# Molecular Organization and Viscosity of a Thin Film of Molten Polymer between Two Surfaces As Probed by Force Measurements

**R. G. Horn***,† **and J. N. Israelachvili**‡

*Department of Applied Mathematics, Research School of Physical Sciences, Australian National University, GPO Box 4, Canberra 2601, Australia.*
*Received June 1, 1987; Revised Manuscript Received February 12, 1988*

ABSTRACT: Measurements are presented of the force between two molecularly smooth mica surfaces immersed in liquid poly(dimethylsiloxane) (Dow Corning 200 of nominal viscosity 50 cS) over a range of film thicknesses from 3 to 200 nm. There is a repulsion, attributed to conformational restrictions, when the polymer molecules are confined to a gap less than about 15 nm thick. In extremely thin films (<5 nm) the force is an oscillatory function of thickness with a repeat spacing corresponding to the width of the polymer molecule, which suggests that the polymer segments are arranged in layers near the solid surfaces. Dynamic force measurements show that the polymer has a viscosity equal to its bulk value even in very thin films, but a region next to each surface, only about one radius of gyration thick, does not flow. Saturation of the polymer with water destabilizes the film when it is very thin.

## 1. Introduction

In recent years direct measurements of the forces acting between solid surfaces[1] have been made in a variety of liquid media. These were originally conceived to measure the interactions which determine colloidal stability, for example, the electrical double-layer repulsion and van der Waals attraction,[2,3] which are the two planks of the DLVO theory. Polymers in solution also have a major part to play in colloidal stability, sometimes coating particles and stabilizing them by osmotic or steric repulsions or in other systems causing flocculation by segment–segment attraction or by bridging between two or more particles. These interactions have been measured by employing the same techniques with model surfaces immersed in various polymer solutions.[4]

Apart from exploring features pertinent to colloidal stability, equilibrium force measurements have also given a lot of information on the manner in which molecules in a liquid are arranged or "structured" near solid interfaces, because that is reflected in the so-called *solvation force*. For example, the rigid, quasi-spherical molecules of a simple liquid have a tendency to lie in layers next to a smooth rigid solid surface, and the force which results between two such surfaces is an oscillatory function of their separation, alternating between attraction and repulsion.[5,6] In aqueous solutions the effects of the surface on water structure can lead to a *hydration repulsion* between hydrophilic surfaces[3,7,8] or a *hydrophobic attraction* between hydrophobic ones.[9]

Dynamic measurements of the force can also be used to probe the *viscosity* of a liquid film between the two solids,[10,11] to ascertain, for example, whether or not the viscosity is modified by structuring in the liquid near a solid boundary.

In this paper we describe the use of the direct force-measuring technique to explore the structure and viscosity of a molten polymer (poly(dimethylsiloxane), PDMS) in a thin film between two smooth solids. Although, as mentioned above, the technique has previously been applied to polymers in solution, we believe these to be the first such measurements on a polymer melt. Apart from its intrinsic interest, the static and dynamic behavior of a polymer at its boundary with another material has obvious importance in a variety of applications, such as moulding, adhesion, coating, composites, and lubrication.

## 2. Experimental Section

The results presented below were obtained by using a modified version of the surface force apparatus developed by one of us.[2] Two thin sheets of molecularly smooth mica are mounted as crossed cylinders whose radius ($R$) is about 1 cm. The shortest distance between the two curved surfaces ($D$) is measured by a sensitive optical interference technique with a resolution of ~0.1 nm. Any force ($F$) between the two micas is measured by monitoring the deflection of a spring on which one of the sheets is mounted, with a sensitivity of $10^{-7}$ N. Further details of the method can be found in ref 2.

By making measurements of the force when the surfaces are in relative motion, the viscosity of the medium between the micas can be determined. This can be done either by driving the surfaces toward each other continuously or by oscillating one of them and measuring the response of the other. These methods are described in ref 10 and 11, respectively. In the former case a numerical simulation of the rate of approach of the surfaces is compared with the experimental measurements to establish the value of the viscosity. In the latter case, if one surface is driven as

$$y = \bar{y} + A_0 \exp(i\omega t) \tag{1}$$

the movement of the other can be written as

$$x = \bar{x} + x_0 \exp(i(\omega t + \phi)) \tag{2}$$

The quantity we measure is the separation

$$D = y - x = (\bar{y} - \bar{x}) + (A_0 - x_0 \exp(i\phi)) \exp(i\omega t) = \bar{D} + A \exp(i\omega t) \tag{3}$$

