

# Universal and System-Specific Features of Surface Forces between Adsorbed Polystyrene in a Near- $\theta$ Solvent

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**ABSTRACT:** Surface forces were measured between mica surfaces bearing polystyrene adsorbed to saturation from dilute cyclopentane solution ( $\theta$  temperature,  $T_\theta = 19.5^\circ\text{C}$ ). The temperatures were 18, 23, 28, and  $34^\circ\text{C}$ . Four conclusions emerge. First, for  $M_w = 515\,000$ , the adhesive minimum grew with the time (up to 14.5 h) that the adsorbed layers were kept together. This suggests the existence of extremely slow chain relaxations. Second, for  $M_w = 490\,000$  and  $515\,000$ , the layer thickness at the point of steep short-range repulsion was substantially less at  $28^\circ\text{C}$  and higher temperature than at  $23^\circ\text{C}$  and lower temperature. This shows that the mass adsorbed was remarkably sensitive to small changes in solvent quality. Third, for  $M_w = 115\,000$ ,  $490\,000$ , and  $1\,080\,000$  at fixed temperatures, the layer thickness at the point of steep short-range repulsion scaled approximately with the radius of gyration,  $R_G$ , just as is expected for the layer thickness at a single surface under poor solvent conditions. Fourth, in comparisons of the long-range forces ( $>R_G$ ) as a function of molecular weight and temperature after forces had equilibrated for up to 2-5 min, the force-distance profiles were reversible, but their sign, strength, and range did not fit a simple pattern. The range of attraction at temperatures above  $T_\theta$  passed through a maximum with increasing molecular weight and increasing temperature. The relative influence of kinetics and thermodynamics on the force-distance profiles is discussed. The initially distinct polymer layers appeared to interdiffuse to only a limited extent over the time scale of the experiment, which implies that the present systems were in metastable states far from thermodynamic equilibrium. A discussion of error and of experimental limitations is included.

## Introduction

New experimental tools open up new fields of investigation. In recent years considerable interest has been excited by the force balance technique, which affords the capability to measure force as a function of separation between two solid surfaces, the distances of separation being comparable to molecular dimensions.<sup>1,2</sup> A review discusses various instrumental approaches that have been taken.<sup>3</sup> Among these, the mica force balance instrument<sup>4</sup> has been used in nearly every recent experiment involving polymers. With this instrument, forces are measured between two cylindrically curved sheets of muscovite mica (radius of curvature ca. 1 cm), the cylinders being oriented at right angles to one another. The Derjaguin approximation (see the Appendix) transforms the measured force into the equivalent interaction energy per unit area of parallel plates at this same separation.

The original impetus to develop this experiment was to test theories of van der Waals forces in air and under vacuum. However, in recent years studies have shifted to the case where a liquid medium separates the two solid surfaces, and many previously unsuspected features of the physics of interfaces have been discovered. In liquids, van der Waals interactions between the solid substrates turn out to be only a small part of the total interaction. Surface-imposed structures of the liquid, of many varieties (electrostatic double layers, hydrophobic and hydrophilic orientation, adsorbed polymers, "structural" ordering of small compact liquid molecules near a flat boundary<sup>1,2</sup>), dominate instead.

A recent paper gives a critical review of prior surface forces experiments concerning polymers.<sup>5</sup> One fruitful theme of research concerns terminally anchored polymers.<sup>6,7</sup> From force-distance profiles in a thermodynamically good solvent, concentration profiles of polymer segments in the direction normal to the substrate have been inferred and compared critically with theory. In this mode of attachment, where anchoring to the surface is either

by covalent bonds or by adsorption comparable in strength to that of covalent bonds, the surface forces between the long dangling chains equilibrate rapidly. On the time scale of this experiment, which is seconds to minutes, the structures of terminally anchored polymers do not appear to depend on the measurement time.

A second theme of research (historically the first to have been studied) concerns adsorbed homopolymers. With homopolymers every segment of the chain is a potential adsorption site whose attachment to the surface is believed to be by weak physisorption, with strength less than 1 kT. The potential adsorption sites adsorb at random. As discussed in several reviews,<sup>8</sup> the concentration profile between solid surface and isotropic solution is described as a statistical distribution of trains, which anchor the chain to the surface, loops of various sizes, which penetrate into the solvent, and dangling tails at the ends of the chains, which may penetrate longer distances into the solvent. One consequence of weak segmental sticking is that the adsorbed chains are not permanently attached. Chains may diffuse about even at overall adsorption equilibrium.<sup>9,10</sup>

Present theories<sup>11,12</sup> to interpret the physics of homopolymer interactions are equilibrium theories. The equilibrium in question is a state of "restricted" equilibrium, since at complete equilibrium, migration of polymer out of the zone of interaction could dissipate any momentary repulsion. The quantity of polymer present is fixed, but chain conformations are assumed to equilibrate as the distance between the solid surfaces is varied. At closest range the forces are determined by considerations of packing the fixed quantity of adsorbed polymer in a restricted volume. At longer range the forces are predicted to be some combination of osmotic interactions (which would depend on the solvent quality) and bridging interactions (the phenomenon that segments on a single chain might adsorb to two mica surfaces at once). In these arguments, the  $\theta$  temperature,  $T_\theta$ , is presumed

to be well-defined and unchanged near a surface.

The original experiments with adsorbed homopolymer involved aqueous poly(ethylene oxide) (PEO), unfortunately an ill-characterized industrial grade.<sup>13</sup> This was followed by studies using clean fractions of PEO in aqueous medium<sup>14</sup> and in toluene.<sup>15</sup> These were thermodynamically good solvents for PEO under the conditions of measurement. Although substantial hysteresis was found over the time scale of a few minutes, reversible measurements were possible with measurement times of 15–30 min per datum. The force–distance profiles were repulsive at all points with the onset of measurable interaction at separation  $(5\text{--}7)R_G$  (radius of gyration in isotropic solution). This range of observed interaction was much larger than predicted by well-known theories<sup>11,12</sup> but, to observe repulsion (not attraction), agreed qualitatively with the expectation that segment–segment osmotic interactions should be repulsive above the  $\Theta$  temperature,  $T_\Theta$ . However, these conclusions were recently challenged by independent experiments,<sup>16</sup> from which it appears that the method of preparing the PEO–toluene solutions can change the outcome of the experiments. These conflicting results have been discussed critically.<sup>5</sup>

Adsorbed homopolymers in binary solution have also been studied at temperatures close to the  $\Theta$  temperature,  $T_\Theta$ . Polystyrene (PS)<sup>17–19</sup> and poly( $\alpha$ -methylstyrene)<sup>20</sup> were studied in cyclohexane ( $T_\Theta = 34.5^\circ\text{C}$ ). Steep repulsion at very short range was found to be combined with attraction at longer range. Attraction developed at separations of  $(2\text{--}3)R_G$ , or even less if coverage of the surfaces by polymer was less than saturated.<sup>19</sup>

The initial experiments were performed in cyclohexane at ca.  $10^\circ\text{C}$  less than  $T_\Theta$ ,<sup>14,15</sup> and the attraction was attributed to osmotic interactions associated with the poor solvent quality. Later, attraction was found to develop even at ca.  $3^\circ\text{C}$  above  $T_\Theta$ , a situation where the osmotic segment–segment interactions were expected to be repulsive.<sup>19</sup> Although in principle this result might have been consistent with an increase in  $T_\Theta$  in confined geometry, experimental support for explanation in terms of bridging was provided by the finding that attraction was larger when the amount adsorbed was less than saturated,<sup>19</sup> a condition expected to facilitate bridging. The experimental difficulty of thermostating this experiment precluded making measurements above  $T_\Theta + 3^\circ\text{C}$  in this system.

Experiments under near- $\Theta$  conditions were also performed with the system PS in cyclopentane ( $T_\Theta = 19.5^\circ\text{C}$ <sup>21,25</sup>). The first experiments,<sup>22</sup> performed at ca.  $3^\circ\text{C}$  above  $T_\Theta$ , found that forces were repulsive at all separations so long as the amount of PS adsorbed had equilibrated. The suggestion was made<sup>22</sup> that different signs of the third virial coefficient might resolve the apparent contradiction that long-range forces at the same temperature of corresponding state were attractive in cyclohexane but repulsive in cyclopentane. The third virial coefficient of PS in cyclopentane is not, unfortunately, known from direct measurement.

