Shear of polymer brushes

Jacob Klein
Weizmann Institute of Science, Rehovot 76100, Israel

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Abstract

We have measured the normal, lateral and hydrodynamic forces that act between polymer-brush-bearing surfaces immersed in a good-solvent medium, both when stationary and when in motion with respect to each other. At low sliding velocities we find a very marked decrease in the frictional force between the surfaces, an effect interpreted in terms of a fluid interfacial layer resulting from the non-interpenetration of the opposing brush layers even when they are compressed against each other. In a different study we measured the lubrication forces between the brush-bearing surfaces, due to hydrodynamic interactions resulting from normal mutual motion. These reveal that, when the surfaces are far apart, the fluid flowing past them penetrates only very slightly into the brush layers. At high compressions, fluid is forced to flow through the brushes; the magnitude of the hydrodynamic forces may then be compared with predictions based on a model for fluid flow through porous media. This is used to discriminate between scaling and mean-field exponents of the composition-dependent hydrodynamic screening length in the semidilute polymer brushes, and shows the results to be much closer to those expected using scaling exponents.

Key words: Polymer brushes; Shear

Introduction

Polymers that do not adsorb at a solid/liquid interface but are densely attached to it by one end only form so-called polymer brushes. Such brushes can profoundly modify interfacial properties [1,2]. In particular, and unlike in the case of adsorbed chains [2], the interactions between two brush-bearing surfaces, across a liquid medium which is a good solvent for the chains, are repulsive at all surface separations and surface coverages. This has obvious implications for the steric stabilisation of colloids [3]. Polymer brushes have been intensively studied in the past few years, and the physics of the brush structure and of equilibrium surface forces between compressed brushes is by now reasonably well understood (see, in particular, references to recent experimental and theoretical work in the comprehensive review by Halperin et al. [1]).

In Fig. 1 are shown schematically three modes of interaction between brush-bearing surfaces. The configuration in Fig. 1(a) illustrates the normal forces \( F_N(D) \) that act between two brushes when they are compressed quasi-statically (surface separation \( D < 2L \), where \( L \) is the equilibrium thickness of an uncompressed brush). This is the configuration most commonly studied in the surface force experiments [1,4–6]. The resulting force–distance profiles have been comprehensively interpreted in terms of the equilibrium normal forces expected between brush-bearing surfaces, as indicated in the inset to Fig. 1(a).

Much less is known about the behaviour of brushes when they are sheared rather than compressed [7–9]. Figures 1(b) and 1(c) illustrate the situation expected when the surfaces are undergoing mutual motion. In Fig. 1(b) the surfaces slide parallel to each other. The layers may be separated \( (D > 2L) \), in which case each layer will be subject
Fig. 1. Illustration of the modes of interaction between curved brush-bearing surfaces a closest distance \( D \) apart. (a) Normal equilibrium forces \( F_\perp(D) \) in static compression. The inset shows \( F_\perp(D) \) profiles, for a typical \( \text{N}^+\text{(CH}_3\text{)}_2\text{(CH}_2\text{)}_4\text{SO}_4^- \) end-terminated polystyrene (PS–X(140)) brush in toluene, taken from Ref. [6]. The solid line is the variation predicted from the Alexander–de Gennes model for the normal force per unit area \( f_\perp(D) \) between two parallel brush-bearing surfaces.

\[
f_\perp(D) = k_BT/s^3[(2L/D)^{9/4} - (D/2L)^{3/4}]
\]

where \( k_B \) and \( T \) are the Boltzmann constant and the temperature, respectively, \( s \) is the mean interanchor spacing of the tethered chains on the surface, and \( L \) is the thickness of each uncompressed brush. The first term in the square brackets represents the change in osmotic pressure due to the segmental interactions within the compressed brushes (increases with decreasing \( D \)). The second term represents the reduction in free energy which occurs on decreasing \( D \) as the stretched chains in the brush (assumed not to interpenetrate) are compressed towards their unperturbed dimensions. In the Derjaguin approximation [6], \( F_\perp(D)/R \) is directly related to \( f_\perp(D) \) (where \( R \) is the mean curvature of the mica sheets). (b) When the top surface slides with velocity \( \nu \) parallel to the bottom one, a shear force \( F_\parallel(D) \) is felt by the bottom surface. At sufficiently high \( \nu \) there is also a sharp increase in the normal forces \( F_\perp(D) \) acting between the surfaces. The inset, adapted from Ref. [8], shows this increase \( AF_\perp(D) \) for two different values of \( D \) (both less than \( 2L \) (a) and greater than \( 2L \) (b), for the PS–X(140) brushes. (c) As the top surface moves (with velocity \( (dD/dt) \)) with respect to the lower one, fluid is forced out of (or into) the intersurface gap. The resulting transverse pressure gradient in the annular region between the surfaces leads to a normal hydrodynamic force \( F_H(D) \) acting to oppose the motion.
to a stress mediated by the fluid being sheared in the gap; or they may be compressed ($D < 2L$) in which case the shear forces $F_\parallel(D)$ between them can, in addition, be transmitted more directly by frictional interactions between the contacting segments.