Assuming that the surfaces are coupled by a newtonian liquid of constant viscosity $\eta$, it can be shown[11] that the measured amplitude of response is

$$A = A_0[(6\pi\omega\eta R^2/K\bar{D})^2 + \delta^2]^{-1/2} \tag{4}$$

where $K$ is the spring constant and $\delta$ is related to the gradient of the surface force at $\bar{D}$

$$\delta = 1 - \frac{1}{K}\left(\frac{dF}{dD}\right)_{\bar{D}} \tag{5}$$

This relation is valid so long as $A$ is much smaller than the mean separation $\bar{D}$. Thus

$$\frac{6\pi\omega R^2}{K[(A_0/A)^2 - \delta^2]^{1/2}} = \frac{\bar{D}}{\eta} \tag{6}$$

and a plot of the left-hand side against $\bar{D}$ should give a straight line whose slope is the inverse of the viscosity.

The PDMS used in these experiments is a commercial silicone oil, Dow Corning 200, of nominal dynamic viscosity 50 cS, used

---

† Present address: Ceramics Division, National Bureau of Standards, Gaithersburg, MD 20899.

‡ Present address: Department of Chemical and Nuclear Engineering, University of California at Santa Barbara, Santa Barbara, CA 93106.

0024-9297/88/2221-2836$01.50/0

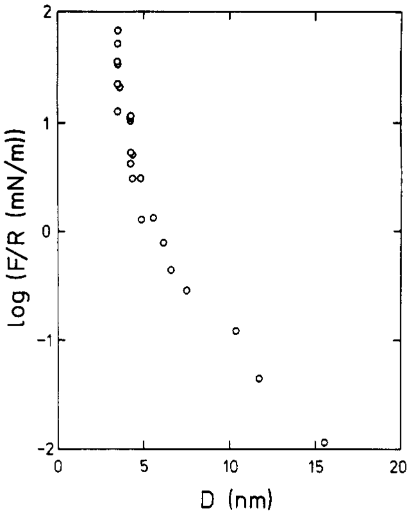

**Figure 1.** Force $F$ measured on approach between crossed mica cylinders immersed in molten poly(dimethylsiloxane) (PDMS), plotted on a logarithmic scale as a function of surface separation $D$. The force is normalized by the radius $R$ (~1 cm) of the cylinders, because this quantity is proportional to the interaction free energy per unit area between two flat plates at the same separation.[15] Points were measured at 1-min intervals. The PDMS has a nominal molecular weight of 3700, corresponding to 50 monomer units, and a mean radius of gyration of 1.6 nm, although there will be a considerable spread in these values due to polydispersity of the sample.

without further purification. PDMS is considered to be a flexible polymer, newtonian, chemically inert, and nonpolar. The viscosity of our sample was measured with an Ostwald tube and found to be (53.8 ± 1.0) cP at 22 °C. According to ref 12 and 13 this value corresponds to a molecular weight of about 3700, or 50 monomer units. The radius of gyration for this molecular weight is estimated as 1.6 nm.[14] However, the material in this form is rather polydisperse. The ratio of weight-average to number-average molecular weight has been measured by Dr. L. Fetters as 2.3 for this particular sample. Furthermore, it may include a significant amount of cyclic and oligomeric dimethylsiloxanes,[12] so not too much significance should be attached to the nominal figures for molecular weight and radius of gyration given above.

A droplet of the sample is injected between the mica sheets and held in place by capillary action. The surrounding vapor is exposed to $P_2O_5$ to ensure that the humidity is minimized, because previous experience has shown that the surface force measured in nonpolar liquids is extremely sensitive to the presence of water. The effect of exposing the sample to humid air is described in section 3.3.

All measurements were made at (22.0 ± 0.2) °C.

## 3. Results and Discussion

**3.1. Surface Structure Deduced from Equilibrium Force Measurements.** The force between two mica sheets separated by a thin film of liquid PDMS is shown plotted on a log scale in Figure 1. The force has been normalized by the radius of curvature of the mica sheets because it has been shown by Derjaguin[15] that this quantity is proportional to the interaction energy per unit area between two flat plates at the same separation

$$F/R = 2\pi E \tag{7}$$

and it is useful to discuss the results in terms of this energy.

The points shown in Figure 1 are from two runs in the same experiment; a repeat experiment gave results in good agreement with these. About 1 min was allowed for equilibration at each separation, which was sufficient time for the surfaces to stop moving (cf. Figure 4). However, we cannot be absolutely certain that the system had reached true equilibrium: with the rather weak forces measured for separations greater than 5 nm it is not practicable to allow a much longer time. The significance of this will be discussed below.