Since that initial study, different findings have been obtained using cyclopentane from different sources. Recently we reported a preliminary account of surface force experiments using two other sources of cyclopentane.<sup>23</sup> Surface forces were measured at 18 and  $28^\circ\text{C}$  between mica surfaces bearing polystyrene ( $M_w = 490\,000\text{ g}\cdot\text{mol}^{-1}$ ) adsorbed from dilute cyclopentane solution. Forces at long range were monotonically repulsive at  $28^\circ\text{C}$  and mildly attractive at  $18^\circ\text{C}$ , in good agreement with previous findings,<sup>19</sup> but only provided that a cyclo-

Table I  
Characterization of the Polystyrene Standards

code	$M_p$ , <sup>a</sup>	$M_w/M_n$ , <sup>a</sup>	$R_G$ , <sup>b</sup> Å
A	115 000	<1.04	98
B	490 000	<1.08	203
C	515 000	<1.07	208
D	1 080 000	<1.05	301

<sup>a</sup> Manufacturer's data. <sup>b</sup> Calculated from ref 44.

pentane containing 5% linear pentanes was used. This contrasted with experiments in a more pure (99%) cyclopentane, in which the range of detectable forces was  $(2\text{--}3)R_G$  at  $18^\circ\text{C}$  and  $(5\text{--}6)R_G$  at  $28^\circ\text{C}$ , and the forces at long range were strongly attractive at  $18^\circ\text{C}$  and weakly attractive even at  $28^\circ\text{C}$ . These latter observations were reminiscent of classical behavior measured previously in cyclohexane.<sup>17–20</sup>

The  $\Theta$  temperature of the PS–cyclopentane system allows convenient measurement farther above  $T_\Theta$  than in cyclohexane. Using this system, we have performed experiments at temperatures that range from below  $T_\Theta$  to farther above  $T_\Theta$  than previously. We also investigated the roles of molecular weight and equilibration time.

## Experimental Section

A surface forces apparatus of Israelachvili type<sup>4</sup> was constructed.<sup>24</sup> The details of the experimental protocol have been reported elsewhere.<sup>4,23</sup> In brief, two atomically smooth, step-free mica sheets are glued onto cylindrical lenses and mounted at right angles to one another. The distance between the sheets is measured by multiple-beam interferometry between the backs of the sheets, and the distance-dependent force between the sheets is measured as the deflection of a weak spring. In the experiments reported below, the distances reported refer to the zero measured in dry nitrogen atmosphere. The spring constant of the force-measuring spring was approximately 100 N/m.

Polystyrene standards were purchased from Polymer Laboratories and were used as received. Their characteristics are listed in Table I. Two fractions with  $M \approx 500\,000$  were used because of the limited quantity of the first one we used.

The muscovite mica surfaces (Asheville-Schoonmaker) were mounted in the apparatus, and the enclosed apparatus was purged with dry nitrogen. To check cleanliness, the sheets were brought together at a slow rate in  $\text{N}_2$  atmosphere to verify the expected jump into contact resulting from attractive van der Waals forces. In the event this attraction was not observed, the experiment was aborted. Cyclopentane (freshly distilled, stored over type 4A molecular sieves, and filtered through an  $0.5\text{-}\mu\text{m}$  PTFE filter immediately before use) was added. The presence of oscillatory structural forces was verified, as will be noted in the Results. Finally filtered PS solution was added to the cyclopentane to form a dilute PS solution ( $150\text{ }\mu\text{g}\cdot\text{mL}^{-1}$ ), and this solution was incubated for at least 1 day at large separation, at the temperature of subsequent measurements, before measurements were begun. It was verified that force–distance profiles did not change with longer incubation times. Experiments were conducted in a room where the relative humidity was controlled to be <20%. The temperature was well-controlled during each run ( $<0.1^\circ\text{C}$ ) but may have differed by  $\pm 0.5^\circ\text{C}$  between repeat runs.

The cyclopentane (Eastman Kodak; 99% pure by GLC) was stored over type 4A molecular sieves and was freshly distilled before use. The different results obtained using a cyclopentane containing linear pentanes (Aldrich reagent grade; 95% cyclopentane by GLC) have been discussed elsewhere.<sup>23</sup> Independent determination of  $T_\Theta$  for the particular source of cyclopentane we used did not prove to be practical; we do note, however, that  $T_\Theta = 19.5^\circ\text{C}$  has been measured twice before using samples of similarly high purity<sup>21,25</sup> (cyclopentane from those sources was unfortunately not available at the time the present study was performed). Use of Aldrich spectroscopic-grade cyclopentane was discontinued at an early stage when it proved to contain approximately 25% linear pentanes.

In the data shown in the figures, pip left denotes measurements made as the surfaces were brought together and pip right denotes measurements made as the surfaces were separated. Agreement of these measurements (after equilibration for up to 2–5 min/data point) indicates reversibility over the experimental time scale.

The equilibration time for each datum was whatever was needed for the forces to stabilize on the time scale of minutes. At the largest separations only seconds were needed, while at small separations (roughly  $<2R_G$ ) up to 2–5 min were needed. After these times, the forces did not change with longer equilibration on the order of minutes (say, 10 min per datum).

The forces were found to be unaffected by the time (up to 30 min) that the adsorbed layers were kept compressed before they were separated, although we will present evidence below that suggests that extremely slow relaxations occurred over periods of hours.

## Results

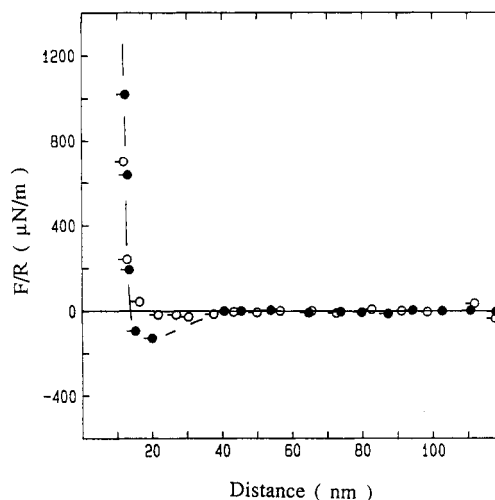
**General Remarks.** In cyclopentane without added polymer, detectable forces were not observed at separations larger than 2–3 nm. At lesser separations, the oscillatory structural forces characteristic of dry liquids<sup>1</sup> appeared for all three sources of cyclopentane we used. Such forces have been studied in detail by others.<sup>26,27</sup> To observe them in the present experiments served as a routine qualitative check, before adding polymer solution, of the cleanliness of the system.

A comment is needed about reliability of the experiments. Because the segmental sticking energy is small in these experiments with adsorbed homopolymers, there is danger of competitive adsorption between segments of the homopolymer and adventitious surface-active contamination. The requirements to maintain a clean system may be appreciated by recalling that the equilibrated amount of polymer adsorbed is typically only 0.1–1  $\mu\text{g}\cdot\text{cm}^{-2}$ .<sup>8</sup> A few nanograms of surface-active contamination can make a significant difference. To collect data is straightforward, but to know that any day's measurements are true is impossible to determine except by the experience gained from repeated experiments.

In addition, because many details of operating the surface forces experiment currently are as much an art as a science, the expertise of the operator is more of an issue than in many other experiments. In our experience, if often happens that reliable measurements are not made until the operator has had experience with the instrument for a year or longer.

These considerations mean that the basic limitations on experimental accuracy are not set by the resolution of distance measurement or by the sensitivity of force measurement. Rather, they are beset by difficulties in defining the experimental system exactly. These issues are discussed in more detail in the Appendix.