In Fig. 1(c) the brush-bearing surfaces are in normal motion with respect to each other. In this situation the liquid between the impermeable solid surfaces must either flow out of the gap (surfaces approaching, as indicated schematically) or into it (surfaces receding). The resultant hydrodynamic interactions $F_\parallel(D)$, arising from the mutual motion of the two surfaces, act to oppose the motion and are referred to as lubrication forces. Such interactions were originally analysed by Reynolds [10] in 1886. For a sphere, radius $R$, moving at velocity $dD/dt$ in a liquid of viscosity $\eta_0$ relative to a plane surface a distance $D$ away, in the lubrication limit $D \ll R$

$$F_\parallel = 6\pi R^2 \eta_0 (dD/dt)/D$$

In the configuration of Fig. 1(c) the brushes are subject to a shear as well as to a normal stress arising from the fluid flow, and their structure and hence the forces acting between the surfaces will be affected by these stresses. The equilibrium normal forces $F_\perp(D)$ (Fig. 1(a)) between compressed chains depend only on the thermodynamics of the end-attached layers [11,12]. In contrast, the shear and lubrication forces $F_\parallel(D)$ and $F_\perp(D)$ (Figs. 1(b) and 1(c)) clearly depend also on the relative velocities of the surfaces, as well as on the dynamics of the chains and on their frictional interactions with each other and with the flowing liquid. The behaviour of polymer-bearing surfaces under shear has implications for several practical phenomena. These include the frictional and lubrication properties of such surfaces as they slide past each other, fluid flow modification and the question of viscous drag, and the more general problem of the rheology of sterically stabilised colloidal dispersions.

We recently developed [2,8] an apparatus designed to measure simultaneously both the normal forces $F_\perp(D)$, and the shear forces $F_\parallel(D)$ that act between polymer-bearing mica surfaces as they slide past each other in the configuration of Fig. 1(b). In a brief earlier account [8], we described an unexpected coupling between the lateral sliding motion and the normal forces between the surfaces: at sufficiently rapid shear rates a dramatic increase $\Delta F_\perp(D)$ in these was observed, as indicated in the inset to Fig. 1(b). The effect has been analysed in terms of stretching of the tethered chains which decreases the screening and thus increases the osmotic repulsions between them [7,9]. This is illustrated in Fig. 2, although a number of other explanations have also recently been proposed [13,14]. In the present work we describe the shear forces $F_\parallel(D)$ that act between brush-covered surfaces as they slide past each other at much lower velocities. In addition, we describe a study of the forces that act between the surfaces as they move in the configuration of Fig. 1(c). Such lubrication forces provide information on the penetration of the fluid into the brushes and on the drag experienced by the fluid as it flows through the brush itself.

### Materials, apparatus and procedure

#### Materials

The end-adsorbing polymers used in these studies were anionically polymerised monodisperse polystyrene (PS) chains of molecular weight $M$, terminated with the zwitterionic group

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**Fig. 2.** Schematic illustration of a possible origin [7,9] of the increase $\Delta F_\perp(D)$ in the normal force (inset to Fig. 1(b)). When the tethered chains (a) are subjected to a sufficiently strong shear so that they stretch, the screening of the excluded-volume interaction between the segments decreases; this leads to increased overall osmotic repulsion and thus to brush swelling, as in (b).
Table 1
Characteristics of end-adsorbing polymers* used in the study

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>$R_g$</th>
<th>$R_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-X(140)</td>
<td>1.41 x 10^5</td>
<td>1.03</td>
<td>105</td>
<td>323</td>
</tr>
<tr>
<td>PS-X(375)</td>
<td>3.75 x 10^5</td>
<td>1.03</td>
<td>173</td>
<td>620</td>
</tr>
</tbody>
</table>

*Details of the synthesis and characterisation are given in Ref. 6. 
$^b$Weight-average molecular weight. 
$^c$Number-average molecular weight. 
$^d$Unperturbed radius of gyration of the molecules. 
$^e$Swollen end-to-end dimension of the molecules in toluene.

