force measurements.

Subsequently, 2 mL of cyclopentane was removed with a syringe, and 2 mL of concentrated polystyrene solution was injected through the PTFE filter. The resulting mass concentration of polymer was 0.155 ± 0.005 g/dm^3, which is less than $^1/_{100}$ of the overlap concentration. The surfaces were kept close together during the injection of polystyrene solution followed by mixing with the syringe. After about 30 min, when any possible dust particles in the solution have settled, the surfaces were separated to 1−1.5 mm to let the polymer adsorb for various times. The thickness of the adsorbed layer was determined from the force measurements at different contact positions after varying adsorption times. The interactions between the adsorbed layers were determined by waiting long enough between measured points to ensure that the movement in or out had completely stopped.

The experimental difficulties associated with long waiting times between points were reduced by controlling the temperature accurately and by waiting long enough with the surfaces close together (but separated more than the range of the interaction) before starting a force measurement. This ensures that any effects of flow or possible mechanical tension in the distance controls (from bringing the surfaces close from a large separation during the adsorption) have had time to relax so as not to cause drifts during the force measurements. The Mark III SFA is constructed so as to minimize drifting, and no systematic drift was observed during the experiments presented here. One observes a somewhat larger scatter than usual in the region where there is no force between the surfaces, an effect possibly due to small, unsystematic thermal drifts during the waiting time between the measured points. This may or may not be present when a force acts between the surfaces.

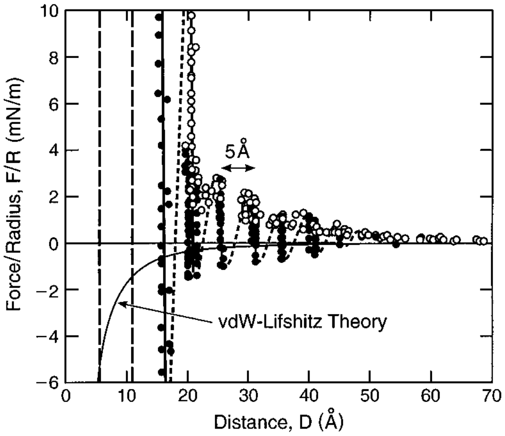

Figure 1. Oscillatory force profile between two mica surfaces in pure, dry cyclopentane at 23 °C, indicating the presence of quasi-layered cyclopentane molecules between the two surfaces. The open symbols represent several measurements on approach, and the filled symbols are the corresponding measurements on separation. The transition from $D = 20$ Å to $D = 15$ Å occurs off-scale at $F/R \approx +30$ mN/m and the corresponding outward jump on separation occurs from $D = 17$ Å at $F/R \approx -15$ mN/m. Layer spacings of 5−6 Å and 10−11 Å were observed upon further compression (dashed vertical lines). The continuous solid curve indicates the theoretical continuum van der Waals−Lifshitz interaction, $F/R = -A/6D^2$, between two cylindrically curved mica surfaces across cyclopentane at 23 °C ($A = 1.05 \times 10^{-20}$ J).

Table 1. Properties of the Polystyrene Samples

M_w (g/mol)	$P = M_w/M_n$^{a}	R_g (Å)^{19,b}
208 000	1.06	132
400 000	1.06	183
650 000	1.05	234

^{a} Manufacturers data (GPC). ^{b} The effect of a 4 °C increase from the Θ-temperature on the radius of gyration of polystyrene in cyclopentane has been found to be negligible.[14,20]

Theoretical Model

We employed a continuum version of self-consistent field (SCF) theory[9] to generate theoretical predictions of polymer adsorbed amounts and interactions between polymer-coated surfaces. Within the framework of statistical mechanics, SCF theory models polymer molecules as idealized chains of segments distributed throughout space. Polymer−solvent and polymer−surface interactions control the statistical distribution of chain configurations and thus the partition function and free energy. Functional minimization of the free energy yields the equilibrium spatial distribution of polymer segments, which in turn governs all of the other characteristics of the adsorbed polymer layers.

The continuum SCF model[9] differs from the related lattice-based approach[4] in its treatment of polymer chain stiffness. The lattice SCF model equates the volume of a polymer segment to that of a solvent molecule. The continuum SCF model defines a segment by requiring that a real polymer molecule and an idealized chain of segments have (1) the same contour length along the backbone, and (2) the same coil diameter in free solution. This ensures that the idealized chain has the proper stiffness. It also creates a difference between the molecular volume of segments and solvent molecules. Both of these factors influence the balance of energy and entropy that control the equilibrium segment distribution and are thus critical for making quantitative comparisons with experimental adsorption data.

For homopolymer adsorption from a pure solvent, the model[9] requires values of eight parameters as input, including temperature (T), polymer segment length and number of segments per chain (l, Z_p), polymer and solvent molar volumes ($\bar{V}_p$, $\bar{V}_s$), polymer volume fraction in bulk solution (φ_p^b), Flory−Huggins parameter (χ), and the segment−surface interaction parameter (χ_s). The parametrization for polystyrene−cyclopentane[6] at 23 °C gives $l = 1.70$ nm; $Z_p = 1.73 \times 10^{-3}$ (mol/g)M_{PS} (where M_{PS} is the polystyrene molecular weight), $\bar{V}_p = 99.1$ cm^3/mol and $\bar{V}_s = 94.0$ cm^3/mol, $\varphi_p^b = 0.953$(cm^3/g)$c_p{}^b$ (where $c_p{}^b$ is the mass concentration of polystyrene in bulk solution), and $\chi = 0.484$. The exact value of χ_s is not known; we use $\chi_s = 1$ in all cases. The calculated force−distance profiles are insensitive to the χ_s value as long as it is O(1). A bulk solution concentration of 0.155 ± 0.005 g/dm^3 corresponds to $\varphi_p^b = 1.477 \times 10^{-4}$. The values of Z_p for the three polystyrene molecular weights shown in Table 1 are 361, 695, and 1130.