**Relaxation of Surface Forces.** Relaxation of forces was observed over two distinctly different time scales, short (up to 2–5 min) and long (hours). Figure 1 illustrates the more rapid relaxation in force–distance profiles measured for polymer C ( $M_w = 515\,000$ ) at 23 °C. Normalized force is plotted against distance for one experiment where measurements were made directly without waiting for forces to stabilize (5–10 s/datum) and a second experiment on the same system after apparent stabilization (up to 2–5 min/data point). These two sets of data share some features and differ in others. The data agree in showing steep short-range repulsion at ca. 10-nm separation, but at longer range the forces were virtually zero in the data taken rapidly. The attraction observed at  $D < 40$  nm took 2–5 min to develop.



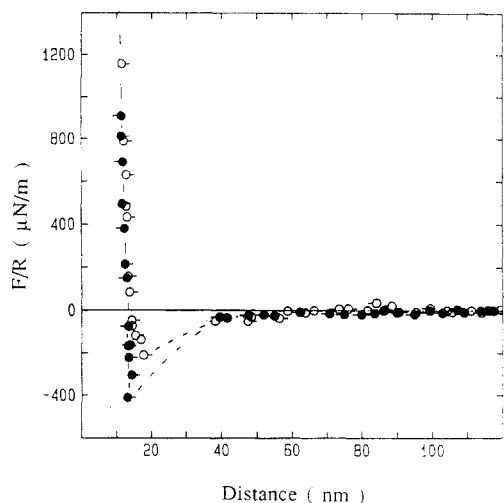
**Figure 1.** Force plotted against distance measured with 5–10-s equilibration per datum (open circles) and up to 2–5-min equilibration per datum (shaded circles). Data are for polymer C ( $M_w = 515\,000$ ) at 23 °C.

Such relaxation has previously been attributed to the slow drainage of solvent through the swollen polymer matrix contained in an exceedingly narrow gap.<sup>18</sup> A similar interpretation, in terms of ultraslow viscous drainage, was recently offered in a reinterpretation of surface force measurements of molten polymer oligomers.<sup>51</sup> However, in the present work the polymer concentration was not very high (say, at a surface separation of 30 nm), and the solvent, which was being forced out of the gap, had a very low viscosity. Moreover, recent experiments involving surface forces between terminally attached polymer chains in a low-viscosity solvent *do not* show this phenomenon,<sup>6,7</sup> though the polymer concentration in the compressed layers is similar to that in the present experiments; equilibration of terminally attached chains is complete after only a few seconds. On these several grounds, we therefore suggest that the phenomenon reflects true relaxation of forces, a manifestation of chain relaxation, not a drainage effect.

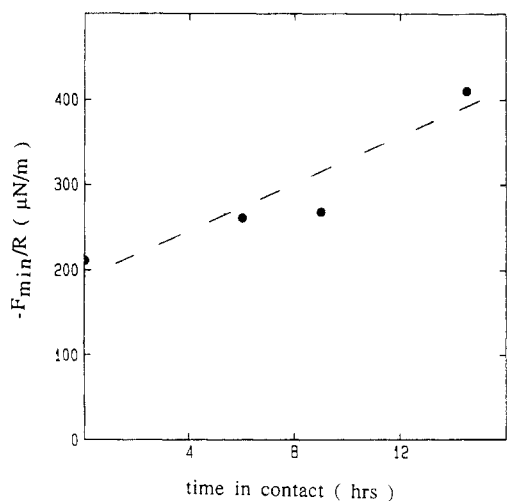
Further study will be needed to elucidate the origin of this relaxation, since at first glance one would expect that molecules should not have to make any drastic configurational changes on compression. However, times could be slower if rearrangements of the surface-hugging trains were involved. We will return to this point below.

Relaxation dynamics for polymers can be exceptionally slow. With this in mind, having observed apparent equilibration of long-range surface forces after 2–5 min, we did not rule out the possibility that forces would continue to change, albeit slowly on a time scale measured in minutes. In order to study what could happen over longer intervals of time, polymer C was adsorbed onto mica surfaces at 23 °C. The polymer-laden surfaces were compressed and then decompressed to the distance where the surface force was zero (approximately 14 nm), and finally the surfaces were left in contact. Because of thermal and mechanical drift, repulsive forces of several mN/m may have resulted before subsequent measurements were made. After 5 min and 6, 9, and 14.5 h, a retreat run and an immediate approach run were taken. Figure 2 compares the results measured after 5 min and 14.5 h in contact. It is obvious that, after 14.5 h, the adhesive minimum had doubled over its value at 5 min and that the distance position of this minimum had moved substantially inward (by approximately 5 nm).

Figure 3 compares the adhesive minima measured at



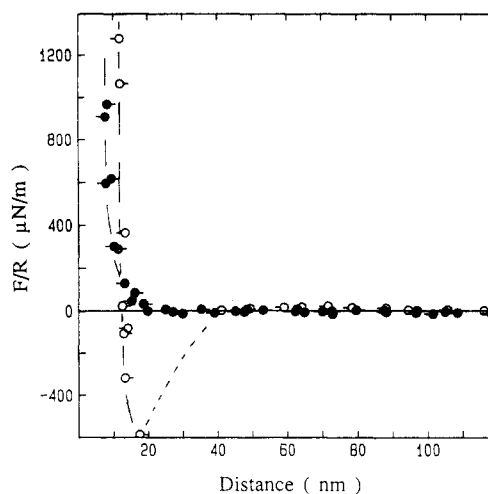
**Figure 2.** Force–distance profiles during retraction and immediate recompression for polymer C ( $M_w = 515\,000$ ) at 23 °C: open circles, 5-min contact time; shaded circles, 14.5-h contact time. Pip left denotes compression; pip right denotes decompression.



**Figure 3.** Minimum attractive force for polymer C ( $M_w = 515\,000$ ) at 23 °C, plotted against time in contact.

four contact times. Although a stable situation must surely be reached sometime, equilibration of the adhesive minima had not occurred even after hours in contact. Because of drift, it was not practical to allow hours-long equilibration at larger separations, but it is reasonable to expect that forces measured at longer range may similarly become much more attractive if measured over longer times.

In the most compressed state (2000  $\mu\text{N/m}$ ), the thicknesses obtained by linear regression to the force–distance data were 11.3 nm initially, 10.6 nm after 6 h, 10.4 nm after 9 h, and 10.2 nm after 14.5 h. It is tempting to attribute the increased adhesion to desorption of polymer,<sup>20,28</sup> since the total decrease in thickness from start to end of the experiment was 10%. However, we emphasize that the total change in thickness between 6 and 14.5 h was only on the order of the thickness of a single polystyrene repeat unit (0.4 nm), during which time the strength of the adhesive minima grew by over 50%. A clean separation of desorption effects from configurational rearrangement effects will require further work. However, the present findings suggest to us that the increased adhesion did not originate primarily in desorption as a function of contact time, which in turn suggests that extremely slow chain relaxations occurred.



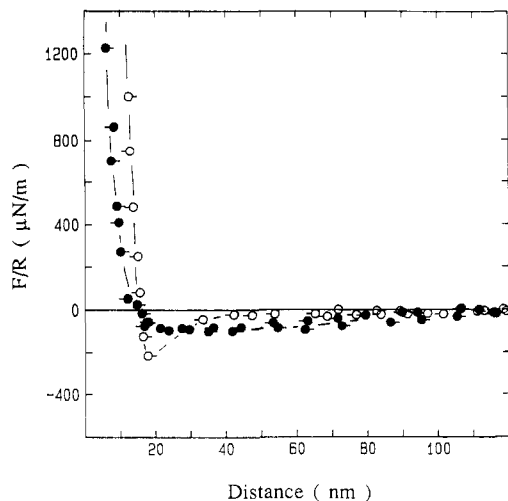
**Figure 4.** Force–distance profiles for polymer B ( $M_w = 490\,000$ ) plotted at 18 °C (open circles) and at 34 °C (shaded circles).