= N^+(CH3)2(CH2)2SO3 (the molecules are designated PS-X). Their characteristics are given in Table 1. These PS-X(M) samples (M in units of 10^3 Da) were from the batches (with the same designation) that were used earlier in extensive surface force measurements [5,6] and surface exchange studies [15,16]. Unfunctionalised polystyrene is known not to adsorb onto mica from toluene [5,17], but the zwitterionic end group adheres to the mica surface with an energy $\Delta \equiv k_BT = (6-8)k_BT$, anchoring the PS-X chains at one end to create the polymer brushes [7].

Apparatus and procedure

Two different experimental approaches are used. For shear forces in the configuration of Fig. 1(b) we used the apparatus described in Refs. 2 and 8. In this the curved mica surfaces are positioned opposite each other, and the distance of closest approach between them, $D$, is measured (via multiple beam interferometry) to $\delta D = \pm 2$ Å. One of the surfaces is mounted on a horizontal leaf spring (spring constant, $K_2$), the bending of which yields the normal force $F_n(D)$ in the usual way. The other surface is mounted via a sectored piezoelectric tube (PZT) on a pair of vertical leaf springs (spring constant, $K_1$). The top mica surface, mounted on the sectored PZT, can be made to move laterally relative to the bottom surface in an extremely parallel fashion (i.e. at an essentially constant separation $D$). A schematic illustration of the configuration is shown in Fig. 3. Any shear force $F_s(D)$ acting between the surfaces as they slide past each other causes a bending $\chi$ of the springs $K_1$; this bending is detected (to $\delta \chi = \pm 2$ Å) by a parallel air-gap capacitor, to provide the shear forces. The sensitivities $K_2 \delta D$ and $K_1 \delta \chi$ of direct measurements of both $F_n(D)$ and $F_s(D)$ respectively are comparable, being around $4 \times 10^{-8}$ N. Such extreme sensitivity is required because the lateral force expected between polymer-bearing surfaces undergoing shear is expected to be several orders of magnitude weaker than for corresponding frictional forces between bare solids in contact (either in air or in a monomeric liquid [18,19]). (The mica force balance has also been used to investigate viscoelastic properties of sheared polymer melts confined between the surfaces; see, for example, Ref. 20.) During a shear experiment the bending of the two orthogonal springs is monitored simultaneously to yield both $F_n(D)$ and $F_s(D)$.

In the second study we measured the normal lubrication forces between curved mica sheets in the configuration of Fig. 1(c). In this experiment [21] a sinusoidal normal motion $A_0 \sin \omega t$ (where $A_0$ is amplitude) is applied to the top surface. For the case of uncoated surfaces immersed in a simple
liquid of viscosity $\eta_0$, and as long as the driving frequency $\omega$ is much lower than the resonant frequency of the supporting spring, the closest distance between the surfaces varies as

$$D'(t) = D + A \sin(\omega t + \phi)$$

(2)

and the following relationship can be shown [23] to follow from the Reynolds Eq. (1).

$$6\pi R^2 \omega / \{K_2 [(A_0/A)^2 - 1]^{1/2}\} \approx G(R, \omega, A_0, K_2) = D/\eta_0$$

(3)

where $R$ is the mean radius of curvature of the two mica sheets. A plot of “effective mobility” $G$ against surface separation $D$ should then yield a straight line with slope $1/\eta_0$ running through the origin ($D=0$). For the case where each surface bears a polymer layer of some effective hydrodynamic thickness $L_H$, Eq. (3) still holds for $D \gg 2L_H$, but the equation is now modified to [23]

$$G = (D - 2L_H)/\eta_0$$

(4)

This is equivalent to shifting the plane of shear of the fluid (defining the no-slip boundary) from the original (polymer free) solid/liquid interfaces to a distance $L_H$ from each surface. A plot of Eq. (3) should then manifest a linear regime at $D \gg 2L_H$, with a slope $\eta_0^{-1}$ and an intercept $D=2L_H$.

Figure 4 defines the geometry and parameters of the experiment. Values of $A_0$ in the range 500–3000 Å and of $\omega$ in the range 0.1–1 Hz were used in these experiments. In practice the interferometric fringes which yield $D$ and hence $A$ (Eq. (2)), are recorded with a VCR during an experimental run and are subsequently analysed to calculate the “effective mobility” $G$ (Eq. (3)).

In both studies the normal force profiles $F_\perp(D)$ were frequently determined during the course of the experiments. These profiles provide a control on the integrity of the brush layers with respect to being detached from the surfaces or otherwise degraded as a result of the measurements.

