Viscoelasticity of Adsorbed Polymer Layers

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ABSTRACT: We discuss theoretically dynamic measurements with a surface force apparatus composed of a plane and a sphere coated with adsorbed polymer layers in a good solvent. The hydrodynamics are studied within a simple two fluids model where the friction between polymer and solvent is described by the so-called Brinkman approximation. In a steady compression experiment the distance between the sphere and the plane varies at a constant velocity and the polymer layers have a hydrodynamic thickness \( \eta_0 \) of the order of their radius of gyration. In a periodic compression experiment, the distance has a periodic modulation of small amplitude at a finite frequency; the results are recast in terms of a complex modulus \( G' \). At a low frequency, the modulus has the standard Maxwell behavior \( (G' \approx \omega^2, G'' \approx \omega) \). The contribution of the polymer to the loss modulus \( G'' \) is small when the polymer layers do not overlap; it is of the same order of magnitude as the pure solvent contribution when they do overlap. The elastic modulus increases with the thickness of the adsorbed layers. At a high frequency, the complex modulus increases as \( G \approx \omega^{\alpha/3} \) and is independent of the thickness of the polymer layers. When the adsorbed polymer layers overlap, there is an intermediate regime where the elastic part of the modulus increases as \( G' \approx \omega^{\beta/3} \), far enough apart, the dynamic repulsion is well described by Reynolds theory (eq 1), after correcting \( h_0 \) by the polymer layer hydrodynamic thickness. The hydrodynamic thickness is of the order of the Flory radius \( R_f \) of the polymer chains (In a good solvent, the Flory radius increases with the degree of polymerization \( N \) as \( R_f \approx N^{1/5} \)). When the distance between the plates is smaller than the Flory radius \( R_f \), the dynamic force is the sum of an "in phase" elastic repulsion due to the elasticity of the adsorbed layers of an "out of phase" lubrication force which includes the viscous friction of the solvent on the polymer.

Experiments in this geometry have been recently performed by Pelletier et al.\textsuperscript{6} An oscillatory motion has been imposed on a sphere-plane apparatus normal to the plane, and the dynamical response of an adsorbed polymer solution has been measured as a function of frequency.

The viscoelastic response of the complex polymeric fluid to oscillatory shearing is characterized by the shear relaxation modulus \( G(t) \), which links the shear stress \( \sigma(t) \) to the shear strain \( \gamma(t) \):

\[
\sigma(t) = \int_{-\infty}^{t} dt' \gamma(t-t') \gamma(t')
\]

In Fourier space, one defines the complex modulus \( G^*(\omega) = G'(\omega) + iG''(\omega) \) by

\[
G^*(\omega) = i\omega \eta + i\omega \int_0^\infty dt e^{-i\omega t} G(p)(t)
\]

where \( \eta \) is the solvent viscosity and \( G(0) \) the polymer contribution to the modulus \( G(t) \). The real part \( G'(\omega) \) is the storage modulus (\"in phase\"-response) and the imaginary part \( G''(\omega) \) is the loss modulus.

The force acting on one plate when the other one moves is related to the modulus by

\[
F(t) = -6\pi R^2 \int_{-\infty}^{t} dt' G'(t-t') \gamma(t'),
\]

\[
F(\omega) = -6\pi R^2 \gamma G^*(\omega)
\]

where the factor \(-6\pi R^2 \gamma \) has been introduced by analogy with the Reynolds formula: the loss modulus of a periodically compressed newtonian fluid if \( G''(\omega) = \eta \gamma (h_0/h_0) = i\omega \eta \).

As depicted in Figure 1, our (theoretical) surface force apparatus is composed of a fixed plane and an oscillating sphere of radius \( R \). The mean separation between the

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Figure 1. Second-order velocity profile in the nonoverlapping geometry ($R_l < h_0/2$). The profile is plotted for three different values of the friction parameter: $l = 3$, $l = 5$, $l = 10$.

surfaces varies along the radial coordinate $r$ as $h(r) \approx h_0 + r^2/2R$ if $R > R_0$ where $h_0$ is the smallest distance between the surfaces.