When the polymer film is less than about 15 nm thick there is a monotonic repulsion between the solid surfaces bounding it, a repulsion which increases steadily as the thickness decreases. A possible explanation is that this repulsion arises from the entropic penalty of confining the polymer chains within a narrow gap. It has been argued recently by de Gennes[16] that this would only occur if there was some pinning of the polymer chains to the surfaces, which may be occurring on the time scale of these measurements. As the two solid walls are brought closer together fewer and fewer conformations are available to the polymer chain, so the free energy has to increase. This is one of the contributions to the force between surfaces in polymer solutions, which have received extensive study both theoretically[17] and experimentally.[4,18-20] For molten polymers the effect has been computed by Barker[21] using a lattice model but has not been measured before. The elegant theory of Dolan and Edwards[22] could also be applied to a polymer melt, although those authors considered molecules terminally anchored to one wall, which is not appropriate to the situation here.

In view of the polydispersity of the PDMS used for these experiments, it would be unwise to attach too much significance to the range of the repulsion, which is almost 10 times the nominal radius of gyration. The repulsion could be partly due to higher molecular weight components adsorbed to the surface. In principle these components ought to be squeezed out of the space between the surfaces as they are forced together, because replacing segments of one molecule at the surface by segments of another of the same chemical composition does not affect the adsorption energy, but entropy favors smaller molecules in the gap. However, it is conceivable that this exchange process (and the diffusion of high molecular weight components out of the gap) could take a long time and that final equilibrium has not been attained in these experiments.

Three points are worth noting about the range of the repulsion. First, it appears to be a roughly exponential function of separation beyond 5 nm, with a decay length of about 2 nm, comparable to the nominal radius of gyration. Second, surface forces are a very sensitive probe of inhomogeneous structure near an interface. From the Derjaguin equation[7] above, the amount by which the average free energy per polymer molecule differs from the homogeneous liquid can be estimated. For the weakest detectable force, at 15 nm, the result is $10^{-4}$ kT per molecule, which is a very small fraction of its average thermal energy. Third, one of us has recently made similar measurements in another polymer melt, polybutadiene.[23] For two monodisperse samples with radii of gyration 1.2 and 2.1 nm, the range of the measured force is respectively less than and greater than the range observed here. Since the original submission of this manuscript we have learned that Montfort and Hadziioannou have also recently measured a monotonic repulsion extending to at least 10 times the radius of gyration in a molten perfluorinated polyether.[24]

At shorter range, below about 5 nm, the force takes on a new character, as shown on a linear scale in Figure 2. It is no longer monotonic but displays a series of alternating maxima and minima as the film thickness $D$ is reduced, with a repeat spacing of about 0.7 nm.

Similar forces have been found in low molecular weight liquids[5,6,8] and attributed to packing constraints of the finite-sized molecules in very thin films. At this scale a liquid cannot be thought of as a continuum; the distance resolution of the force-measurement technique is finer than

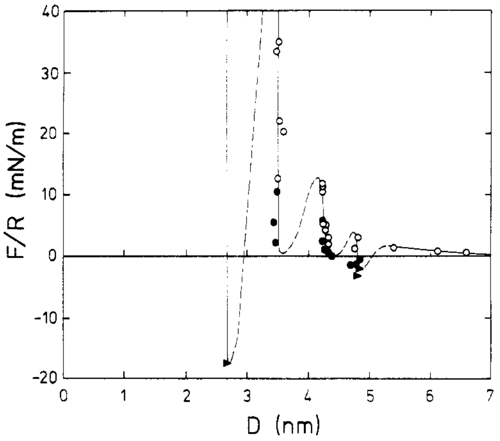

**Figure 2.** Force at short range, plotted on a linear scale. Because one of the mica surfaces is mounted on a spring there is an instability which can be exploited in measuring an oscillatory force such as this. Regions where the force has a steep positive slope are unstable, so the surfaces jump either inward from a force maximum or outward from a force minimum, to the next stable part of the curve. These jumps are used to detect and locate the maxima and minima.[5] Open circles indicate points measured as the surfaces are brought together, closed circles are measured on separation, and triangles indicate the start of outward jumps. Dashed lines show the unstable regions of the force curve where no measurements are obtainable.

the diameter of even small molecules, with the result that it detects the arrangement of the molecules themselves. Close to a smooth solid surface the molecules tend to lie in layers parallel to the surface. When two surfaces approach, there are distances (approximately multiples of the molecular diameter) at which the molecules can pack into an integral number of layers, which is favorable, but at intermediate distances this is not possible, so an unfavorable situation arises. The free energy alternates between maxima and minima, whose magnitude decreases as the number of layers increases. In simple liquids typically eight to ten "oscillations" in the energy (or force between curved surfaces) can be measured.