Results

Forces in Pure Cyclopentane. At small separations, below about 50 Å, the force between two mica surfaces in pure, dry cyclopentane (Figure 1) is an oscillatory function of distance, with a period of 5.1 ±

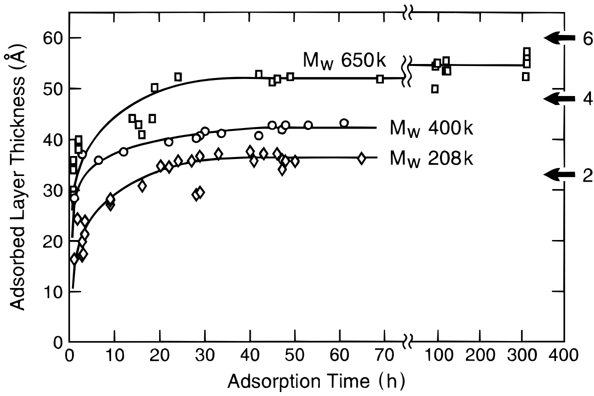

Figure 2. Thickness of the adsorbed polystyrene layer on each mica surface measured at a compressive force of $F/R = +0.5$ mN/m, as a function of adsorption time at 23 °C. The thickness was determined by halving the "hard-wall" separation measured during the force runs (see Figure 3). Diamonds represent $M_w = 208\,000$, circles represent $M_w = 400\,000$, and squares represent $M_w = 650\,000$ in this and all following figures. The arrows indicate the corresponding thicknesses predicted by the SCF model.

0.5 Å, corresponding to the thickness of semiordered layers of cyclopentane molecules.

Oscillatory forces have also been observed for other systems consisting of spherical or unbranched short-chain molecules.[21,22] Since the presence of water or other contaminants is known to disturb the layering and thus the oscillations, the observation of oscillations extending to ∼10 molecular layers served as a check of the purity of the solvent and the surface cleanliness of that particular contact position. The oscillations at smaller separations (below 15 Å) were not studied in detail, since there is a risk of damaging the mica surfaces when separating them from strongly adhesive contacts and/or dragging in particulates with the inward flow of liquid just after a jump apart from a strongly adhesive contact. If one chooses to press the surfaces hard into contact, an incompressible 5−6 Å thick layer, corresponding to one layer of cyclopentane, remains between the surfaces.

Adsorption Times of Polystyrene to Mica. Polymer was added to the solvent, as described earlier, and allowed to adsorb for different times as shown in Figure 2. We find that the thickness of the compressed layer as measured at a particular compressive force ($F/R = +0.5$ mN/m) becomes constant only after adsorption times longer than 24 h, especially for the sample with the highest molecular weight.

The equilibrium thickness of the adsorbed layer remained constant over the time of the experiment, which in general was 3−4 days. The longest time studied was 10 days for the highest molecular weight. In the following figures, all force measurements shown as examples of interactions occurring at adsorption equilibrium are for layers adsorbed for at least 42−45 h. Interactions at nonequilibrium adsorption will also be shown for comparison.

Figure 2 (arrows) also shows values of the compressed layer thicknesses predicted by the SCF model. Layer thicknesses of 33, 48, and 60 Å are predicted for $M_w = 208\,000$, 400 000, and 650 000, respectively.

Measurements of Bridging Forces. When two previously undisturbed adsorbed polystyrene layers are brought together slowly (approach rate < 1 Å/s) for the first time, a long-range, linear, attractive interaction is observed (Figure 3). Since the polymer is in a near-Θ solvent, where there are no attractive segment−segment interactions, and the bulk concentration of polymer is very low, which excludes depletion forces, the probable cause for the attraction is polymer bridging from one surface to the other. As can be seen from Figure 3, with increasing molecular weight, the range of the bridging attraction and hard-wall repulsion increases, while the magnitude (depth) of the attractive force and adhesive well decreases. Similar attractive minima have been measured in previous studies of this system.[12,14] These results are as expected: the longer polymer forms a thicker adsorbed layer, and its tails and loops extend further out into the solution, thus giving rise to a longer-ranged interaction. With increasing molecular weight, though, there are fewer tails per unit area and the adsorbance and surface occupancy are higher, so the attraction becomes weaker.

It was found that, on approach, *each* measured point on the attractive part of the force curve required *several minutes* for the force to develop completely. We found that for the three molecular weights studied, longer waiting times were necessary to ensure that the inward movement of the surfaces toward their new equilibrium position had completely stopped. For $M_w = 208\,000$, 400 000, and 650 000, waiting times of 2.0, 2.5, and 3.5 min, respectively, were required for typical steps of 100 Å. The actual movement occurred during a somewhat shorter time, but an additional waiting time of 30−60 s for each system was allowed to exclude the possibility that the measurements were being influenced by any slowly continuing attraction or a thermal drift. This slowly equilibrating interaction, requiring surfaces to approach each other more slowly than 1 Å/s, is most likely due to entanglement relaxations during the re-equilibration of polymer in the adsorbed layer and, at smaller separations, additional hydrodynamic interactions whose contributions cannot be easily separated. The slow approach to equilibrium (actually constrained equilibrium since the polymer probably remains in the gap) is not due to a high viscosity of the medium, since the concentration of polymer at large separations is very low and the solvent has a low viscosity. Furthermore, there is no resistance to any additional incremental movement in (which would have been the case in a viscous medium) from any separation within the attractive regime, whether the surfaces have already equilibrated at that particular separation or not.

The corresponding force−distance profiles predicted by SCF theory (Figure 3A−C) are in good agreement with the experimental data for the repulsive regime. They also display the correct qualitative features of the attractive regime but do not give accurate estimates of the onset of attraction or depth of the attractive minima. The depth of the minimum decreases with increasing polystyrene molecular weight in both the experimental data and the model predictions. For the 400 000 and 650 000 molecular weight cases, the SCF predictions of the locations of the minima agree with the measured locations at separations of $D = 0.5{-}0.7R_g$. The lattice-based SCF model[4] gives similar values. However, the predicted location of the onset of the attraction is much less than the measured location. This is probably due to the "ground state" approximation made in the solution of the SCF equations.[7,9] In effect, this approximation leads to the exclusion of tails, leaving only loops to form bridges. Since the loops do not extend as far from the surfaces and must pay a higher entropic penalty to form bridges, the predicted range and magnitude of the bridging attraction are seriously underestimated.