**Dependence on Temperature.** We compare the measurements at 18 and 34 °C for polymer B ( $M_w = 490\,000$ ), shown in Figure 4. (In this and all succeeding figures, the equilibration time was up to 2–5 min/datum.) At 18 °C ( $\theta - 2$  °C), note that attraction began abruptly at 40 nm ( $\approx 2R_G$ ), with a minimum at 17 nm ( $\approx 1R_G$ ) and strong repulsion beyond  $\approx 12$  nm. These features of scaling with the radius of gyration agree well with previous measurements<sup>17–19</sup> involving PS in cyclohexane at similar temperatures of corresponding state below the  $\theta$  temperature in that system.

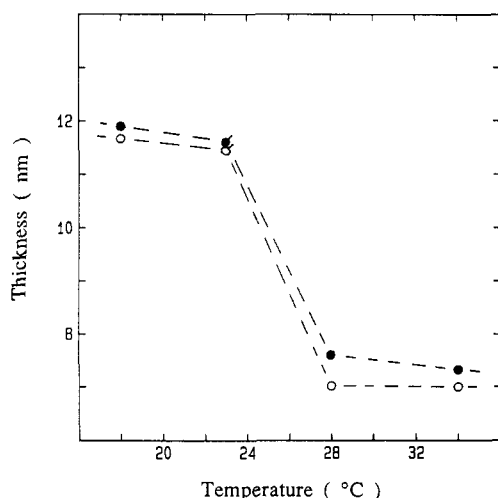
The behavior of this same adsorbed polymer at 34 °C,  $T_\theta + 14$  °C, was decidedly different. The range of forces was substantially less (see also Figure 6, discussed below). We will argue below that to find short-range repulsion at a smaller separation than at the lower temperature suggests that the amount adsorbed was less. At longer range, to observe repulsion rather than attraction suggests that osmotic interactions dominated, as might be expected from the positive second virial coefficient at a temperature above the  $\theta$  temperature. It is noteworthy to find monotonic repulsion at 34 °C. Attraction, resulting from enhanced bridging relative to 18 °C because of the lesser mass adsorbed, might have been expected on the basis of prior experience,<sup>17–20,22</sup> as will be discussed below. Finally, it is remarkable to observe no detectable forces at  $D > 1R_G$ , a much shorter range of interaction than at 18 °C.

Figure 5 shows force–distance measurements made at the intermediate temperatures of 23 and 28 °C. The trend continued that the point of steep repulsion fell at lesser separation, the higher the temperature. Also consistent with the trend in Figure 4 is that the strength of attraction decreased with increasing temperature. Finally the range of attraction at longer range continued to vary in a complex fashion. The range of forces at  $\theta - 2$  °C was comparable to that at  $\theta + 2$  °C, approximately  $2R_G$ . But before shrinking to approximately  $1R_G$  at  $\theta + 14$  °C, as discussed above and illustrated in Figure 4, the range was  $(5\text{--}6)R_G$  at  $\theta + 8$  °C.

Relative values of the mass adsorbed can be estimated from the layer thickness at the point of steep repulsion, as we will discuss below. In Figure 6, thickness in this region is plotted against temperature at two levels of repulsive force. At the highest compression of 2000  $\mu\text{N/m}$ , the biggest drop in thickness (by a factor of 1/4) was between 23 and 28 °C, both temperatures above the  $\theta$  temperature. This level of compression works out, accord-



**Figure 5.** Force-distance profiles for  $M \approx 500\,000$  plotted at 23 °C (open circles, polymer C) and at 28 °C (shaded circles, polymer B).



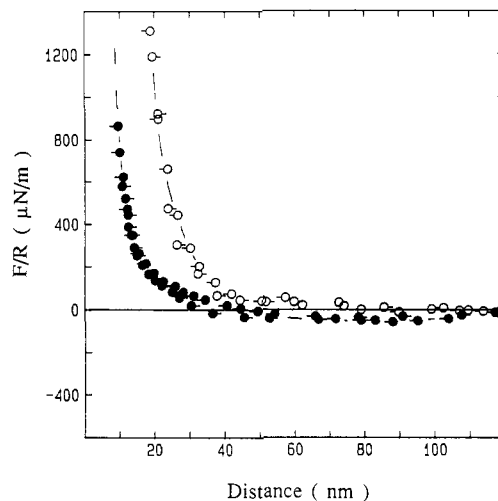
**Figure 6.** Compressed thickness for  $M \approx 500\,000$  plotted against temperature at specified repulsive forces: shaded circles, 1500  $\mu\text{N/m}$ ; open circles, 2000  $\mu\text{N/m}$ . No pip denotes polymer B; pip denotes polymer C.

ing to the Derjaguin approximation, to a substantial compression per unit area, 3  $\text{kT}/\text{nm}^2$ .

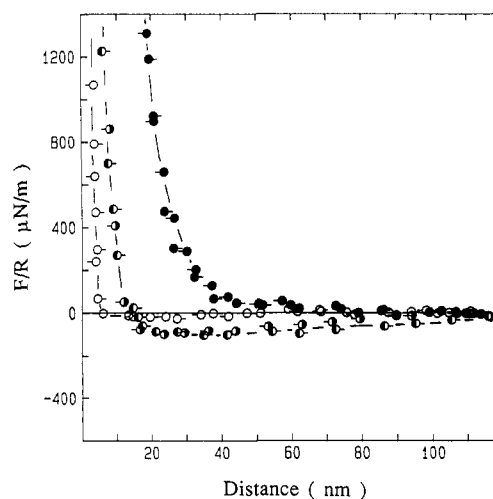
The temperature dependence of force-distance profiles for polymer D ( $M_w = 1\,080\,000$ ) is plotted in Figure 7. At 28 °C no interaction was apparent until  $D < 60$  nm, and at lesser separations the forces were monotonically repulsive. At 34 °C, very weak attraction appeared in the region 40–120 nm.<sup>29</sup> The thickness at steep repulsion, evaluated at the normalized repulsive force of 1000  $\mu\text{N/m}$ , was 21 nm at 28 °C and 10 nm at 34 °C.

**Dependence on Molecular Weight.** At the set temperature of 28 °C, Figure 8 compares the force-distance profiles of polymers A, B, and D ( $M_w = 115\,000$ , 490 000, and 1 080 000, respectively). It is evident that thickness at the point of steep repulsion was larger, the higher the molecular weight. This thickness will be shown below to scale approximately with the radius of gyration of the polymer (see Figure 11). The sign and range of longer range interactions were more complex, however.

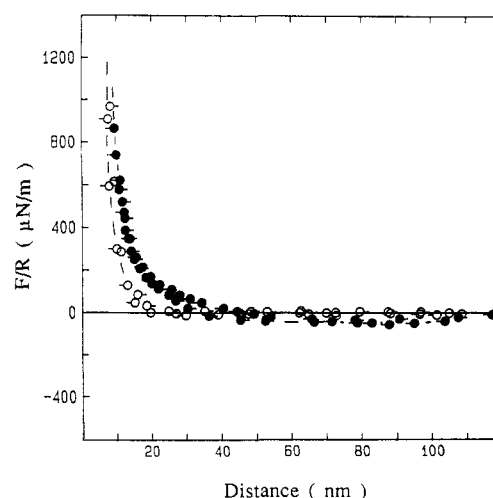
At the set temperature of 34 °C, Figure 9 compares the force-distance profiles of polymers B and D ( $M_w = 490\,000$  and 1 080 000, respectively). At this temperature also, the point of steep repulsion increased with increasing molecular weight, approximately according to the radius of gyration of the polymers (see Figure 12).



**Figure 7.** Force-distance profiles for polymer D ( $M_w = 1\,080\,000$ ) plotted at 28 °C (open circles) and at 34 °C (shaded circles).



**Figure 8.** Force plotted against distance at 28 °C for polymer A ( $M_w = 115\,000$ ; open circles), polymer B ( $M_w = 490\,000$ ; left-half shaded circles), and polymer D ( $M_w = 1\,080\,000$ ; full-shaded circles).



**Figure 9.** Force plotted against distance at 34 °C for polymer B ( $M_w = 490\,000$ ; open circles) and polymer D ( $M_w = 1\,080\,000$ ; shaded circles).

For both polymers all forces of magnitude  $>50$   $\mu\text{N/m}$  were now repulsive. The thickness at the point of steep repulsion was remarkably small.