The spacings observed in Figure 2 correspond to the *width* of the dimethylsiloxane chain, abouut 0.7 nm, rather than some average diameter of the molecule such as $2R_g$, which is much larger. The polymer molecules are not rolled into tight, independent balls which then have packing constraints akin to the smaller molecules of simple liquids. As is well-known, they are interpenetrating, entangled, and indistinct. But the chains are not infinitely thin and flexible: their finite width becomes apparent in very thin films.

As the solid surfaces are brought close together the polymer chains are obliged to occupy a narrow gap, and some gaps can be filled more efficiently than others. It is easy to see that a gap one chain diameter wide can be filled by a set of flexible chains which never cross each other or themselves. Only when the gap is two diameters or wider can chains cross; for gaps between one and two diameters it would be impossible to fill the space without significant voids, and this would be expensive in free energy. It becomes increasingly difficult to visualize the chain arrangements as the film becomes thicker, but our results show that favorable packings are possible only when the thickness is an integral number of chain widths and that the effect is significant up to about seven or eight widths.

This is easier to explain if we assume that short sections of neighboring polymer chains (which could belong to the same molecule) tend to lie parallel to each other, and furthermore tend to lie parallel to the mica surface. In that case, if there is a reasonably high density of chain segments forming a layer next to the surface, chains in the next layer will be obliged to lie parallel to the surface even if they are not parallel to the chains in the first layer. The argument is repeated for the next layer, and so on, until beyond some short-range coherence length the chains will no longer "feel" the presence of the surface. To use a different language, the segment density distribution function normal to the surface would show a pronounced maximum at one chain radius from the wall, a lesser maximum one diameter beyond that, and a still smaller one beyond that, until it decayed to the average density in bulk. It is exactly the overlap of such density distribution functions from neighboring walls that leads to oscillatory force laws.[25]

Recently we reported similar force measurements for mica surfaces separated by the even-numbered liquid *n*-alkanes from hexane to hexadecane.[26] There, too, we found an oscillatory force law with the spacing of the force minima comparable to the *width* of the alkane chains, about 0.4–0.5 nm, independent of the carbon number, and drew similar conclusions about the arrangement of the chains near the solid surfaces. No long-range monotonic repulsion was observed, indicating that the entropic penalties of confining chains of up to 16 segments to narrow gaps are not too serious when the thickness is more than a few chain widths.

From the discussion above about the spacing of density oscillations being determined by chain diameters and from the close similarity of all the force curves measured in the different linear alkanes, it is clear that the oscillatory force would not be greatly affected by the presence of chains of the same width but different lengths, in other words by the polydispersity of the liquid.

No oscillatory force law has ever been observed in any of the measurements so far reported on polymer solutions; why do we find one in a polymer melt? One reason may be related to the absence of solvent in this case. The measurements showing oscillatory force laws in simple liquids were made on pure, i.e., one-component, systems and explained in terms of the constraints on packing a collection of identical molecules into a confined space. Subsequent measurements on liquid mixtures[27-29] have shown that the oscillations in the force become much less pronounced when two molecular species of different sizes are present and the range of the "oscillatory" part of the force is considerably reduced. This is because the packing constraints are much less severe when molecules of two different diameters are available to occupy voids: the density would then vary less dramatically as a function of gap width. In a polymer solution there are two species present, polymer and solvent, and a similar effect would be expected. If the diameter of the solvent molecule did not match the width of the polymer chain, it would tend to disrupt the modulation of the density and reduce the strength of the oscillatory force. Only if the gap were reduced to one or two solvent diameters or polymer chain widths might any oscillations become apparent, but that is such a small distance that it has never been attained in those experiments, the repulsion due to entropic or osmotic effects always preventing the surfaces from being pushed so close together. With a pure polymer, however, the magnitude and range of the oscillatory force are much greater, so that in the present case we are able to measure it out to seven or eight chain widths (about 5 nm), and because of the low moleculear weight of the polymer chosen for this study the entropic repulsion is of relatively short range and not strong enough to mask out the oscillations.