Results and discussion

Shear forces

Normal force profiles $F_\perp(D)$ for brushes formed by the PS–X(140) sample are indicated in Fig. 5. Data points are presented for profiles determined both prior to and following shear measurements; the similarity of the profiles demonstrates clearly that, within the scatter, the brushes are unchanged by shear. These $F_\perp(D)$ profiles are closely similar to those described for the same brushes in the

![Fig. 4](image_url)

Fig. 4. The configuration used for the measurement of lubrication forces [21] between curved interacting surfaces (mean radius of curvature $R$) bearing PS–X chains attached by one end (via the zwitterion $-$X at that end), with mean interanchor spacing $s$ and brush thickness $L$. In these experiments the upper surface is moved sinusoidally with frequency $\omega$ and amplitude $A_0$ normally with respect to the lower one, so that the distance of closest approach $D$ also varies sinusoidally (Eq. (2)).
comprehensive earlier study by Taunton et al. [6]. The stability of the polymer brushes to shear is of interest and may have practical implications. The reasons for this robustness have been discussed in more detail earlier [2,9]; they are related to the fact that even under conditions where the tethered chains are considerably stretched by shearing, the tension in them is weak relative to that required to remove the adhering zwitterions from the mica surface. (In contrast, long tethered PS–X chains may be readily removed and replaced on the surface by shorter PS–X chains [15], even when the latter are present at much lower concentrations [16].)

A convenient way to monitor the shear forces at different values of $D$ is to display, as a function of time, the relative lateral displacement $\Delta x_0$ applied to the top surface by the sectored PZT, together with the corresponding bending $\Delta x$ of the spring $K_1$ due to the shear force between the surfaces (see Fig. 3). The shear force is then obtained directly as $F_{\parallel}(D) = K_1 \Delta x$. Typical $\Delta x_0(t)$ vs. $\Delta x(t)$ runs are shown in Figs. 6 and 7 for different configurations. In Fig. 6 the mica surfaces are in molecular contact in air. As evident from the traces, the bending of the vertical springs $\Delta x$ exactly follows the applied motion $\Delta x_0$. This implies that the two surfaces move rigidly together, i.e. that the static frictional force between the surfaces is larger than $F_{\parallel}(D)$ over the range of $\Delta x_0$ applied. (Later we demonstrate how, at sufficiently large amplitudes of the applied motion, the lateral force $F_{\parallel}(D)$ exceeds the frictional force and the surfaces slide over each other, i.e. $\Delta x < \Delta x_0$.) Very similar "rigid-coupling" profiles are obtained also when the polymer-free mica sheets are in contact in toluene; in this case there is a strong attraction between them due to capillary condensation effects arising from trace water in the undried solvent. Thus the interaction of the bare mica surfaces in air or in a simple monomeric liquid such as toluene is characterised by a strong adhesion and by a large resistance to being slid past one another.

The presence of polymer brushes on the surfaces modifies these features dramatically. This is true not only for the normal forces (e.g. Fig. 1(a) inset

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**Fig. 6.** Variation with time of the lateral displacement $\Delta x_0(t)$ applied to the upper mica surface by the sectored PZT, together with the corresponding bending $\Delta x(t)$ experienced by the spring $K_1$ (see Fig. 3) in response to the shear forces between the surfaces. The mica sheets are in molecular contact in air. The two displacements are of the same amplitude and in phase, showing that the surfaces move rigidly together (no sliding) over the range of motion displayed. The broken horizontal lines (marked with arrows) represent the "equilibrium" position: zero lateral displacement and zero shear force.