## Discussion of the Results

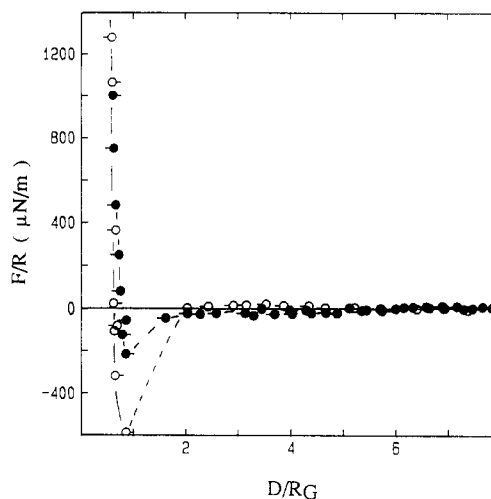
Most force–distance profiles between adsorbed polymers look alike; they differ in their quantitative features. At large separations, where forces between the adsorbed layers first appear, the forces are moderate in strength. These forces change slowly with separation, and often an attractive well is observed. At short range the repulsion is steep. When force–distance profiles are discussed, it is useful to distinguish *hard contact* from *soft contact*. Hard contact reflects the low compressibility of adsorbed polymer layers when they are highly compressed. Soft contact reflects more elusive interactions, which are poorly understood.

**Dependence of the Position of Hard Contact on Temperature.** If the harsh repulsion measured in hard contact reflects a high degree of compression, a rough estimate of the *relative* mass adsorbed can be made by comparing the layer thicknesses at a fixed repulsive force. At first glance this interpretation might seem to be complicated by the possibility that the adsorbed polymer configurations might relax faster at the higher temperatures, so that thickness at the point of short-range repulsion might depend on the degree of relaxation. However, as mentioned in the Results, the changes that were observed for polymer C over a period of hours in hard contact were a few percent, fractional changes that would not significantly affect the conclusions below. Also, as mentioned in the Experimental Section, periods in contact up to 30 min did not change this final layer thickness.

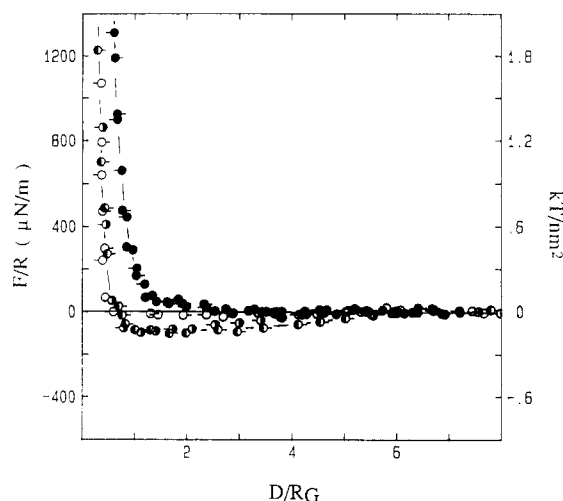
Using the layer thicknesses plotted in Figure 6 at compression  $F/R = 2000 \mu\text{N/m}$  ( $3 \text{ kT/nm}^2$ ) and assuming the density of bulk PS for simplicity leads to the estimate that the mass adsorbed for  $M \approx 500\,000$  was approximately  $0.5 \mu\text{g/cm}^2$  at 18 and  $23^\circ\text{C}$  and that it was approximately  $0.35 \mu\text{g/cm}^2$  at 28 and  $34^\circ\text{C}$ . To be sure, these estimates are upper bounds because solvent was surely retained within the compressed layers, probably to a degree that increased with improved solvent quality at temperatures above  $T_\theta$ . However, the large relative decrease with increasing temperature is striking.<sup>30</sup>

To find so much less adsorbed at the higher temperatures implies, as Klein has emphasized,<sup>31</sup> that the segmental sticking of PS to mica was weak under the conditions of this experiment. The assumption of weak segmental sticking is a feature of the existing theoretical models,<sup>11,12</sup> a point to which we will return in the discussion of equilibration below.

Unfortunately, it is not possible at present to assess how common a phenomenon this large temperature effect may be. Few studies have been made of the dependence of mass adsorbed on temperature near the  $\theta$  temperature. Most studies of the influence of solvent quality on adsorption have taken the approach of changing solvents entirely or the approach of dissolving the polymer in mixed solvents of varied composition, so that the resulting mixture was ternary. A study by Kawaguchi and Takahashi did study the temperature-dependent adsorption of PS from cyclohexane onto chrome plate, using ellipsometry.<sup>32</sup> Curiously enough the mass adsorbed was almost independent of the molecular weight. However, the mass adsorbed was consistently (and reversibly) some 30% less at  $\theta + 10^\circ\text{C}$  than it was at  $T_\theta$ , in general agreement with the present findings. An earlier surface forces study, of PS adsorbed onto mica from cyclohexane,<sup>19</sup> also reported changes in the position of hard contact with temperature, which are consistent with the present ones. The same conclusion also emerges<sup>52</sup> when a direct infrared mea-



**Figure 10.** Comparison of force–distance profiles for polymer B at  $18^\circ\text{C}$  (open circles) and  $23^\circ\text{C}$  (shaded circles). Distances are normalized by the radius of gyration ( $R_G$ ) of the respective polymer fractions.

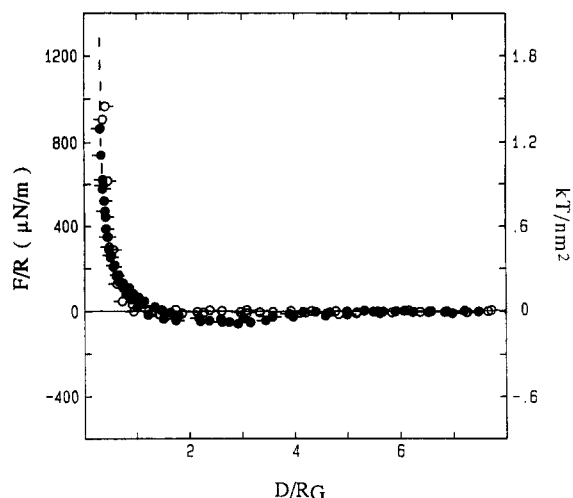


**Figure 11.** Comparison of force–distance profiles for polymer A ( $M_w = 115\,000$ ; open circles), polymer B ( $M_w = 490\,000$ ; half-shaded circles), and polymer D ( $M_w = 1\,080\,000$ ; full-shaded circles) at  $28^\circ\text{C}$ . Distances are normalized by radius of gyration of the respective polymer fractions. On the right-hand ordinate is shown the equivalent energy of interaction calculated using the Derjaguin approximation.

sure of the mass of PS adsorbed onto silicon is used.<sup>10</sup>

**Scaling of Distance with Radius of Gyration.** If the concentration gradient of homopolymer between surface and solution is approximated as a single number, this thickness scales approximately with the radius of gyration ( $R_G$ ) of the polymer.<sup>8</sup> Therefore, in surface force experiments one might perhaps expect to see onset of interaction at approximately  $2R_G$  (one  $R_G$  per layer). That this indeed occurs at temperatures from  $\theta - 8^\circ\text{C}$  up to  $\theta + 3^\circ\text{C}$  was shown already some years ago,<sup>17–19,22</sup> and it is confirmed here by experiments on a different system. Figure 10 shows the successful scaling with  $R_G$  for polymers B and C measured at 18 and  $23^\circ\text{C}$ , respectively. The normalized data agree nearly quantitatively with earlier data from other laboratories regarding polystyrene adsorbed onto mica from cyclohexane.<sup>17–19</sup>

Figures 11 and 12 show forces plotted against distance in  $R_G$  units at 28 and  $34^\circ\text{C}$ , respectively. When the distance scales were normalized by  $R_G$ , the slight increases in  $R_G$  at temperatures above  $T_\theta$  were estimated for completeness, though the corrections from the unperturbed



**Figure 12.** Comparison of force–distance profiles for polymer B ( $M_w = 490\,000$ ; open circles) and polymer D ( $M_w = 1\,080\,000$ ; shaded circles) at 34 °C. Distances are normalized by radius of gyration of the respective polymer fractions. On the right-hand ordinate is shown the equivalent energy of interaction calculated using the Derjaguin approximation.