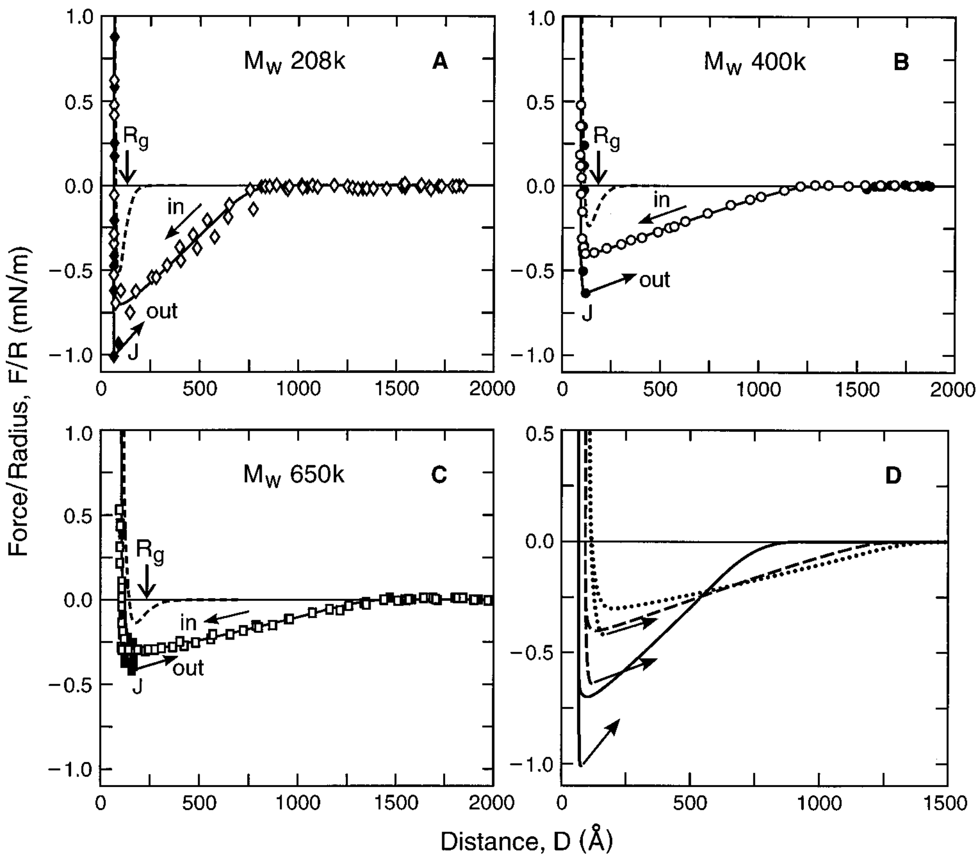

Figure 3. Bridging attraction measured on the first approach (open symbols) and first separation (filled symbols) of not previously compressed polystyrene layers adsorbed for 42−45 h at 23 °C from solutions of concentration 0.155 ± 0.005 g/dm^3. Jump-out positions are indicated by "J", and the radius of gyration by "R_g". The dashed curves in parts A−C are the SCF results for each M_w. The solid curves are drawn as a guide only. Key: (A) results from two measurements at different contact positions for M_w = 208 000, waiting time between each data point 2.0 min; (B) M_w = 400 000, waiting time 2.5 min; (C) two measurements on M_w = 650 000, waiting time 3.5 min; (D) summary of the experimental data in parts A−C, with all data points omitted. In Figures 3−7 it should be noted that since different spring constants were used in the force measurements, the arrows indicating instability jumps out (whenever $\partial F/\partial D > k$) point in somewhat different directions.

Adhesive Minima. As shown in Figure 3, upon decompression, an adhesive force keeps the surfaces together at the "hard-wall" until they jump apart (from positions marked "J"). This adhesion is stronger for the lower molecular weight polymer. Since the waiting time between each point on the curves was kept the same (2−3.5 min) during compression and decompression in the repulsive/adhesive regimes as when measuring the bridging attraction at larger separations, the total time in "hard" contact was about 30−40 min. No change in the interactions from a possible desorption of polymer was measured for different short times (less than 40 min) in contact, which is consistent with the observations reported previously by Hu and Granick.[14]

In a few experiments, the surfaces were kept at separations within the purely attractive regime, i.e., at distances between $1R_g$ and $6R_g$, and never compressed to the "hard-wall". Generally, the force curves were reversible and no additional adhesion was observed upon separation. On a subsequent approach of the surfaces, a similar attraction would develop as during the previous approach.

Repulsion. On compressing the surfaces beyond the attractive regime, one finds a steeply repulsive regime representing a layer of adsorbed polymer which does not appear to change its "hard-wall" thickness with time at the adsorption times (up to 10 days) and low compressions (F/R < 2 mN/m) we have studied. Only when forcing the surfaces closer at high pressures (using the coarser distance controls of the Mark III SFA) at the end of an experiment, i.e., applying a pressure of about 5×10^5 Pa, which is 1 order of magnitude larger than during an ordinary experiment, does one observe a gradual diminution in thickness until an incompressible layer remains, having a thickness of about 60% of the "hard-wall" thicknesses shown in Figure 3. The thickness of the compressed layer on one surface is thus 60% of the thicknesses shown in Figure 2. A separate set of experiments, the results of which are shown in Figure 4, was done for M_w = 400 000 and 650 000 with a higher spring constant ($k = 9 \times 10^5$ mN/m) to show the full force curves at high pressures. An incompressible layer is reached at $F/R \approx 60{-}100$ mN/m. At these large compressions, the separations observed (either during a force measurement or by compressing the polymer layers manually with the coarse distance controls) correspond to layers with thicknesses of approximately 3, 4, and 5 polymer chain diameters (segments widths) on each surface for M_w = 208 000, 400 000, and 650 000, respectively.

The SCF model provides predictions of the location and steepness of the repulsion that agree well with the measured repulsion. At constant interaction energies as large as 40 mN/m, the predicted range of the repulsion is within 1 nm of the measured range. For larger interaction energies, the predicted repulsion has a shorter range than the measured one. The discrepancy could be due to lack of equilibration: given the extreme level of compression, it seems likely that polymer molecules would become trapped in nonequi-

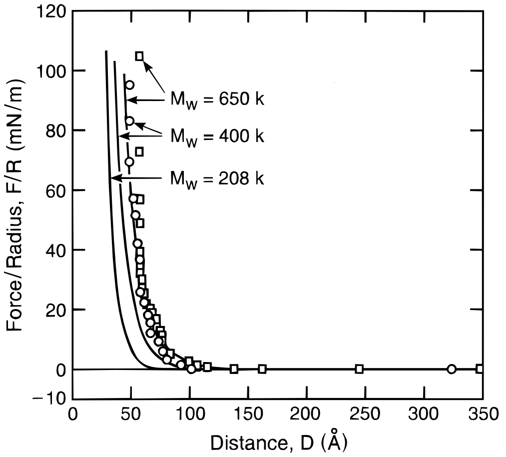

Figure 4. Compression to $F/R \approx 100$ mN/m, i.e., to 60% of the thickness in Figure 3, for M_w = 400 000 (circles) and 650 000 (squares). The corresponding SCF results for M_w = 208 000, 400 000, and 650 000 are shown as solid curves.

librium configurations, at least on the time scale of the experiments.