**Fig. 7.** $\Delta x_0(t)$ vs. $\Delta x(t)$ plot as in Fig. 6, for two mica surfaces bearing a PS–X(140) brush under strong compression ($D < D_{\text{conc}}/10$). The applied motion $\Delta x_0(t)$ has a sawtooth shape. At each change of direction the two surfaces are initially rigidly coupled, but when the extension $\Delta x(t)$ exceeds a certain $\Delta x_{\text{crit}}$ (at the point marked with an arrow), so that the shear force exceeds $F_{\parallel}(D) = K_1 \Delta x_{\text{crit}}$, they begin to slide past each other with a characteristic stick–slip motion. The broken horizontal lines (marked with arrows) represent the zero lateral displacement corresponding to zero shear force.
and Fig. 5), but especially with respect to the frictional forces between them. Shear measurements between brush-bearing surfaces were carried out from the respective separations $D_{\text{onset}}$ where the surfaces first begin to repel each other, and at progressively higher compressions $D < D_{\text{onset}}$. We find that over a range of increasing normal compressive forces $F_{\perp}(D)$, from $D = D_{\text{onset}}$ down to $D = xD_{\text{onset}}$ where $x \approx (1/6) - (1/10)$ (dependent somewhat on the applied shear velocity $v = \partial A x_{0}/\partial t$) the shear forces as measured by our apparatus are so weak as to be within the noise level of the $Ax_{0}$ signal. To take a specific but characteristic example, we find that for two compressed PS-X(140) brushes sliding past each other at low velocities ($v \approx 100 \text{ nm s}^{-1}$) the shear forces are less than the noise in our signal for surfaces separations down to some 160 Å (i.e. $D_{\text{onset}}/8$ for this system, Fig. 5). For typical noise levels (due to vibrations) of some $\pm 5$ Å in the bending of the springs $K_{1}$ measuring the shear forces, this shows that these forces must be weaker than about 0.15 μN under these conditions. From the force profiles, such as those appearing in Fig. 5 (or in the inset to Fig. 1(a)), we may estimate the corresponding normal force $F_{\perp}(D = 160 \text{ Å}) \approx 100 \text{ μN}$. This gives an effective “friction coefficient”, defined as $\mu_{\text{eff}}(D) = F_{\parallel}(D)/F_{\perp}(D) < 0.0015$ for all surface separations $D > 160 \text{ Å}$. At progressively smaller $D$ values (and correspondingly stronger compressions), detectable shear forces are manifested, and indeed increase very rapidly as $D$ decreases. The surfaces then slide past each other with a characteristic “stick–slip” behaviour, as illustrated in Fig. 7. This shows the change in the shear force, when the brushes are highly compressed ($D < D_{\text{onset}}/10$) as the top mica surface is moved back and forth (with amplitude $x_{0}(t)$) via the PZT (Fig. 3). At each change of direction the surfaces are initially rigidly coupled ($Ax = A x_{0}$, the “stick” cycle) because the static frictional force between them exceeds the applied shear force. Eventually, at some displacement $A x_{0,e}$ of the top surface, the bending of the vertical springs results in a shear force $K_{1}A x_{0,e}$ which exceeds the static frictional force resisting the sliding motion. At that point the surfaces commence to slide past each other (the “slip” cycle) with an erratic (possibly low amplitude stick–slip) motion, seen as the horizontal portion of the $x(t)$ plot in Fig. 7.

It is of interest to estimate the normal pressures between the compressed mica sheets corresponding to these regimes. In the Derjaguin approximation, the normal force–distance profiles $(F_{\perp}(D)R)$ give the interaction energy per unit area between flat parallel plates a distance $D$ apart obeying the same force law, and from this we may evaluate the mean pressure in the region of closest approach $D$ between the surfaces. For $D = 160 \text{ Å}$ a pressure of about 5–10 atm may be estimated. A similar value is obtained if one assumes, based on Fig. 5, that (at high compressions) most of the load is born by those polymer chains squeezed to between $D$ and $D + 50$ Å say. The effective area bearing the load is then $A_{\text{eff}} \approx 10^{-11} \text{ m}^{2}$, corresponding to an effective pressure $F_{\perp}(D)/A_{\text{eff}}$, for $D = 160 \text{ Å}$ this approach gives a value of around $10^{6} \text{ N m}^{-2}$ (10 atm). Thus up to moderate pressures between the surfaces we find the polymer brushes serving as extremely efficient lubricants. Indeed, the value of $\mu_{\text{eff}}$ remains low (below 0.05) up to much higher normal pressures. This contrasts with the case of air or of simple liquids between mica surfaces, where the surfaces come into spontaneous adhesive contact even in the absence of any applied pressure and the frictional force is very high (as in Fig. 6 and in earlier studies [18,24]).

The origin of this lubricating effect is suggested in Fig. 8. The chains in each brush tend to stretch normal to the substrate, in order to reduce segmental interactions between the tethered chains; the equilibrium brush thickness is then determined by the balance between these osmotic effects and elastic constraints on chain stretching. When the brushes press against each other, the initial tendency is for each of them to undergo compression, with only little interpenetration of the opposing chains (Fig. 8(a)): this reduces the elastic energy in the brushes by bringing the stretched chains closer to their equilibrium dimensions [11,12], as noted...
in the caption to Fig. 1(a). As the compressed brushes slide over each other, therefore, they are only weakly entangled, so that the sheared interfacial region between them remains highly fluid. Qualitative support for this idea — that the weakness of the shear forces observed in this study is related to the non-interpenetration of the brushes — is provided by experiments described elsewhere [25], where the mica surfaces were covered not by tethered chains in a good solvent, but by adsorbed chains in a theta solvent. Under these conditions the opposing chains undergo considerable interpenetration on being compressed (see Ref. 26 and the schematic diagram in Fig. 8(b)). We found [25] that the shear forces between the compressed polymer layers in the theta solvent case (considerable interpenetration) were very much larger (for corresponding compressions) than in the good solvent study described here (little interpenetration), consistent with the discussion above.