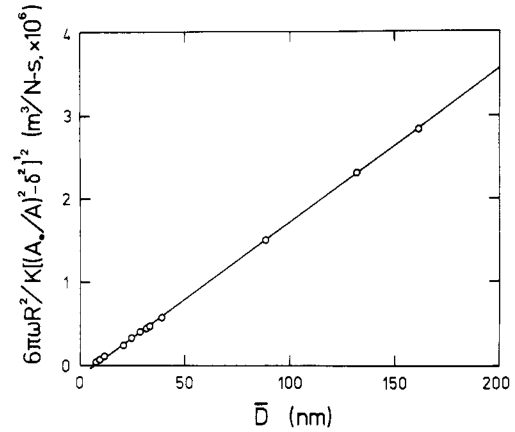

**Figure 3.** Dynamic response of the surface separation when one surface is driven sinusoidally, plotted in the form given by eq 6. The straight line has a slope (1/0.0538 (N s)/m$^2$), corresponding to the measured viscosity of 53.8 cP but does not pass through the origin. The intercept at $\bar{D} = 2D_s$ = (6.0 ± 1.0) nm suggests that the shear plane is located at 3.0 nm from the solid surface.

An alternative explanation for the absence of oscillatory forces in the polymer solutions studied so far has been offered by one of the referees. The density of adsorbed polymer near the surface could become very high, especially when the films are compressed to narrow gaps, and if they were compressed enough the polymer could become solid. It may not be possible for them to rearrange into anything other than a glassy structure on the time scale involved,[30] and such a structure would not give an oscillatory force.

We cannot entirely dismiss the possibility that the oscillations we have observed arise only from low molecular weight components remaining between the surfaces if higher components are evicted from the gap at small separations, and thus they would not be found in a monodisperse linear polymer melt. However, we believe this suggestion to be inconsistent with the long-range repulsion observed (Figure 1). Interestingly, Israelachvili and Kott[23] observed no oscillations in the force measured in molten polybutadiene, but a satisfactory explanation for their absence is presented in terms of the significant branching of that polymer. Further credence is given to this explanation by more recent work of the same authors on a set of branched alkanes[31] in which no oscillations are found, in contrast to the linear alkanes.[26]

**3.2. Viscosity.** Information on the effective viscosity of the thin polymer film can be obtained from measurements of the dynamic response of one surface to a given displacement of the other. Using an oscillatory driving function,[11] we obtain the results shown in Figure 3. They are plotted in the form suggested by eq 6, whereby a newtonian liquid of uniform viscosity would display a straight line through the origin of slope $1/\eta$.

A line of slope 1/(0.0538 (N s)/m$^2$), corresponding to the measured viscosity of our PDMS sample, gives a good fit to the measured points in Figure 3 but does not pass through the origin. Instead, it intersects the $D$-axis at $2D_s$ = (6.0 ± 1.0) nm. This is the behavior expected for a liquid having a uniform viscosity but with the plane of shear (the plane at which the stick boundary condition applies) placed at a distance $D_s$ = 3.0 nm away from the solid surface (toward the liquid). In other words, this is the hydrodynamic layer thickness of the polymer at the mica surface.

An alternative method[10] of establishing the viscosity of the film is to drive one surface toward the other continuously and measure their separation as a function of time.

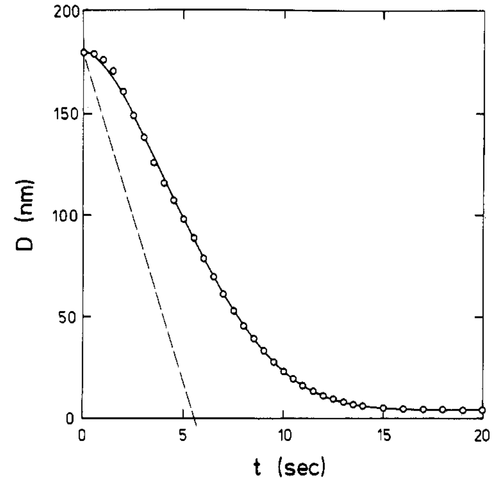

**Figure 4.** Response of the surface separation $D$ as a function of time $t$ when one surface is driven toward the other at a constant speed of 32.5 nm/s (dashed line). Open circles are measured points and the continuous line is the theoretical response for a liquid of viscosity 53.8 cP, a shear plane at $D_s$ = 2.0 nm from each surface, and the appropriate surface force (Figure 1).

Results of one such experiment are shown in Figure 4. The equation of motion of the surfaces can be worked out from Reynolds lubrication theory for a newtonian liquid, including a term due to the equilibrium surface force.[10] The solid line in Figure 4 shows this theoretical response for a newtonian liquid of viscosity 53.8 cP, including the surface force shown in Figure 1, and assuming that a layer of thickness $D_s$ = 2.0 nm next to each solid surface does not undergo shear. Apart from some problems at small $t$ due to start-up imperfections in the motor drive used, there is excellent agreement between theory and experiment. This shows that both types of dynamic measurement can be fitted with the same model, although there is minor disagreement between them in establishing the precise position of the plane of shear.