Subsequent Force Measurements. Once the polymer layers have been compressed slowly during the first force measurement as in Figure 3, the layers remain compressed upon separation and subsequent compressions (Figure 5) and do not appear to re-expand over periods of 3−4 days (up to 10 days in one experiment with polystyrene of M_w = 650 000). The second and subsequent force measurements for the different M_w values were done with the same waiting times between data points as in Figures 3A−C.

Generally, during a second compression, no force—either attractive or repulsive—is observed at the separations where a bridging attraction was seen during the first compression. Occasionally, a very weak attraction or repulsion or an unsystematic combination of alternating attraction and repulsion sets in at separations corresponding to the range of the bridging interaction, but the magnitude of this force was always much less (≤5%) than the bridging attraction measured on the first approach.

However, the hard-wall repulsions arising when compressing the already compressed adsorbed layers were found to be at the same separations as on the first approach. In addition, when separating the polymer layers after applying a similar compressive pressure for the same total time in “hard contact” as during the first approach, a similar adhesion force was measured on the second and all subsequent force measurements.

It was also found that the slow second and subsequent approaches and separations of two previously compressed polymer layers are in most cases totally reversible, with no adhesion observed, if the layers are not compressed to more than about $F/R \approx +0.1$ mN/m during the approach. In addition, leaving two previously compressed surfaces in contact at the hard-wall separation without applying a force (i.e., at the smallest separation where $F/R = 0$ for each molecular weight in Figure 5) for the same length of time as surfaces were compressed during the force measurements above (30−40 min) does not give rise to adhesion. The adhesion minima shown in Figure 5 obviously develop only when the polymer layers are compressed above some critical value around $F/R \approx +0.1$ mN/m.

Once compressed, the interactions of the polymer layers are reproducible for up to 4 days; i.e., the long-range bridging attraction seen during the first approach does not develop again, indicating that the polymer layers remain in the compressed state for up to 4 days and, in one single case, for the highest molecular weight, for 10 days. The relaxation processes in this system are therefore either very slow, or the layers are compressed to an equilibrium state on the first slow compression and then remain there.

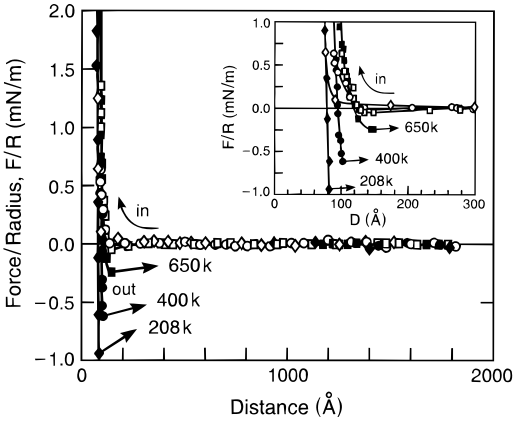

Figure 5. Force profiles during the second (and subsequent) approaches and separations of the previously compressed polymer layers of Figure 3. Symbols and waiting times are as for Figure 3. The inset shows the interactions at small separations. The forces on approach were always very small compared to the bridging force observed during the first approach (shown in Figure 3) and were sometimes zero all the way in to the repulsive “hard-wall”, sometimes very slightly repulsive or attractive in the regime below 250 Å (as seen in the inset), independent of the molecular weight. In contrast, the hard-wall repulsion and the adhesion on separation were identical to the ones observed during the first approach.

Incomplete Adsorption. We have established that the thickness of the layer adsorbed on each surface, as measured at $F/R = +0.5$ mN/m, reaches a constant value after 24−40 h, as shown in Figure 2. Before the adsorbed layer reaches its equilibrium thickness, the forces, shown in Figure 6, are qualitatively similar to the “equilibrium” forces, but the range of the bridging attraction is shorter, the adsorbed layer (hard wall) is thinner, and the depths of the attractive minima on the first approach and separation are deeper. The effect of the shorter adsorption time on the properties of the polymer layer appears to be similar to the effect of lower molecular weight on the interactions at equilibrium adsorption.

In Figure 6, the development of the attraction and adhesion during the first hours of adsorption is more apparent for the lower molecular weight and the development of the range more pronounced for the higher molecular weight. The bridging attraction between these incompletely adsorbed layers, which are far from adsorption equilibrium, also disappears after the first slow compression.

Effects of Approach Rate. If one brings the surfaces toward each other on the first approach faster than the rate needed for the bridging attraction to fully develop, several different, nonequilibrium phenomena may be observed (Figure 7). These include a weaker and approximately *exponential* long-range attraction, with a shorter range than obtained in “slow” measurements (such exponential, as opposed to linear, force profiles have been measured in previous studies, cf. ref 11 on the cyclohexane and ref 12 on the cyclopentane system), or, in particularly rapid measurements, hardly any attraction at all until the hard wall is reached (as noted for rapid measurements in ref 14). In both cases,