**Lubrication forces [21]**

The measurement of lubrication forces in the configuration of Fig. 4 was carried out in pure toluene, and also in toluene to which unfunctionalised polystyrene had been added; finally PS–X(375) amphiphiles were added to the solution to form brushes at the mica/toluene interface. As usual, $F_\perp(D)$ profiles were determined as a control throughout the experiments. Figure 9 shows the normal force–distance profile for these brushes, which is very similar to earlier profiles obtained by Taunton et al. [6] (broken line) for the same end-functionalised chains. In particular, the quasi-static $F_\perp(D)$ profile gives a measure of the thickness $L$ of each brush, $L = \frac{D_{\text{onset}}}{2} = 1130 \pm 50$ Å. The inset to Fig. 9 shows clearly the absence of interaction between the bare surfaces (both in pure toluene and in the presence of unfunctionalised PS), and the emergence of long-range repulsive forces once brushes form.

In Fig. 10 are shown the dynamic $G(D)$ profiles, defined in Eq. (3). The broken line passing through the origin summarises data in the absence of surface-attached chains (i.e. with pure solvent, and with unfunctionalised PS). The slope of this line is equal, within errors, to the inverse viscosity of bulk toluene, as expected from Eq. (3). The fact that the line passes through the origin $G=0$, $D=0$ shows that the plane of shear in the absence of surface-attached chains is at the mica/liquid interface. The very different behaviour following the formation of the PS–X(375) brushes is shown by the data points. Different symbols correspond to different combinations of the applied motion $A_0$ and frequency $\omega$. 
Several features are immediately apparent. At surface separations larger than $2L$, the data lie (within the scatter) also on a straight line. The slope of this line is again equal, within its estimated uncertainty, to the inverse viscosity of bulk toluene. The intercept of the line at $G=0$ is at some 2200 Å. From our earlier discussion and from Eq. (4), this defines the plane of zero shear and yields the hydrodynamic thickness as $L_H = 1100 \pm 50$ Å. The fact that $L_H \approx L$ as obtained from the $F_A(D)$ profile is of considerable interest. It implies that, as the surfaces approach and recede, and the liquid in the gap is thus expelled or sucked in, there is little interpenetration of the velocity field of the solvent into the brushes as it flows past them.

As the brushes come into overlap so that $D < 2L$, solvent must flow within the layers as the surfaces approach or recede, and the behaviour becomes more complicated. It is then of interest to examine more closely the form of the $G(D)$ profile in the highly compressed region. Very recently Fredrickson and Pincus [27] have analysed the form of the lubrication forces expected between two polymer-bearing surfaces in mutual normal motion at separations $D$ much less than $2L_H$ (i.e. under strong compression). In their treatment the solvent flow throughout the polymer layer is modelled by the Brinkman equation [28] for flow through porous media:

$$\eta_0 \nabla^2 v - \eta_0 \xi^{-2} \nabla P = 0$$  \hspace{1cm} (5)

In this equation, $v$ is the solvent velocity field, $P$ is the pressure and $\xi$ is the hydrodynamic screening length. Physically, $\xi$ is the length scale on which a localised solvent velocity disturbance in the polymer layer decays due to multiple scattering from the polymer segments. Like the static correlation length in a semidilute polymer solution, $\xi$ is approximately independent of polymer molecular weight and scales in the semidilute regime ($\phi \ll 1$) of moderately overlapping layers as

$$\xi = \xi_0 \phi^{-\alpha}$$ \hspace{1cm} (6)

where $\xi_0$ is a length comparable to the monomer size and $\alpha$ is a positive scaling exponent. Although there remains some uncertainty in the values of $\alpha$, it is generally believed that for semidilute solutions (this is the relevant concentration regime within the compressed brushes) $\alpha$ takes the value $3/4$ in good solvents and the value $1$ in theta solvents [29–31]. A value for $\xi_0$ may be obtained explicitly by comparison with neutron scattering studies of hydrodynamic interactions in semidilute polymer solutions [31].

Fredrickson and Pincus solved the Brinkman equation above for steady compression of a sphere of radius $R$ against a flat surface in the lubrication limit, $D/R \ll 1$. This corresponds closely to the conditions of our experiments. They obtained a modified expression for the Reynolds lubrication force and, in particular, derived the analogue of Eq. (3) for the effective mobility $G$, as

$$G = \frac{D}{\eta_{\text{eff}}}$$ \hspace{1cm} (7)
with an effective viscosity given by

\[ \eta_{\text{eff}} = \frac{2}{9} \frac{\rho}{\zeta} \eta_0 \]  

(8)

Since the surface excess of polymer in our study remains constant (and its absolute value may be readily evaluated from the \( F_\perp(D) \) profiles), the mean volume fraction \( \phi \) of the polymer in the compressed brushes must vary inversely with \( D \). From Eqs. (6)–(8) it is then possible to evaluate \( G \), yielding an expression which has no adjustable parameters but depends strongly on the value of \( x \).