$R_G$  were small.<sup>33,34</sup> The approximate collapse of data taken at 28 °C and the excellent collapse at 34 °C illustrate that hard contact scales approximately with  $R_G$ , just as the layer thickness at a single surface is known to do for this range of molecular weight.<sup>8</sup>

Behavior in the zone of soft contact was more complex. We consider first the measurements made at 28 °C (Figure 11). The range of soft contact was from  $1R_G$  to  $6R_G$ . For  $M = 115\,000$ , forces in soft contact were zero or attractive at an extremely low level. For  $M = 490\,000$ , the attraction was stronger and extended up to  $(5\text{--}6)R_G$ . Finally, for  $M = 1\,080\,000$ , the sign of forces in the zone of soft contact switched to repulsion, and with a compressed range: forces were nil all the way down to  $2R_G$  and they were monotonically repulsive upon closer approach.

At the still higher temperature of 34 °C (Figure 12), the data in the zone of soft contact were again of short range. For  $M = 490\,000$ , no forces at all were measured except at distances less than  $1R_G$ . For  $M = 1\,080\,000$ , forces were attractive at a very low level up to  $4R_G$ .

**Sign and Range of the Forces in Soft Contact.** A striking feature of the data in Figures 11 and 12 is how weak were all the interactions except, of course, those measured in harsh compression. Most of the interesting differences in range and in sign pertain to forces less than  $200\ \mu\text{N/m}$ . With the Derjaguin approximation,  $F/2\pi R = W(D)$ : this corresponds to equivalent energies per unit area between parallel plates ( $W(D)$ ) less than  $0.2\ \text{kT/nm}^2$ . On the one hand, it is clear that subtle effects were being measured; on the other hand, as Klein has emphasized,<sup>31</sup> effects of this magnitude can become important compared to  $kT$  with respect to the overall interaction between colloidal particles when the effective area of interaction is large, and therefore these effects can have significant implications for the stability or instability of colloidal suspensions.

The only possible source of attraction above the  $\theta$  temperature, at distances too large to result from significant van der Waals attraction between the mica,<sup>35</sup> is believed to be bridging of chains between the two solid surfaces so that they attach to both surfaces at once. The resulting entropic force should be attractive. The other conceivable sources of surface forces, physical compression and osmotic interactions, should be repulsive.

One might surmise that low surface coverage and strength of long-range attraction may be strongly correlated: the less the mass adsorbed to a surface, the thinner the layer, so the more opportunity for chains on an opposing surface to bridge to it. This view is also the theoretical prediction even if restricted equilibrium holds.<sup>11,12,28</sup> There is experimental support for this if the solid surfaces are *starved* so that the mass adsorbed is less than saturated;<sup>19,20,22</sup> in comparisons in which the temperature is not changed and the same molecular weight polymer is under study, enhanced attraction is found when the adsorption is less than the saturated amount.<sup>19,20,22</sup>

The present experiments, under conditions of saturated adsorption, found a more complicated pattern when the temperature and molecular weight of the polymer were varied. We did not find that attraction was necessarily stronger when the mass adsorbed was less. The range of net attraction at temperatures above  $T_\theta$  appeared to pass through a maximum with increasing molecular weight and increasing temperature, as we now discuss.

Consider the same polymer fraction measured at different temperatures. For  $M = 490\,000$ , the attraction measured in soft contact decreased as experiments were conducted at higher and higher temperatures, until at 34 °C no attraction was measured at all on the time scale of this experiment. Under these conditions of differing solvent quality, low mass adsorbed and the presence of attractive forces did not go hand in hand.

Unfortunately, unambiguous interpretation of this observation in terms of relative extents of bridging is not possible because of the possible trade-off between attractive (bridging) and repulsive (osmotic) forces. With increasing temperature both probably increase in strength: bridging because there is less mass adsorbed and osmotic effects because the solvent quality is improved. In principle, the net result could be attractive or repulsive depending on subtle differences in the experimental conditions; the weak *net* forces measured could result from the near cancellation of two forces of opposite sign.

The second experimental conclusion we are faced with is that, in comparisons of different molecular weight fractions measured at the same temperature, the net attraction did not vary monotonically with the mass adsorbed. This is seen most clearly for the measurements made at 28 °C (Figures 8 and 11). For the least mass adsorbed ( $M_w = 115\,000$ ), forces were extremely low, close to zero, all the way to hard contact. With more mass adsorbed ( $M_w = 490\,000$ ), attraction was stronger and it extended to larger separations. With still more mass adsorbed ( $M_w = 1\,080\,000$ ), only repulsion was observed and it occurred only at short range.

An interesting complication is that the bridge density might depend on time and molecular weight. As surfaces were brought close together, surely the adsorbed chains on one mica sheet took some time to establish bridges with the other mica sheet. The higher the molecular weight, the greater the mass adsorbed, therefore, the thicker the adsorbed layer that must be penetrated to establish a bridge and the less likely that penetration could occur during a given time. By the same token, the higher the molecular weight, the fewer dangling tails were available (per area) to contribute to bridging, so the less the resulting force (per area). The experiments at 28 °C showed that the force switched from attraction to repulsion with increased polymer molecular weight. The degree to which this could reflect a lower density of bridges achieved over the experimental time scale is difficult to assess and remains a real problem in interpreting force-

distance profiles between adsorbed homopolymers.

What of the distance range? If bridging is initiated by tails on the fringes of the concentration profile of adsorbed segments, one might anticipate that the distance range of bridging would scale with the extension of these tails. The average extension of tails is predicted to increase proportional to the molecular weight, i.e., more rapidly than proportional to  $R_G$  (or to  $M^{1/2}$ ).<sup>36</sup> This suggests that soft contact might occur at longer range (in units of  $D/R_G$ ), the higher the molecular weight.

Indeed, in the measurements made at 28 °C, forces in soft contact did fall at longer range for  $M = 490\,000$  than for  $M = 115\,000$ . Forces were zero or attractive (suggesting bridging) for both these fractions. Not so on either count for  $M = 1\,080\,000$ . An inviting possibility is that the greater adsorbed amount of this polymer was too large to allow sufficient bridging, over the time scale of the experiment, to dominate over osmotic repulsion. In this view, the attraction caused by bridging passed through a maximum as a function of molecular weight.

Speculations along similar lines can be made regarding the findings at 34 °C. For  $M = 490\,000$  the range of measurable interaction was shorter than at the lower temperatures. Perhaps osmotic repulsion impeded measurable bridging over the time scale of the experiment. The shorter range of repulsion compared to the findings at 28 °C, observed both for  $M = 490\,000$  and for  $M = 1\,080\,000$ , suggests the possibility that the chain conformations were more flattened than at lower temperatures, perhaps because the adsorbed amount was less, but no quantitative explanation is offered at this time.

The temperature 34 °C is significantly above  $T_\theta$ . It is interesting to compare the findings of these experiments conducted under marginally good solvent conditions to findings obtained under definitively good solvent conditions. The extensive measurements by Klein and co-workers, of poly(ethylene oxide) in aqueous salt<sup>14</sup> and toluene<sup>15</sup> solutions, showed monotonic repulsion starting at the large separation of  $(5-7)R_G$ , as noted in the Introduction. This long range of soft contact was rationalized in that study by considering that the second virial coefficient is significant under good solvent conditions but not under near- $\theta$  conditions. In this view, which was elaborated later,<sup>37</sup> strong forces of osmotic origin may result as soon as opposing layers begin to touch in a good solvent, but considerable overlap may be required to produce significant forces of osmotic origin under conditions of poor solvent quality.