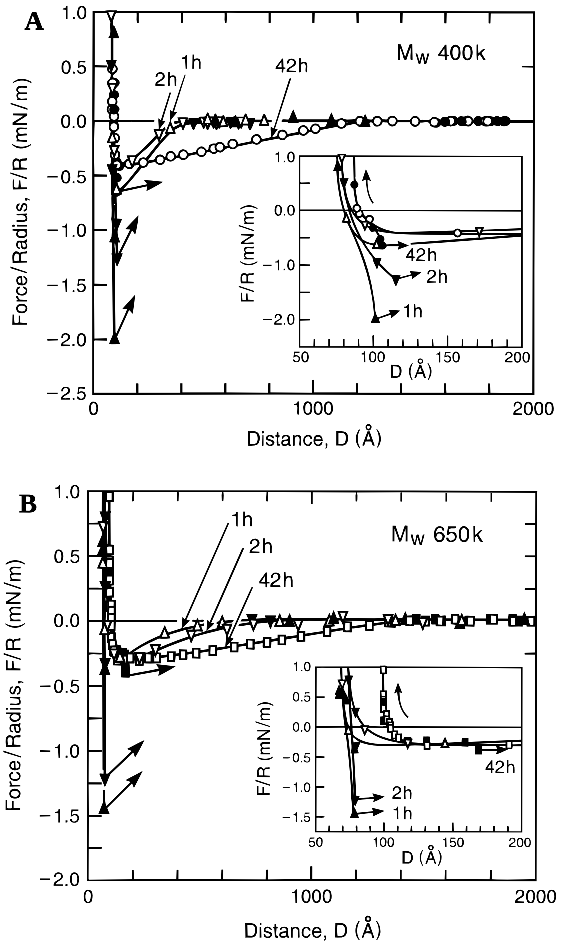

Figure 6. First approach interactions after adsorption times of 1 and 2 h (triangles “up” and “down”, respectively), compared to the equilibrium interactions from Figure 3 (with symbols as in Figure 3) for (A) $M_w = 400\,000$, waiting time between data points 2.5 min, and (B) $M_w = 650\,000$, waiting time 3.5 min. Open symbols denote approach, and solid symbols, separation. The inset in each figure shows the interactions at small separations in greater detail. (Since different spring constants were used in the experiments, the jump-out arrows point in different directions).

there is generally a slow but distinct instability (an inward jump, which takes a couple of minutes) at smaller separations, as indicated by the inward arrows in Figure 7.

The interactions observed during a fast run are quite reproducible, including the long-range attraction, during the second and subsequent approaches. This may explain why some of the effects seen above, such as the “permanently” compressed layers after a first, slow approach, have not been previously observed in experiments where the force measurements were done more rapidly.[11,12] In our “fast” measurements, the force was somewhat varying, as can be expected for a nonequilibrium situation, but the attractive part had an exponential shape with a decay length of 150−250 Å, which happens to be on the order of R_g for the polymer samples studied. In Figure 7 the onsets of the attraction for the different molecular weights almost coincide. This is probably an effect of the differences in time needed for the forces to develop for the different molecular weights.

After several “fast” compressions and separations, the range of the bridging forces and the depths of the attractive minima become gradually smaller until the layers have become completely compressed and only a hard-wall repulsion remains. It was interesting to note that, even after a fast compression, the adhesion force measured on separation is similar in magnitude to that found after a slow compression.

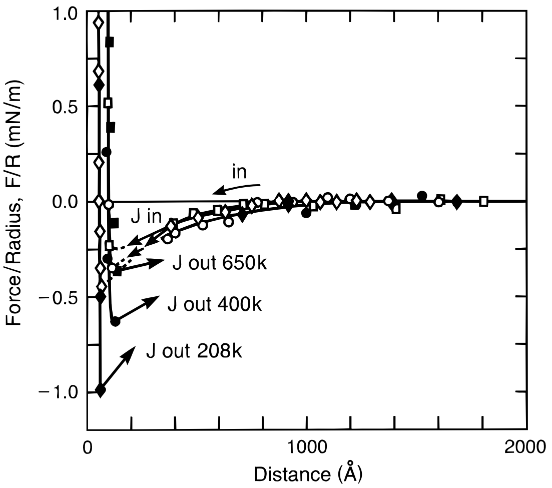

Figure 7. Force profiles at adsorption equilibrium during a first approach at a rate of 10−20 s between data points (approach rate 5−10 Å/s). Symbols are as in Figure 3. These measurements show a nonlinear long-range attraction (exponential, decaying approximately as D/R_g) and instability jumps (“J in”) at smaller separations. The adhesion and jumps apart on separation (“J out”) were similar to those observed during slow measurements (cf. Figure 3).

Effects of Water. The oscillatory force observed across pure, dry cyclopentane indicates that the solvent does not contain water, but one may deliberately introduce water into the solution at any stage during the experiment. We did not find a significant effect on the adsorbed amount of polymer or the magnitude of the long-range forces in a system where the solvent was saturated with water after the adsorption. However, in the presence of water, the adsorbed polymer layers can, unlike in the dry solvent, be displaced from the surfaces by applying a large compressive force of approximately 50−100 mN/m (corresponding to a pressure in excess of 5×10^5 Pa). A similar monotonic decrease in the thickness of the adsorbed polymer layer was observed during the compression as in Figure 4 (which shows the compression of a water-free system) until the whole polymer layer suddenly is displaced from the gap between the surfaces. The adhesion between the two surfaces after the polymer has been removed is stronger than the one measured when polymer remains between the surfaces (i.e., stronger than the adhesion shown in Figures 3, 5, and 7). The effects of water, which have been studied in detail by Marra and Christenson[23] for polystyrene adsorbed on mica from mixtures of cyclohexane and polar solvents, are most likely due to the hydrophilicity of the mica surfaces, which allows water to displace or compete with the polymer for the polar surface binding sites on mica.[23]

Discussion

Equilibrium Adsorption. The time needed to reach equilibrium adsorption, or a layer thickness that does not change with time, was found to be longer than previously expected. The rate of adsorption is determined by the diffusion of polymer to the surfaces and the rate of binding and desorption. The rate of polymer diffusion through a very narrow gap has been discussed by Almog and Klein, who found experimentally that the adsorption of polystyrene from cyclopentane onto mica surfaces kept at a separation of 30−100 μm at 23 °C was significantly restricted.[12] Similar experiments have also been carried out for polystyrene in cyclohexane under poor solvent conditions.[11] Almog and Klein estimated the characteristic time needed for saturation adsorption in a small gap of 30 μm, from the diffusion constant ($\sim 10^{-7}$ cm^2 s^{-1} for polystyrene in bulk solution[24]), to be on the order of several days.[12] (It appears, however, that most experiments were not done after initial adsorption times longer than 16 h.) In our experiment, we have taken care to keep the surfaces at a large separation (1−1.5 mm) during the adsorption, and the solution was also well stirred by mixing the entire solution with the syringe while injecting the polymer. The adsorption on each surface should thus be equivalent to adsorption on a single, isolated surface, unaffected by the presence of another.

The compressed layer thicknesses, as estimated from the separation at which $F/R = +0.5$ mN/m, are comparable to the results obtained by others[14] for similar molecular weights at identical solution conditions and similar adsorption times. For the same level of repulsion, the SCF model predicts compressed layer thicknesses that are in reasonable agreement.