In the following, we consider two different types of compression: steady squeezing with a constant (small) velocity difference between the plates, and oscillatory squeezing, where the upper plate has small oscillations around its mean position, with a shear strain $\gamma(t)$. The time-dependent thickness is $h(r,t) = h(r) + h_0\gamma(t)$.

The spirit of our calculation is similar to that of Fredrickson and Pincus for compressed grafted polymer layers. In this approach, the chains are considered as an elastic porous medium through which the solvent flows. The friction between the solvent and the polymers induces an extra viscous dissipation and an elastic deformation of the network formed by the polymer chains. The main difference between the two problems lies in the polymer density profile. The concentration profile in a grafted layer varies smoothly and can be approximated by a constant (a more accurate description is a parabolic profile). In an adsorbed layer, the concentration profile decays as a power law of the distance from the adsorbing surface. In order to describe in a simple manner the polymer concentration in the adsorbed layers, we use the scaling picture introduced by de Gennes where an adsorbed polymer layer is described as a self-similar grid. In an adsorbed layer, the concentration profile has the same scaling behavior with the local concentration $c(z) \sim c(z')$. In the scaling analysis, the adsorbed layer is considered locally as a semidilute solution which becomes denser in the vicinity of the adsorbing surface. The solution has locally no characteristic length scale and the local correlation length must be proportional to the distance to the adsorbing surface $\xi(z) \sim z$. The concentration varies then as $c(z) \sim z^{-3/2}$. In the case where the adsorbed layers on the two plates are not overlapping, the two adsorbed layers are independent and the self-similar concentration profile is cut at a distance from the adsorbing surface equal to the size of the largest loops, i.e. at a distance of the order of the Flory radius. When the two adsorbed layers are moderately overlapping, we can use the Derjaguin approximation according to our hypothesis of large sphere radius. We consider the two plates to be locally parallel and assume that the concentration profile is self-similar on each adsorbing surface and symmetric with respect to the midplane.

The paper is organized as follows. In the next section we introduce the general framework of the two fluids model and the lubrication approximation that allows the derivation of the viscoelasticity of the adsorbed polymer layer. Section 3 studies nonoverlapping polymer layers. We first discuss steady compression and then oscillatory compression in the limit of low pulsation $\omega$ where the internal modes of the adsorbed polymer loops do not contribute to the viscoelasticity. This is the case when $\omega R < 1$ where $\tau_R$ is the Zimm relaxation time of the largest loops with a size of the order of the Flory radius of the chains. Overlapping layers are considered in section 4 and oscillatory compression at high frequency is briefly studied in section 5. The last section presents some concluding remarks and comparisons with experiments.

2. Two Fluids Model

The viscoelastic properties of the confined solution are described within the framework of a two fluids hydrodynamic model. The two fluids are the solvent considered as a Newtonian fluid and the network formed by the adsorbed polymer loops. The displacement of the sphere induces a pressure gradient in the radial direction $r$ and a radial flow of solvent. The drag of the fluid through the network then creates viscous dissipation and an elastic strain of the polymer. The drag is described here by the Brinkman equation, that approximates the polymer solution by a porous medium with a permeability of order $\eta/\xi^2$. The hydrodynamic equation for the solvent flow is the Stokes equation:

$$\eta \nabla^2 \mathbf{u} - \nabla P = 0$$

where $\mathbf{v}$ and $\mathbf{u}$ are the solvent velocity field and the polymers displacement field. The first term is the viscous stress, and the last one the pressure gradient. The second term describes the friction between polymer and solvent in the Brinkman approximation. The permeability has here been written as $\eta/\xi^2$ where $\xi$ is a length proportional to the local correlation length $\xi$. Since in each adsorbed layer the correlation length is proportional to the distance to the adsorbing surface $z$, it is convenient to define a dimensionless number $l$ such that $\xi^* = l(l-1)/2 l^* = (l-1)/h_0$ if $z < h_0/2$ and $\xi^* = l(l-1)/h_0$ if $z > h_0/2$. The number $l$ measures the friction of the solvent of the polymer and is larger than 1 (if $l=1$ the friction vanishes). This number is mainly dependent on the quality of the solvent. The equation of motion of the polymer is a balance between the elastic stress in the solvent and the friction force:

$$\nabla(E(z)\nabla \mathbf{u}) + \frac{\eta}{\xi^*} (\mathbf{v} - \mathbf{u}) = 0$$

where $E(z)$ is the local Young modulus of the polymer solution which in a scaling approach is proportional to the osmotic pressure $E(z) \sim k_BT/\xi^2(z) = \alpha k_BT/z^3$ where $\alpha$ is a numerical constant.

Locally the adsorbed polymer layer can be considered as an isotropic elastic medium and is characterized by two elastic moduli, the Lamé coefficients. At the level of scaling arguments, it can be argued that the two elastic moduli have the same scaling behavior with the local concentration and that the Poisson ratio is a number independent of the
polymer concentration. Following Fredrickson and Pin-  
cus, we have introduced here only the shear modulus  
and we have implicitly assumed that the Poisson ratio  
vanshishes. It is shown at the end of section 3 that  
extact at very low frequency, the contribution to the  
elastic stress considered here is dominant even for  
incompressible layers.

In the case of steady squeezing with slow displacement  
of the upper plate, the polymer has time to relax toward  
equilibrium configuration; we thus only need to consider  
the motion of the solvent through a fixed network (u = 0).  
If the squeezing is obtained by an oscillatory motion  
of the plates, the displacement of the polymer network  
has to be taken into account. Equations 5 and 6 are then  
coupled.

In the case where the distance between the sphere and  
the plane h is much smaller than the radius of the sphere,  
the two fluids model can be further simplified by using  
the lubrication approximation. The typical length scale  
for the variation of the velocity in the z direction is much  
smaller than the typical length scale in the radial direction.  
This imposes that the velocity is essentially radial (u_r  
<< u_z) and that the pressure does not depend on the transverse  
coordinate z; the pressure gradient is also radial. The  
equations of motion in this approximation reduce to

\[ \begin{align*}  
\eta \frac{\partial^2 v_z}{\partial z^2} - \frac{\lambda^2}{\eta} (v_z - \bar{u}_z) - \frac{\delta}{\partial P} &= 0 \\
\eta \frac{\partial}{\partial z} \left( \frac{v_z}{\eta} \right) + \frac{\lambda^2}{\eta} (v_z - \bar{u}_z) &= 0  
\end{align*} \]  

The solvent incompressibility equation can be written  
as \[ \nabla \cdot \mathbf{v} = 0 \]  
or \[ \partial_z v_z = -(1/r) \partial_r (r v_r). \]

This allows a determination of the motion of the upper  
plate from the velocity field:  

\[ v_z(h) = h_0 \dot{z} = \int_0^h \partial_z v_z \, dz = -\frac{2}{r} \partial_r (r \int_0^h v_z \, dz) \]  

we thus obtain

\[ \int_0^{h/2} v_z \, dz = -\frac{1}{4} \dot{h}_0 \]  

The velocity field and the displacement field are obtained  
by integration of the coupled eqs 7 and 8 for a given  
pressure gradient. The pressure gradient is then derived  
from the continuity eq 10, and the hydrodynamic force  
is obtained by integration of the stress tensor over the radial  
surface:

\[ F = \int_0^\infty 2 \pi r dr (P(r) - \bar{P}_a - 2 \eta \partial_z v_z|_{z=0}) = \]  

\[ 2 \pi R \int_0^\infty dh (P(r) - \bar{P}_a - 2 \eta \partial_z v_z|_{z=0}) \]  

The complex modulus is finally obtained from eq 4.