The present measurements did not fit this pattern. A shorter range of soft contact was observed at 34 °C (best solvent quality) than at lower temperatures. A recent account of surface forces between polystyrene layers adsorbed from toluene<sup>38</sup> reports a similar range of forces: repulsion starting at  $(1-2)R_G$  and scaling approximately with  $R_G$ . The range of soft contact measured under good to moderate solvent conditions was thus of far shorter range in these two polystyrene systems than in two PEO systems.<sup>14,15</sup> The differences might reflect strong segmental sticking in the case of PEO and weak segmental sticking in the case of PS, but this is not clear yet in view of the conflicting measurements on PEO systems (discussed in the Introduction). What behavior may prove to be typical of generic behavior in good solvent conditions is not possible to say yet.

**Scaling of Forces by the Mass Adsorbed.** Scheutjens and Fleer have calculated that the magnitude of force-distance profiles scales approximately with the mass adsorbed,<sup>11</sup> i.e., with the number of adsorbed segments

per unit area. This suggested normalizing the ordinate by the mass adsorbed in the comparisons made in Figures 11 and 12. The normalization was performed (not shown) by approximating the relative adsorptions by the relative square roots of the radii of gyration. The collapse of the data in the zone of hard contact was improved for the data shown in Figure 11 but was worsened for the data shown in Figure 12. It may go without saying that this normalization of the ordinate scale could not reconcile the differences we noted above in the sign and range of the forces measured in soft contact for the various adsorbed polymer fractions.

**Questions of Equilibration.** A theme that emerges from this study is that the equilibration time of the surface forces experiment was a significant variable. In the discussion above, we have rationalized the complex pattern of observations as possibly reflecting differing degrees of equilibration.

Lack of hysteresis is sometimes cited as evidence that a state of equilibration was reached. However, the present measurements were also reversible over *short times* (2–5 min/data point), as shown by the pips pointing right and left in the figures. We emphasize that this does not speak to the possibility that other modes of relaxation could take place at significantly longer times. That dynamics did occur over longer times is suggested by the data in Figures 2 and 3.

At equilibrium, the structure of the adsorbed layers would, of course, be independent of sample history. Consider the dynamic processes that must precede equilibrium. There might exist complete equilibrium (in which case only attractive forces would result) or constrained equilibrium (equilibrium under the restriction of constant adsorbed amount).<sup>11,12</sup>

If constrained equilibrium were to describe the situation, adsorbed polymer chains within the zone of contact would be intermingled completely. No distinction would remain between chains that originally were adsorbed to one surface or the other. At each separate distance measurement in the force-distance profile, this state of constrained equilibration would be accomplished over the experimental time scale of 2–5 min. This is a strong assumption.

We suggest that the bridging interaction may represent the first stages in achieving this condition. Bridging requires that a chain attached to one surface invades the opposing adsorbed layer, penetrating it so deeply as to become physically attached to both mica surfaces at once. In this view, bridging may reasonably be expected to depend on such considerations as the chain molecular weight and the mass adsorbed, as we have argued above. The process is an early stage of interdiffusion.

Much effort devoted to the fit of data to models based on the state of constrained equilibrium<sup>11,12,39,40</sup> shows that the qualitative patterns of force-distance profiles are reproduced successfully but that quantitative agreement is poor. The predicted ranges of distance and magnitudes of force appear to underpredict experiment by a factor of at least 2–3 for any reasonable choice of parameters.<sup>11,12,39,40</sup> This is despite the fact that the theoretical assumption of weak segmental sticking to the wall ( $<kT$ ) does seem to be satisfied, as discussed above and indeed measured directly in a previous study.<sup>20</sup> We conclude that these experiments may be far from thermodynamic equilibrium. To describe these experiments, the difficult task of modeling *variable* degrees of interdiffusion of two initially distinct layers seems to be required.

As de Gennes has emphasized,<sup>8</sup> virtually all the avail-



able theories of adsorbed polymers are based on the assumption of a state of thermodynamic equilibrium. It is interesting to observe that these theories describe successfully some features of experimental data, such as the dependence on molecular weight of the mass adsorbed<sup>8</sup> and the shape of the force–distance profiles, but fail to describe others, such as the range and strength of force–distance profiles. The rich variety of force–distance profiles we observe suggests that relaxation times are long and that these experiments do not completely satisfy the assumption of constrained equilibrium. Elucidation of more difficult nonequilibrium questions of motion and relaxation in surface layers seems required for a full explanation.

The essential physical reasons for this slow relaxation are not yet clear. There are questions of diffusion under constraints: diffusion of an adsorbed polymer molecule over long distances surely requires concerted motion at the many points where the chain is attached to the surface. This process may be expected to be slow compared to relaxation of the free chain. The glass transition temperature ( $T_g$ ) of the polymer might also play a role. Kremer has proposed<sup>41</sup> that the polymer concentration directly at the mica surface might become high enough for the PS ( $T_g \approx 100$  °C for bulk PS) to reach a glasslike state in a thin volume of liquid near the surface. Regardless of whether one accepts this argument, it is true that other experiments involving the shear of polymer liquids confined between mica sheets<sup>42</sup> do suggest remarkably slow relaxation times, even at temperatures unequivocally above  $T_g$ , raising the possibility that the local geometrical packing of polymer segments and solvent molecules in the restricted space close to the surface might be relevant to this problem also.

### Concluding Remarks

The measurements described above of the surface forces between adsorbed homopolymer layers under near- $\theta$  solvent conditions cover a wider range of time, temperature, and molecular weight than appear to have been studied previously. Four chief findings may be summarized:

(a) The adhesive minima of force–distance profiles increased with time, at a rate at least proportional to the elapsed time (up to 14.5 h) that the adsorbed layers were kept together before they were separated. This suggests that extremely slow chain relaxations occurred in these layers.

(b) The layer thicknesses at hard contact scaled approximately with the radius of gyration,  $R_G$ , i.e., approximately with the square root of the molecular weight. This is the scaling expected for the layer thickness at a single surface under poor solvent conditions.

(c) The layer thicknesses at hard contact were substantially less at the higher temperatures. This suggests that the mass adsorbed was remarkably sensitive to small changes in the temperature near  $T_\theta$ , as one might expect when the solvent quality changes rapidly with temperature.

(d) The forces measured in soft contact were weak, corresponding according to the Derjaguin approximation to the equivalent energy of interaction between parallel plates of 0.2 kT or less. In comparisons of the sign and the range of the surface forces in soft contact as a function of the molecular weight of the adsorbed polymers at a set temperature, the results were complex as to the sign and even the range of the surface forces measured over the time scale of this experiment. Possible reasons for this were discussed in terms of bridging and of variable degrees of equilibration over the experimental time scale.

On the basis of these findings, we have argued that the special features of homopolymer adsorption—weak sticking by any single segment combined with the possibility that any segment might stick, either to its original surface or to a second surface that is brought nearby—can lead to difficulties in unambiguous interpretations and comparisons of surface force experiments with homopolymers. The relative influences of bridging and osmotic interactions are difficult to separate when these two sources of force have opposite sign. A common feature of existing theoretical models is to assume that the segment density profile is equilibrated and therefore independent of sample history. The present experiments suggest, however, that the initially distinct adsorbed layers interdiffused to only a limited extent, an extent which depended on the molecular weight, the equilibration time, and the adsorbed amount.

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### Appendix

Experimental details and assumptions of this experiment have been little discussed since the pioneering publication of Israelachvili and Adams.<sup>4</sup> With this technique it is possible, in principle, to measure forces with a force sensitivity of 10–100 nN and a distance sensitivity of 1–2 Å. However, workers in the field are well-aware, from experience and from word-of-mouth, that the basic limitations on experimental accuracy are often stronger than this; they are often set not by sensitivity of the measurements but by difficulties in defining the experimental system exactly. In what follows, we mention briefly some of these considerations.

**Derjaguin Approximation.** Comparison of experiment (forces measured between crossed cylinders) with theoretical predictions (energy of interaction between flat plates) is possible using the Derjaguin approximation.<sup>2,35</sup> According to the Derjaguin approximation,  $F(D)/R = 2\pi W(D)$ , where  $R$  is the local radius of curvature of the crossed mica cylinders (typically 1 cm in these experiments) and  $W(D)$  is the equivalent energy of interaction, per unit area, between flat plates at the same point  $D$  of closest approach. The result is based on a continuum argument and assumes that the surface forces depend only on distance, i.e., that the forces are field forces. However, when the distance becomes comparable to the dimensions of polymer and solvent molecules, questions arise of how well this is described by the continuum argument. We are not aware of a careful discussion of the Derjaguin approximation in this context.