As discussed below, the adsorption is also qualitatively similar to what has been observed by Terashima[25] for the adsorption of polystyrene with $M_w = 775\,000$ on mica plates from cyclohexane at the Θ temperature 34.3 °C. In ref 25, the increase in the adsorbed amount starts to level off after 5−10 h, which is similar to our results obtained from the force measurements. One may, however, note that the scatter in the measured mass adsorbed in ref 25 became smaller only after an adsorption time of about 24 h, which we also observed.

The adsorbed mass/area for each M_w was estimated from the experimentally determined thickness of the maximally compressed layer at $F/R \approx 100$ mN/m (see Figure 4), which gave thicknesses that were about 60% of the “hard-wall” thickness for each surface at $F/R = +0.5$ mN/m, shown in Figure 2. Careful measurements of the refractive index by Klein[10] on polystyrene in cyclohexane also point toward the conclusion that the compressed “hard-wall” layers at low F/R (around 0.5−1 mN/m) do not consist of pure polystyrene but include some solvent, even under the poor solvent conditions studied in ref 10. Assuming that the density of polystyrene is 1.05 g/cm^3,[24] the equilibrium mass adsorbed on each surface, calculated from the thickness of the incompressible layer at $F/R \approx 100$ mN/m (which, however, probably still contains some solvent), is 2.1, 2.6, and 3.5 mg/m^2 for $M_w = 208\,000$, 400 000 and 650 000, respectively. This extrapolates to approximately 4 mg/m^2 for $M_w = 775\,000$, which is slightly lower than the value of approximately 5 mg/m^2 obtained by Terashima for $M_w = 775\,000$ in cyclohexane at the theta temperature.[25] This result is in fact expected, since the adsorption in our experiment was from a better-than-Θ solvent, which is expected to give a lower adsorption than that at Θ conditions. In previous SFA experiments on polystyrene in cyclopentane at 23 °C, it was found from measurements of the refractive index that the amount adsorbed was 2.5 ± 1.5 mg/m^2 for $M_w = 600\,000$.[12] In another investigation, the adsorbed amount, determined from the thickness of the compressed layer at $F/R = 2$ mN/m, was 5 mg/m^2 for $M_w = 500\,000$.[14]

The corresponding values of the adsorbed amount predicted by the SCF model are 1.08, 1.31, and 1.47 mg/m^2 for the three polystyrene molecular weights. The differences between these values and the experimental ones could be due to a failure of the model. Previous comparisons for polystyrene−cyclohexane[9] indicated that the SCF model predictions for the adsorbed amount were too low, but only by about 0.5 mg/m^2. Alternately, the discrepancy could be caused by a substantial amount of cyclopentane remaining in the strongly compressed polymer layers, leading to an overestimate of the adsorbed amount from the measured force−distance curves. The model presented in ref 8 predicts a smaller adsorbed amount than the SCF model: 0.4 mg/m^2 for $M_w = 600\,000$.

The SCF model gives good quantitative predictions of the location of the steep repulsive wall (Figure 3). The model employs no adjustable parameters; all input data are obtained from experimental conditions or independent experiments. The success of the model probably results from its ability to describe the structure of layers containing mostly loops. The repulsive force at small distances is probably dominated by the entropy loss associated with the compression of loops. However, the accuracy of the predicted force decreases at extreme compressions (Figure 4), perhaps because the adsorbed polymer molecules can no longer equilibrate within the time scale of the experiment.

Bridging Attraction. Bridging attraction can occur only when adsorption sites are available on the opposing surface, i.e., when the coverage is below saturation.[4] On the basis of our measurements of the adsorbed layer thicknesses and interactions after different adsorption times, and on the observations by Terashima[25] on the *lateral* compressibility and stability (or lack thereof) of adsorbed polystyrene films removed from mica surfaces after different adsorption times, we propose that the significantly stronger bridging attraction and adhesion at low adsorption times are due to the low adsorbed amount of polymer and low coverage of the mica surface, which exposes more sites available for bridging than at equilibrium adsorption.

As additional polymer molecules adsorb onto the surfaces from solution, the polymer will extend further out into the solution and fewer sites will be available for bridging. This gives rise to a longer ranged but weaker attractive force, similar to the effects of higher molecular weight on the equilibrium interaction. The balance between desorption and rearrangement of segments of already adsorbed molecules, together with the adsorption of new ones, develops slowly in time, eventually leading to the equilibrium thickness and structure. When the adsorption has leveled off, i.e., after adsorption times longer than 40 h, the interactions between the layers, shown in Figures 3−5 and 7, appear to be independent of further adsorption time for at least up to 4 days.

The bridging attraction at equilibrium adsorption has a significantly longer range ($\sim 6R_g$) and is of larger magnitude than that predicted by the SCF model. The ground state approximation employed in the solution[7,9] leads to the elimination of tail configurations. Since loops are less extended and are less able to form bridges, the underestimate of the attraction is not surprising. Similar SFA measurements, performed by Hu and Granick,[14] allowed sufficient time for equilibration and identified attractions that began at distances of $5-6R_g$. However, they observed weaker attractive minima. These data were compared with predictions from the same SCF model;[7] in that case, the model predicted deeper attractive minima[7] than were observed experimentally.

Our experimental data and the SCF model predictions suggest that these long-range interactions are at least initially (at large separations) due to bridging of *tails* from one surface to another. The contribution of tail interactions to the bridging attraction is generally neglected, since the mass of monomers in the tails is a very small part (at high M_w only a few percent) of the total mass of adsorbed polymer. The tails may, however, dominate the interactions at large separations. Recent theoretical work by Semenov and Joanny[26] has shown that in calculations of the monomer density profile for a "saturated" layer adsorbed from a good solvent, tails dominate over loops at distances greater than lZ_p^ν, where ν is the Flory exponent. For $l = 17$ Å and $\nu = 0.6$ (good solvent conditions), tails dominate over loops at distances of approximately 580, 860, and 1150 Å from the surface for $M_w = 208\,000$, 400 000 and 650 000, respectively. This also provides an approximate lower limit for the range of the bridging interaction between *two* adsorbed layers. The onset of our experimentally observed bridging attractions (Figure 3) occurred at separations of about this range.