The two types of viscosity measurement were conducted in the same experiment, but with different opposed regions of the mica surfaces. It was observed that the monotonic repulsive force had a longer range in the region where the oscillatory-drive measurements were made; the force shown in Figure 1 and subsequently confirmed in a separate experiment was measured in the same region as the continuous-drive viscosity measurements. The difference may be attributable to adsorption of higher molecular weight polymer in the former region, which may also account for the difference in the values of $D_s$ obtained from the two measurements.

Our results clearly show that although the polymer melt is inhomogeneous in very thin films, it can still be treated effectively *as if* it had a uniform viscosity equal to its bulk value. The same thing is true of simple liquids.[10,11] The only question is the precise location of the shear plane at or near a solid surface. These measurements show that the liquid behaves as if there is no shear occurring in a thin layer adjacent to each solid, and the thickness of the layer—the hydrodynamic thickness—is commensurate with the radius of gyration of the polymer molecule, estimated as 1.6 nm. It is interesting to note that this is much less than the measurable range of the surface force in this case. (This "layer" is a construct of the model used to discuss these viscosity results and has nothing to do with the layers discussed in section 3.1.) In similar experiments on a solution of polystyrene in cyclohexane the hydrodynamic thickness was found to be equal to the radius of gyration,[32] and a similar correlation was observed in a crude oil system.[33] Further work will be required to prove the generality of this conclusion, but it would appear that the flow of polymers in narrow capillaries can be modeled very simply and successfully by adopting the stick boundary condition at a plane approximately one radius of gyration from the solid interface and allowing the rest of the liquid to have a uniform viscosity equal to that of the bulk. It should, however, be borne in mind that this is an oversimplified picture of what really happens in extremely thin films; one should not take the "infinite viscosity" of the surface layer too literally. It can be seen from Figure 2 that it is possible to push the surfaces to within $2D_s$ of each other in a finite time.

As can be seen from Figure 4, the approach of the mica surfaces becomes very slow once their separation is down to 5 nm or less. In such thin films the flow of the polymer is severely restricted, and one consequence of this is that the repulsive force barriers shown in Figure 2 may be overestimated if they are partly kinetic in nature. We have noted before that this leads to difficulty in obtaining reproducible values for the force maxima even in simple liquids;[5,10,26] in the present case it makes it very hard to establish the true equilibrium force maxima at short distances. However, measurements of the force minima do not suffer from the same problem and are determined more accurately.

**3.3. The Effect of Water.** The presence of water even at very low concentrations has been found to have a dramatic effect on the surface forces measured in nonpolar liquids.[5,6,28] The important criterion is the chemical activity, or relative degree of saturation of the water, so that even, say, 100 ppm is enough to have a significant effect on the interaction between hydrophilic surfaces if the solubility of water in the nonpolar liquid is 200 ppm. The water tends to "erase" the short-range oscillatory forces typically measured in such systems, giving rise to a strong adhesion.[28] When the liquid is saturated a water bridge can sometimes be observed to form between mica surfaces.

Allowing PDMS to become saturated with water also leads to a reduction in the force barriers at short range and an increased adhesion. Interestingly, the longer-range "tail" of the force appears unaffected. As the surfaces are brought together there is at first a repulsion as shown in Figure 1, but at a separation of about 8–10 nm a strong attraction between the surfaces suddenly appears and they are pulled abruptly into contact. The adhesion between them is measured as $F/R$ = (330 ± 10) mN/m. If the contact angle of water on mica immersed in PDMS is assumed to be small, this corresponds to a water–PDMS interfacial energy of $\gamma_i$ = (26 ± 1) mJ/m$^2$.[34]

This fact—that despite its radical effect on the short-range force water does not affect the long-range force—has not been observed before, for the simple reason that none of the other nonpolar liquids investigated has had any long-range force. The effect on the oscillatory part of the force has been explained[28] in terms of the packing efficiencies of two species of molecule as outlined in section 3.1, but evidently the presence of a small concentration of water does not affect the conformational restrictions which give rise to the monotonic repulsive tail found in the polymer melt.

The dynamic approach of two surfaces in water-saturated PDMS is shown in Figure 5. The curve can be fitted very well, down to the point at which the surfaces jump abruptly into contact, by assuming the bulk value of viscosity for PDMS and including the equilibrium surface force, as in Figure 4. However, in this case the best fit is obtained if the shear plane is placed *at the surface*, i.e., $D_s$ = 0. Why this should be so is not clear, especially since the equilibrium force measurements imply that the polymer conformations near the surface are not greatly affected by the water. There may be an accidental cancellation of drag enhancement due to a hydrodynamic layer of the polymer and drag reduction due perhaps to some slipping at the surface with water present. Further experiments will be required to explore this.