The mica sheets are shaped as crossed cylinders by gluing them onto silica cylinders. There are two potential problems if the repulsion is large.

First, the forces may reflect a complicated mixture of modes of deformation, as Zapas, McKenna, and Brenna have emphasized.<sup>43</sup> If chains are firmly attached to the surface, then their state of deformation varies. It varies from pure compression at the midpoint between the cylinders to shear at the point of attachment.

Second, a large repulsion may cause local flattening of the flexible mica sheets, owing to mechanical compliance of the underlying glue, in which case the Derjaguin approximation would not apply. The extent of this defor-

mation can be estimated from the calibrated modulus of the mechanical system (mica on silica with supporting glue), as Horn, Israelachvili, and Pribac have shown.<sup>45</sup>

To minimize these potential difficulties, the measurements reported above have emphasized observations made for weak forces. Forces larger than  $F/R \approx 3000 \mu\text{N}/\text{m}$  (absolute force corresponding to roughly 6 mg) were not measured.

We note parenthetically that it is possible to take advantage of the fact that the mica sheets flatten under large compression. Flattened mica permits measuring of the shear between parallel plates of mica at constant separation.<sup>43,46</sup>

**Mechanical and Thermal Stability of the Instrument.** The determination of force is based on measurement of the deflection of the spring to the end of which the bottom surface is rigidly attached. As the base of the spring is displaced by a known amount and the associated displacement of the bottom surface is measured, discrepancies are attributed to forces acting between the surfaces. This assumes that the distance between the top and the bottom surfaces would be stable if no forces acted. Difficulties in achieving stability were discussed elsewhere.<sup>24</sup>

**Cleanliness.** The strict requirements for cleanliness were noted above (Results). In experiments where polymer segmental adsorption is weak, adsorption is a competition between polymer and even trace levels of surface-active impurities, an effect that we find can change the force-distance profiles qualitatively. In our experience, the sensitivity to trace contamination is especially large in measurements near the  $\Theta$  temperature and usually shows up as repulsion at unusually large separations.

Cleanliness can only be checked by repeated measurements on the same system prepared again and again, checking for consistency. The levels of potential contamination are too low to detect conveniently by usual analytical means.

Since mica is cleaved in the ambient atmosphere of a laminar flow cabinet, one must consider the propensity of airborne contaminants to find the cleaved surface during preparation. The mica surface appears to be relatively inert to the chemisorption of airborne gases. LEED studies indicate that  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$  do not adsorb to the surface in vacuo.<sup>47</sup> The main contaminant in air cleavage appears to be carbon compounds, presumably "of human origin", present as atmospheric dust,<sup>48</sup> and water adsorption appears to promote the binding of carbon compounds to the mica surface.<sup>48</sup> Although it is routine to cleave and handle mica inside a laminar flow cabinet, differences in the levels of airborne contaminants may be expected to differ from laboratory to laboratory.

In experiments with nonpolar organic liquids, it has been well-established by Israelachvili, Horn, Christenson, and co-workers<sup>26,27</sup> that water forms a condensed film on the mica unless the liquids have been dried. In the present study the liquids were dried to the extent possible, but in some other polymer studies the liquids were used as received, i.e., not dried. A systematic comparison of polymer behavior in "wet" and "dry" organic liquids does not seem to have been made, but one would expect a difference in the segmental sticking energy to mica.

With multiple-beam interferometry one can discriminate changes in the mica-mica separation with a resolution down to 1–2 Å.<sup>4</sup> However, since the mica sheets are

necessarily calibrated in gas atmosphere, adsorbed gases cause uncertainty in the absolute separation. Because the mica-mica contact thickness is typically on the order of 5 Å larger after cleavage in a dry atmosphere than it is before cleavage or in the presence of water,<sup>4</sup> one definition of zero adopted by many workers is to take the thickness measured at the end of an experiment after water has been added.<sup>49</sup> When this is done in experiments of the present type where the liquid is nonpolar, the assumption is made that the nonpolar liquid under study had displaced the adsorbed gases already during the experiment. Another consideration is that water induces ion exchange; protons exchange with  $\text{K}^+$  ions in the cleaved mica basal plane, and this also may contribute to a diminished thickness, though by less than 5 Å.<sup>49</sup>

In the present study, the zero has been referred to the thickness measured before the experiment in dry nitrogen atmosphere. There appears to be some arbitrariness in either choice of zero. This systematic uncertainty in the zero distance does not, of course, affect the form of a force-distance profile but only the exact position on the distance axis.

**Random Errors.** There are two main sources. There is uncertainty in measuring by multiple-beam interferometry the mica-mica separation. Under optimum conditions this can be as low as 1–2 Å, but this is not routine; in our experience the uncertainty is often 5 Å or even 10 Å unless great pains have been taken with the measurement. There also is uncertainty in calibrating the base line of zero force, i.e., the hypothetical position at which the bottom surface would rest if zero net force prevailed between the top and bottom surfaces. A good base line requires exceptional mechanical stability of the surface forces instrument.<sup>24</sup> The uncertainty in force is typically not less than 10% at 1000  $\mu\text{N}/\text{m}$ , as Christenson has noted<sup>26</sup> and Asthana has calculated in detail.<sup>50</sup>

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- (29) It is true that the weak attraction in Figure 7 was not much larger than a conservative measure of the experimental uncertainty; if the experiments had been less stable, it might have been an artifact from a drift in the base line. However, it was reversible and reproducible in different experiments, so we report the data but do not rely upon it in the discussion.
- (30) Mass adsorbed is sometimes gauged from the refractive index measured in hard contact. We attempted to do this, but unfortunately in our hands the measurements were too scattered to give a reliable estimate.
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## Chain Length and the Cosolubility of *n*-Paraffins in the Solid State

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**ABSTRACT:** Within the constraints of rectangular layer chain packing and the orthorhombic perpendicular methylene subcell imposed by the crystal structure, a chain length series of *n*-paraffins from C<sub>28</sub>H<sub>58</sub> to C<sub>60</sub>H<sub>122</sub> was used to form binary solids. If chain length differences fall within limits similar to those found in earlier analyses, solid solutions are formed. As indicated by theoretical calculations of the melting point line, they are nearly ideal in their behavior. Outside of this chain length difference eutectics are formed, with liquidus curves also corresponding closely to the freezing point depression of an ideal liquid solution. Depending on chain length difference, the eutectic solid will be composed of an incommensurate layer structure (crystallized from a metastable solid solution) coexisting with the longer chain component. If no cosolubility is possible, a mixture of the two pure components separates. A boundary domain also exists before strict eutectic separation when a critical temperature is reached. Here, at the miscibility gap, metastable solid solutions fractionate, with a structure very similar to that of a secondary eutectic solid for binary combinations where limited solid solubility still exists. However, the incommensurate solid changes continuously with concentration unlike the mixed lamellar stacking in the eutectic, which has a constant composition. It is therefore possible to describe a progression of crystalline arrays between the stable solid solution and fully separated eutectic.

### Introduction

*n*-Paraffin binary solids have received considerable attention for many years<sup>1-16</sup> as models for the polydisperse polymethylene chain packings found in polyethylene lamellae as well as the mixed acyl chain layers in biomembrane lipids. From numerous calorimetric and diffraction studies, a number of factors can be envisioned that could affect the solid solubility of two paraffins, includ-

ing the space groups of the pure components as well as their relative chain lengths (i.e., respective molecular volumes), as stated formally by Kitaigorodskii.<sup>17</sup>

Recently<sup>18,19</sup> we have found that the symmetry rules thought to govern the stability of an *n*-paraffin solid are somewhat restrictive, and indeed, within a series of solid solutions composed of paraffins that crystallize in the same space group, there is no continuity of space group symmetry, but only a continuum of methylene subcell