In Fig. 11 we magnify the region of high compression, corresponding to the broken rectangle in Fig. 10. Also shown are the predicted \( G(D) \) curves based on the Fredrickson–Pincus treatment outlined above, for the two values of \( x \) corresponding to mean-field (\( x = 1 \)) or to scaling (\( x = 3/4 \)) expectations. Inspection of Fig. 7 shows that neither theoretical prediction is a good fit to the data in the relevant region of high compression (at separations below \( D = 800 \) Å, say). This is not entirely surprising, given the simplification of the model relative to the actual system. Thus the model takes no account of the real volume of the polymer segments or of the approach to the glass transition as the polymer concentration increases with compression (a bulk polystyrene–toluene solution at room temperature becomes glassy at some 85% polymer content). These effects account in part for the fact that the experimental \( G(D) \) profiles appear to intercept the \( D \) axis at \( D \approx 400 \) Å rather than at \( D = 0 \), i.e. that the compressed polymer layers appear to behave in a quasi-solid-like manner at that separation. However, it is important to bear in mind that there are no adjustable parameters involved in calculating the absolute values of the hydrodynamic forces (and hence of the predicted \( G(D) \)). The fact that the magnitude of these \( G(D) \) values predicted using the value \( x = 3/4 \) is very much closer to the data (in the highly compressed region where the model applies) than that using the exponent \( x = 1 \) is then of some significance. It implies that the hydrodynamic screening length does indeed vary with concentration (in the semidilute concentration regime of the compressed brushes) in a manner much closer to the scaling than to the mean-field exponent. This is a gratifying observation, since there are few experimental methods that are sensitive to the precise form of this exponent. Indeed, even the most systematic attack on the problem, via small-angle neutron scattering [31], could not discriminate incisively between the two exponents.

**Summary**

Earlier studies of normal forces \( F_\perp(D) \) between surfaces (at separations \( D \)) bearing polymer brushes in good solvents yielded the brush thickness and its scaling behaviour with tethering density and chain length, as well as the nature of the force–distance laws themselves. These have now been extended to the case of shear and lubrication forces between the surfaces, using an apparatus capable of measuring simultaneously and with great sensitivity both normal and shear forces. Our findings reveal several new features.

When sliding over each other, even at limitingly low velocities, the brush-bearing surfaces can
undergo considerable compression (and support significant pressures) before any lateral forces \( F_\parallel(D) \) are detected between them. This contrasts strongly with the large frictional resistance to motion encountered between sliding surfaces in air or in a simple liquid at similar velocities and pressures. At pressures of up to the order of 10 atm at the point of closest approach \( D \), we find effective friction coefficients \( \mu_{\text{eff}}(D) = F_\parallel(D)/F_\perp(D) < 0.0015 \). This lubricating effect is thought to arise from the non-interpenetration of the brushes as they are pressed against each other; a thin highly fluid layer at the interface between the brushes facilitates the sliding, while at the same time there is a strong normal repulsion between the surfaces, which is maintained owing to the osmotic interactions of the polymer segments within the gap. Within the parameters of our experiments, the brush layers are robust as they slide past each other.

In a somewhat different experimental configuration, hydrodynamic lubrication forces were measured between brush-bearing surfaces moving (sinusoidally) normally with respect to each other. When the brushes are not in contact \( (D > 2L) \), the results show that the velocity field of the liquid penetrates only very slightly into the brushes themselves as it flows past them into and out of the intersurface gap, i.e. the plane of no-slip of the fluid is close to the edge of the brush \( L \). When the brushes are highly compressed \( (D \ll 2L) \), the fluid is forced to flow through them; the resulting surface forces depend strongly on the way in which the hydrodynamic screening length within the brushes varies with segmental concentrations. A model for these forces, based on the Brinkman equation for flow through porous media, provides predictions that are much closer to experimental values when scaling rather than mean-field behaviour is assumed for this variation.

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References

Discussion

Speaker: J. Klein
Questioner: D. Morantz
Q. Would the force versus distance intercept at force zero be a function of time? If one could extrapolate to an “equilibrium” condition would that give a different result compared with measurements (or parameters) made with short time constraints, that is, short in relation to the viscosity of the polymer?
A. I am not sure I understand your question in relation to the lubrication measurements; it is necessary for the two surfaces to be moving with respect to each other. It is this motion which provides the Reynolds “lubrication force”, which for our geometry is given by the effective mobility term $G$ (Eq. (3)). This expression is plotted in Figs. 10 and 11 for a range of frequencies, $\omega$, and applied amplitudes, $A_0$, and as far as we can tell it does not vary systematically with $\omega$.