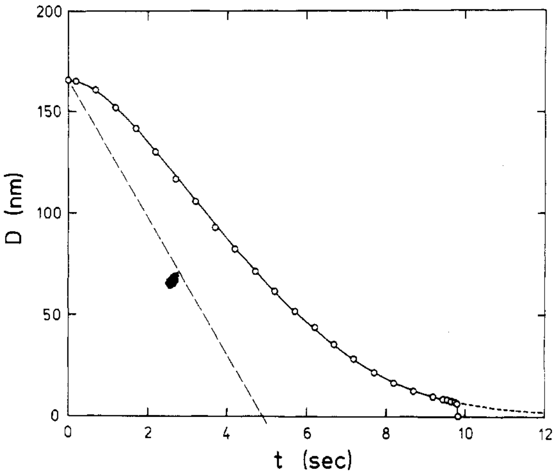

**Figure 5.** Similar experiment to that shown in Figure 4, conducted on PDMS saturated in water. Although the water concentration is very low, it has a dramatic effect on the drainage of the polymer film. In contrast to the earlier results, the film is now unstable, as shown by the abrupt jump into contact at $t$ = 9.8 s. The best-fit theoretical curve is obtained when the shear plane is placed at the surface ($D_s$ = 0), although this may be a coincidence due to the cancellation of opposing effects (see text).

It is clear that without careful precautions to remove water from a nonpolar polymer, it will behave "normally" in moderately thin films, but not in extremely thin films where (between hydrophilic surfaces) it will collapse rapidly, in marked contrast to the stability observed in dry polymer. Since the lubricating effect of PDMS depends on its ability to prevent contacts between solid surfaces, we can surmise that this property is seriously degraded by the presence of water.

## 4. Conclusions

Measurements of the force between smooth surfaces across a film of molten PDMS of viscosity 54 cP have shown a monotonic repulsion extending to 15 nm. The significance of this range is open to debate in view of the polydispersity of our sample, and measurements on a more monodisperse material will be required to confirm it. It is likely that this force results from the molecules being *pinned* to the surface[16] on the time scale of the measurements.

At short range the force is found to be an oscillatory function of film thickness, with alternate maxima and minima separated by a distance corresponding to the width of the polymer chain. These features resemble those found in simple low-molecular weight liquids, where the force has been explained in terms of the quasi-spherical molecules being arranged in layers between the two solid surfaces. Our results indicate that in a molten polymer having flexible, linear chains there is still a layering phenomenon, with the polymer *segments* arranged in layers. A measurement of the segment density distribution normal to a solid surface would show oscillations akin to those found in the familiar radial distribution function of a simple liquid, but a given molecule could occupy several layers. It is difficult to conceive of such an arrangement unless sections of the chain have a tendency to lie parallel to the solid surface, at least in the first layer or two.

It is suggested that the oscillatory region of the force is measurable in the present system because only one molecular species is present in the polymer melt. The layering of segments, giving a spacing equal to the chain width, would still occur in a polydisperse sample. However, if solvent molecules in a polymer solution had a diameter different from the chain width they would be able to smooth out the maxima and minima in the segment density distribution function and so reduce the range of the oscillatory force to only one or two molecular widths, rendering it undetectable.

Recent measurements of surface forces in the liquid $n$-alkanes from hexane to hexadecane[26] showed a similar short-range oscillatory force, but no long-range repulsion. This suggests that the arrangements of the alkane chains in the narrow gap between solid surfaces resemble those of the polymer molecules, but the entropic penalty of confining a chain molecule to that gap only becomes significant (beyond the range of the oscillatory force, about six to eight chain widths) when the number of segments is somewhat more than 16.

Two different methods of determining the viscosity in thin films both show that the polymer melt can be *modeled* very accurately as a newtonian liquid having a uniform viscosity equal to its bulk value, except in a narrow region adjacent to each solid surface, where the viscosity is effectively infinite. The thickness of this "immobile" region is about one radius of gyration of the molecule. It must be stressed that this gives a model for the effective viscosity of the film in squeeze flow, rather than a true picture of the flow which occurs in an inhomogeneous film.

This strong repulsive force barriers encountered at short distances, which may be partly kinetic in nature, could explain the fact that PDMS serves as an excellent release agent and as a lubricant. However, our results suggest that both these properties would be seriously degraded (at least between hydrophilic surfaces) if the polymer becomes saturated with water. In that case the repulsive force barriers disappear, to be replaced by a strong attraction and adhesion due to water condensing and forming a bridge between the surfaces. A squeeze film of the polymer ruptures abruptly at a thickness of about 10 nm, in contrast to the very stable film observed in dry PDMS. These effects occur even though the absolute concentration of water is low and does not affect the viscosity of a thicker film or the long-range part of the surface force.