Is it possible that bridging between tails and the opposing surface alone gives rise to the observed attraction? The interaction energy between two flat surfaces, E_f, can be calculated from the measured force between two curved ones, F_c, using the Derjaguin approximation $F_c(D) = 2\pi RE_f(D)$.[27] For a change in separation of one monomer length, approximately 6 Å, in the linear, attractive regime of the force curves in Figure 3, the experimentally measured change in interaction energy (i.e., the slope of the linear part of the force curve) is 1.0×10^{-6}, 0.4×10^{-6}, and 0.2×10^{-6} J/m^2 for $M_w = 208\,000$, 400 000 and 650 000 g/mol, respectively. Assuming an interaction energy of $1kT$ per segment, the number of bridges needed to achieve this interaction over one segment length is 2×10^{14}/m^2, which is about 2% of the maximum number of tails exposed per surface of approximately 10^{16}/m^2, calculated from the experimental mass/area estimate above and assuming two tails per molecule. The adsorption energy for polystyrene from cyclopentane onto mica is not known, but results from adsorption thin layer chromatography with polystyrene in CCl_4 and cyclohexane on silica at 25 °C give $1.0-1.9kT$ per segment.[28] Measurements by Granick et al.[29] on the adhesion between one poly(α-methylstyrene) covered surface and one bare mica surface in cyclohexane at 25 °C suggest that the interaction energy per segment in that system is $^1/_3kT$ (it was assumed that the whole area (100%) was covered with polymer segments, and because of this the estimate probably represents the lower limit for the adsorption energy per segment). Thus, the interactions observed at large separations could well arise from the bridging of tails only.

In the simple model for the bridging attraction applied above, the change in energy as a function of separation ($\partial E_f/\partial D$) associated with bridging attraction between two *flat* surfaces as a function of separation is a constant, which indeed is what we observe experimentally at large separations as a linear interaction force of constant slope $\partial(F_c/R)/\partial D$ between two *curved* surfaces. At smaller separations (below about $2R_g$), there should be additional bridges arising from interactions between loops and the opposite surface.

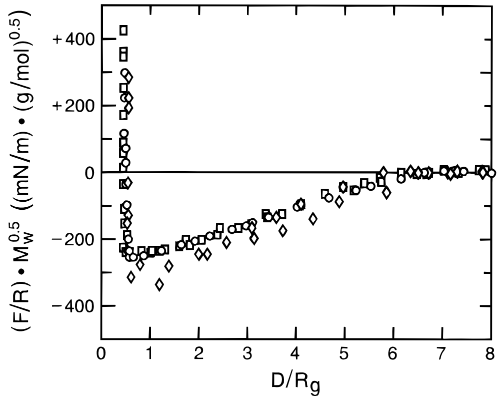

Figure 8. The data in Figure 3 plotted as $(F/R)/(1/M_w^{1/2})$ vs. D/R_g. Symbols are as in Figure 3.

It has been suggested that the magnitude of the minimum in the bridging attraction should scale as $1/M_w$.[4,8] It has also been predicted that the root-mean-square thickness of a layer adsorbed at constant solution concentration (i.e., not effected by the vicinity of another surface) should be proportional to $M_w^{1/2}$.[4] We found that the magnitude of the bridging attraction, i.e., the minimum in the force curve on approach, at equilibrium adsorption is proportional to $1/M_w^{1/2}$, i.e., to $1/R_g$, rather than $1/M_w$, but that the range (bridging force and hard-wall repulsion) is indeed proportional to $M_w^{1/2}$. In a plot (Figure 8) of $(F/R)/(1/M_w^{1/2})$ *vs* D/R_g, the data from Figure 3 collapse to one curve.

As the two surfaces with adsorbed polymer were brought together, the range and magnitude of the bridging attraction were found to depend not only on the adsorption time (discussed above) but also on the time allowed for the interaction to fully develop at each separation. This effect has been noted earlier for this system by Hu and Granick.[14] Apparently, the differences in layer thickness for the three molecular weights, combined with the slow chain relaxations in the adsorbed layers, led to different times needed for the forces to develop. This would include the time needed for penetration and formation of bridges, which requires polymer to diffuse through the opposing layer, and the time needed for desorption, rearrangement, and readsorption of the adsorbed trains on each surface. One may expect this time to depend on the molecular weight and on the availability of exposed sites for bridging after each incremental approach of the surfaces. Experimentally, the time needed for the force to develop, not counting the extra waiting times of 30−60 s, was found to scale approximately as M_w, i.e., as the rate of "snaking" motion in reptation (in the melt or in concentrated solution), which is proportional to $1/M_w$.[30]

Irreversibly Compressed Layers. The interactions during the second and subsequent approaches are distinctively different from the first compression of previously undisturbed adsorbed layers, indicating that an irreversible change in the adsorbed layer occurs during the first slow compression. Compressed adsorbed layers do not relax back to their original state during the times we have studied (days), and the bridging attraction seen on the first approach does not reappear. We ascribe this change to slow relaxations in the high molecular weight system. The possibility of a glass transition in the compressed layer, reducing the mobility of the chains, has been considered.[31] As described above, we estimate the composition of the layer to approximately 60% polystyrene in cyclopentane (by volume). T_g for pure polystyrene is ~100 °C, but a 60% mixture of polystyrene in various solvents appears to have a T_g below 23 °C.[32] A 60% mixture should remain a one-phase system at 23 °C (estimated from refs 18 and 33). A compression of the adsorbed layers to this composition should thus not cause a glass transition or phase separation. Both the glass transition temperature and the phase separation could be significantly altered by the presence of the surfaces or contaminants, which could locally alter the segment−solvent interactions. Examples of the interactions observed between adsorbed polystyrene layers in cyclopentane[13] and in cyclohexane[23] in the presence of other compounds that change the solvent quality have been published. As mentioned in the Experimental Section, care was taken in choosing a high-purity solvent, which was further dried and purified by distillation. It is expected that a worsening of the solvent quality would result in a thicker adsorbed layer and a stronger, more short-ranged attraction than in a near-Θ solvent. We find that our results on thickness and range agree well with the careful experiments under near-Θ solvent conditions by Hu and Granick,[14] and we find no reason to suspect that contamination would be responsible for the irreversibly compressed layers, which were observed in every experiment. Neither should the occurrence of a phase separation or glass transition at a particular compression (i.e., concentration) be dependent on the approach rate, which the formation of "irreversibly" compressed layers was found to be.