Speaker: J. Klein
Questioner: B. Costello
Q. You have considered the relative amplitudes of the applied motion and the response, but not the phase angle between them. But for viscoelastic materials, as one would imagine you are dealing with here, the phase angle will be between 0° and 90°. In fact on compression of the surfaces a transition should be observed from liquid to elastic behaviour. I wonder if you have considered this.
A. There is certainly a phase difference between the applied motion $A_0$ and the observed separation $A$ (see for example Ref. 23 for an analysis of this). In our experiments we record $A$ on a VCR, and use it, via the expression for the effective mobility $G$, to analyse our data. The expression for the effective mobility does not require a knowledge of the phase difference between $A$ and $A_0$, but only of their magnitude.

Speaker: J. Klein
Questioner: E. Kiss
Q. Is it possible to compare the structure of a grafted layer in a good solvent to the case of a poor solvent?
A. In principle it is possible, and there are theoretical papers on brushes in poor solvents (see for example Ref. 1 for a review which includes references to these papers). In practice, changing the solvency conditions from “good” to “poor” often leads to a situation where the end-attached chains also undergo adsorption, i.e. segments along the chain contour tend to stick to the substrate surface.
I do not know of a system where unambiguous brushes, i.e. where only the end is attached to the surface, have been formed in poor solvents.

Speaker: J. Klein
Questioner: J.A. Waters
Q. You compared systems with “adsorbed” polymer with “grafted” polymer. How effective is the grafting which appears to arise from a single zwitterionic group? Can you confirm that there is no desorption of the “grafted” species during the compression?
A. The sticking energy of the single zwitterionic group to the mica from toluene is around 6–8$kT$, which appears ample to anchor the chains at reasonable high density (see for example Refs. 6 and 7 in our paper). Since the force profiles on compression–decompression do not change even after several cycles at different pressures, rates etc., we conclude that little detachment of chains occurs. We reach the same conclusion from the reproducibility of force–distance measurements following our shear experiments. The reasons for this have to do with the fact that the tension in the chains appears to be insufficient to pull the zwitterions
off the mica, whether in compression or in stretching. This is discussed at length, for example in Ref. 2 of our paper.

**Speaker:** J. Klein  
**Questioner:** T. van de Ven

Q. With your experimental technique you can measure and manipulate the normal and tangential forces independently. In general, for surfaces coated with polymers these forces are coupled, i.e., applying a tangential force affects the normal force. Is it possible to measure these coupling effects?

A. It is, and we have done it. It turns out that at low sliding velocities little happens, but above some “critical” shear velocity (which depends on $D$ and the brush thickness) the normal force suddenly increases. This effect is illustrated in Fig. 1(b) (inset) and discussed at length in Refs. 2 and 9, as well as in several recent theoretical papers.

**Speaker:** J. Klein  
**Questioner:** M. Cohen Stuart

Q. In the simple scaling approach to the permeability $\zeta \sim \xi_0 \phi^{-z}$ the limit of $\phi \to 1$ is not correct since you then get a finite permeability rather than zero. We were more successful by using $\xi \sim (1 - \phi)/\phi$, which was also suggested by experimental data. What is your comment on this?

A. There are several simplifications in the application of the Brinkman model for flow through porous media to our system of compressed brushes. Using the simple relation $\xi \sim \phi^{-z}$ is one of them, as it does not allow for the effect of finite PS-segment volume at high $\phi$ — it is in any case not really valid outside the semidilute regime if one wants to use a scaling exponent $z = 3/4$. Your suggestion that a modified $\xi$ allowing for finite volume should be used is certainly a good one. One should also allow for the fact that at high $\phi$ at room temperature the PS solutions become glassy. These issues are discussed at greater length in our full paper (Ref. 22).

**Speaker:** J. Klein  
**Questioner:** M. Tirrell

Q. In comparing your data on Reynolds lubrication with the Brinkman theory, you find that the magnitude of the response with scaling exponents is reasonable, but the shape looks wrong; any ideas why?

A. There are a number of simplifications in applying the Brinkman equation to our actual system of a compressed brush (see also my reply to M. Cohen Stuart’s question). For example, we ignore the real volume of the PS segments, which allows the theoretical lines to pass through the origin, and we ignore the fact that PS–toluene solutions approach “glassiness” at about 80% volume fraction of PS at room temperature. Finally, we assume that the brush network structure responds instantaneously to the applied pressure. These are all simplifications compared to the real situation. Nonetheless, it is important to stress that using different exponents $\alpha$ for the hydrodynamic screening length leads to very different values for the lubrication force — and the value obtained with a scaling exponent is far closer to the data. I do not anticipate that adjusting the theory to take account of the simplifications is likely to change that conclusion.