**Acknowledgment.** We are grateful to Fred Pribac for assistance with data analysis and viscosity measurements, to Lew Fetters for measuring the polydispersity of our sample, to Georges Hadziioannou for giving us a preprint of ref 24, to Hugo Christenson and Matt Tirrell for valuable discussions, and to the two referees for important suggestions. Partial support was provided by NSF Grant CBT86-16599.

**Registry No.** Water, 7732-18-5.

## References and Notes

(1) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic: New York, 1985.
(2) Israelachvili, J. N.; Adams, G. E. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 975.
(3) Pashley, R. M. *J. Colloid Interface Sci.* **1981**, *83*, 531.
(4) Klein, J. *J. Colloid Interface Sci.* **1986**, *111*, 305.
(5) Horn, R. G.; Israelachvili, J. N. *J. Chem. Phys.* **1981**, *75*, 1400.
(6) Christenson, H. K. *J. Chem. Phys.* **1983**, *78*, 6906.
(7) LeNeveu, D. M.; Rand, R. P.; Parsegian, V. A.; Gingell, D. *Biophys. J.* **1977**, *18*, 209.
(8) Pashley, R. M.; Israelachvili, J. N. *J. Colloid Interface Sci.* **1984**, *101*, 511.
(9) Pashley, R. M.; McGuiggan, P. M.; Ninham, B. W.; Evans, D. F. *Science (Washington, D.C.)* **1985**, *229*, 1088.
(10) Chan, D. Y. C.; Horn, R. G. *J. Chem. Phys.* **1985**, *83*, 5311.
(11) Israelachvili, J. N. *J. Colloid Interface Sci.* **1986**, *110*, 263.
(12) Lichtenwalner, H. K.; Sprung, M. N. In *Encyclopedia of Polymer Science and Technology*; Wiley-Interscience: New York, 1970; Vol. 12, pp 464–569.
(13) Hunter, M. J.; Warrick, E. L.; Hyde, J. F.; Currie, C. C. *J. Am. Chem. Soc.* **1946**, *68*, 2284.
(14) Brandrup, J.; Immergut, E.H. *Polymer Handbook*; Wiley: New York, 1975.
(15) Derjaguin, B. V. *Kolloid Z.* **1934**, *69*, 155.
(16) de Gennes, P.-G. *C. R. Acad. Sci. Paris, Ser. 2* **1987**, *305*, 1181.
(17) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic: New York, 1983.
(18) Klein, J. *Nature (London)* **1980**, *288*, 248.
(19) Klein, J.; Luckham, P. F. *Macromolecules* **1984**, *17*, 1041.
(20) Israelachvili, J. N.; Tirrell, M.; Klein, J.; Almog, Y. *Macromolecules* **1984**, *17*, 204.
(21) Barker, J. A. IBM Research Report RJ 4206 (46284), 1984.
(22) Dolan, A. K.; Edwards, S. F. *Proc. R. Soc. Lond., A* **1974**, *337*, 509.
(23) Israelachvili, J. N.; Kott, S. *J. Chem. Phys.* **1988**, *88*, 7162.
(24) Montfort, J. P.; Hadziioannou, G. *J. Chem. Phys.* **1988**, *88*, 7187.
(25) Grimson, M. J.; Rickayzen, G.; Richmond, P. *Mol. Phys.* **1980**, *39*, 61.
(26) Christenson, H. K.; Gruen, D. W. R.; Horn, R. G.; Israelachvili, J. N. *J. Chem. Phys.* **1987**, *87*, 1834.
(27) Christenson, H. K. *Chem. Phys. Lett.* **1985**, *118*, 455.
(28) Christenson, H. K.; Blom, C. E. *J. Chem. Phys.* **1987**, *86*, 419.
(29) Horn, R. G.; Evans, D. F.; Ninham, B. W. *J. Phys. Chem.*, in press.
(30) Kremer, K. *J. Phys. (Les Ulis, Fr.)* **1986**, *47*, 1269.
(31) Israelachvili, J. N.; Gee, M. L.; Kott, S. J., manuscript in preparation.
(32) Israelachvili, J. N. *Colloid Polym. Sci.* **1986**, *264*, 1060.
(33) Christenson, H. K.; Israelachvili, J. N. *J. Colloid Interface Sci.* **1987**, *119*, 194.
(34) Fisher, L. R.; Israelachvili, J. N. *Colloids Surf.* **1981**, *3*, 303.