Adhesion. Unlike the long-ranged bridging forces, the adhesion force observed on separating two polymer layers which have been pressed together was the same on the first and subsequent decompressions (Figures 3, 5, and 7) and was not affected by the separation rate. It was interesting to note that a compression larger than $F/R \approx +0.1$ mN/m was needed for the adhesion to fully develop during a second and subsequent compressions. We found that the compressed layers expanded somewhat (10−40%, see below) during the decompression, right before the jump apart. This effect was more pronounced for the higher molecular weight, and a similar trend can be found upon inspection of previously published results for similar systems.[10−14,29]

We have estimated the van der Waals attraction between two identical layers consisting of polystyrene (the total amount in the layer being 60 vol % of the volume at $F/R = \pm 0.5$ mN/m for each M_w; cf. section on equilibrium adsorption) and cyclopentane. The adsorbed layers were modeled as consisting of cylindrical polystyrene molecules with a radius of 3 Å in a hexagonal packing in cyclopentane. We estimated the mean separation between planes in the hexagonal structure (with a polystyrene volume fraction of 0.53, 0.45, and 0.37, which is the composition of the layers at the jump-out separations for $M_w = 208\,000$, 400 000 and 650 000, respectively) to be 6.8, 7.4, and 8.1 Å, respectively. We then assumed that the separation of the two mixed layers occurs within such a plane. The attractive van der Waals forces $F_c/R = -A/6D^2$ between the mixed layers at the above layer separations are −1.0, −0.7, and −0.4 mN/m, respectively, which is in surprisingly good agreement with the measured adhesion forces. (The Hamaker constants, A, across pure cyclopentane were estimated from the composition above, using the relation[34] $\epsilon_{\mathrm{mixture}} = \phi_1\epsilon_1 + \phi_2\epsilon_2$, where ϵ_i is the dielectric constant and ϕ_i is the volume fraction of component i). This very simple model does not account for the effect of polymer protruding out from the surface layers, which would act to decrease the attractive force.

An adhesion due to van der Waals interactions should not be sensitive to the rate of approach and separation, as was confirmed experimentally, and should only be dependent on the composition of the interacting layers, i.e., in this case on the surface separation and polymer conformation adopted on compression and decompression. As a result, there is no significant difference in the adhesion observed on the first and subsequent compressions, and neither did the rate of the measurements or the waiting times between each approach effect the adhesion, so long as the amount of adsorbed polymer was constant and the applied pressure was the same.

Polymer Equilibration during Interactions. No change in the amount of adsorbed polymer was observed during the short times in contact (30−40 min) in these experiments. A previous study[14] of this system at 23 °C ($M_w = 500\,000$) showed that the adhesion doubled over 14.5 h in contact at $F/R \approx 0$, while the jump out separation decreased by about 50 Å. Although a decrease in polymer adsorption could explain this result, polymer rearrangements were cited as the probable cause since the corresponding "hard-wall" separation measured on compression decreased by only ~10 Å during this time. In another investigation of the system poly(α-methylstyrene) ($M_w \approx 90\,000$) in cyclohexane at 25 °C (poor solvent conditions),[29] a significant decrease of the "hard-wall" thickness to about half of the original and an increased adhesion by a factor of 2 were observed as polymer layers were left in contact at $F/R \approx 1$ mN/m for about 12 h. The more rapid rearrangement of the shorter poly(α-methylstyrene) molecules and the larger applied pressure are the probable explanations for the significant temporal evolution of the force as a function of distance for the poly(α-methylstyrene) system, despite the poor solvent conditions. There are, however, experimental difficulties associated with long times in contact, since thermal drifts and deformation (flattening) of the surfaces may occur that can significantly change the applied force.

At these high molecular weights, the polymer can be considered to be irreversibly adsorbed on the time scale we have investigated. This is because the probability of total desorption of a long chain attached to several places on the surface is very low, and desorption is thus much slower than the adsorption of the same coil from solution. We consider the experimental results to be representative of constrained equilibrium interactions.

In theory, the polymer confined between the surfaces freely rearranges its configurations so as to establish an equilibrium distribution for each incremental approach of the surfaces. Rapid dynamic exchange of polymer segments between the surfaces should result in a strong interdigitation; on separation, the adhesion would be stronger than the van der Waals attraction. The surfaces would also adhere out to large surface separations, since long molecules could be pulled out from the entangled structure. Experimentally, the compression rate needed to allow high molecular weight polymers to achieve a "true" constrained equilibrium is probably very slow. In our experiments, there is no indication of strong interdigitation between the polymer layers. Instead, we observed a separation from an adhesive minimum at small surface separations and "irreversibly" compressed layers which do not give rise to a long-range interaction on a second approach. A slight expansion of the polymer layer on each surface on decompression was observed, but the polymer layers most likely separate along their contact interface in the middle of the gap between the surfaces. Our results suggest that the two adsorbed polymer layers do not have the time to completely rearrange to form their real equilibrium structure within the gap during the compression, in contrast with the assumptions in the theoretical model.

Times much longer than a few hours would be needed to observe changes in the two-layer distribution and in the total amount of adsorbed polymer (the distribution between the layer and the bulk solution). A recent investigation[35] using neutron reflectivity shows that the interdiffusion between polystyrene layers in contact may be slow even at elevated temperatures (∼120 °C). Long measurement times are not practical with our current instrumentation, since long-term thermal drifts would affect the accuracy. In order to study these effects, a relatively low molecular weight polymer would probably be more suitable, especially if one wants to study changes in the thickness of the confined (but not compressed) layer and development of adhesion as a function of time. However, some recent experiments on polyethylene−propylene of $M_w = 5800$ g/mol in a good solvent indicate that even for such low molecular weights, equilibration times in adsorbed layers may still be many hours.[36] Alternately, a more flexible polymer, such as poly(ethylene oxide), might equilibrate faster than polystyrene.[1,3]

It is possible that rearrangement and continuous adsorption/desorption on the surfaces slowly evolve after the initial adsorption and that no real equilibrium is ever reached. However, the interactions measured on first approach did not appear to change once the adsorption has leveled off. Discrepancies between the measured and calculated force−distance curves at large applied pressures (Figure 4) are probably due to experimental difficulties in attaining equilibrium conformation in a confined polymer layer. Nevertheless, the general agreement between the measured force−distance curves with theoretical predictions under constrained equilibrium conditions, highlights the importance of nonequilibrium effects in understanding polymer-mediated colloidal interactions. Future modeling efforts must be able to accommodate different kinds of constraints in space and time in order to fully describe such interactions.

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