The hydrodynamic force is due to the drag of fluid on  
the polymer network. However this is not the only force  
between the sphere and the plane induced by the adsorbed  
polymer. There is a static force arising from the overlap  
of the two adsorbed layers. At a given spacing between  
the sphere and the plane, the force is compensated by the  
spring of the surface force apparatus and is thus not  
obsorable in a dynamic experiment. It is directly  
proportional to the osmotic pressure of the polymer  
solution at the middle of the gap. In a semidilute polymer  
solution, the osmotic pressure scales as:

\[ \Pi_{osm} = k_B T/\xi^3(z) \]  

and the static force:

\[ F_s = 2\pi \int_0^\infty \frac{k_B T}{\xi^3} \sigma(r) dr \]  

The variation of the static force with the distance  
between plates gives rise to a finite contribution to the  
storage modulus G' at zero frequency. Note that the static  
force and thus the zero frequency limit of the storage  
modulus vanish in the limit where the two adsorbed  
layer do not overlap. At a finite frequency, the force  
between the plates also has a contribution from the  
normal component of the elastic stress of the polymer  
network:

\[ F_N = -2\pi R \int_{h_0}^{\infty} E(z = 0) \partial_z u_z |_{z=0} dh \]  

In the limit where the curvature of the sphere is small,  
this elastic force and the component of the hydrodynamic  
force coming from the viscous stress tensor (\eta \partial_z v_z)  
can be neglected against the pressure contribution.

The Brinkman description of the hydrodynamics of the  
adsorbed polymer layers is valid only in the low frequency  
limit where the internal modes of the loops are not excited  
so that the adsorbed polymer layers can be considered as  
a porous medium. This requires that \( \pi \tau_B < 1 \) where  
\( \tau_B \) is the Zimm relaxation time of the largest loops  
with a size of the order of the Flory radius. This low frequency limit  
seems to be the most relevant for the experimental results  
of Pelletier et al. The higher frequency limit is discussed  
briefly in section 6.

3. Nonoverlapping Polymer Layers

A. Steady Compression. When the distance between  
the sphere and the plane in the surface force apparatus  
decreases at a constant slow velocity, the polymer has time  
to relax toward its equilibrium configuration and there is  
no elastic strain. We discuss here the case where the two  
adsorbed polymer layers do not overlap (Rf/h0 < 1).

We separate the gap between the sphere and the plane  
into three regions, two adsorbed layers of thickness Rf  
and the free solvent in between. The velocity field is found  
in each of these regions from eq 5 with an elastic deformation  
\( u = 0 \). The viscous friction between polymer  
and solvent is finite in the adsorption layers but vanishes  
in the free solvent. At the boundaries between the  
adsorbed polymer and the free solvent (z = Rf), the radial  
velocity \( v_r \) and the transverse viscous stress \( \partial_z v_r \)  
are continuous. The boundary conditions for the hydrody-  
amic motion are the no-slip condition on the walls \( v_z (z  
= 0) = 0 \) and the vanishing stress at the midplane \( \partial_z v_z|_{h/2} = 0 \)  
(for symmetry reasons). We find inside the layers (0  
< z < Rf)

\[ v_z(z) = \frac{\partial_z P}{(l+1)(2-l)\pi} \left\{ \frac{z^2 - (l-1)R_f^{-1} + \frac{(l+1)(2-l)}{2l} h(r) R_f^{-1}}{(l+1)(2-l)h(r) R_f^{-1}} \right\} \]
and between the layers

$$v_z(z) = \frac{\partial P}{\eta} \left\{ \frac{1}{2} \left( z^2 - h(r)z \right) + \frac{l - 1}{2l} h(r) R_f + \frac{l - 1}{2(l + 1)} R_f^2 \right\}$$

(16)

The dynamic force between the sphere and the plane is then calculated from the velocity field using the procedure detailed in the previous section.

$$F = -6\pi R^2 \eta \frac{h}{h_0} \left[ 1 + \frac{2(l - 1) R_f}{l} h(r) + O\left( \frac{R_f}{h_0} \right)^2 \right]$$

(17)

If we introduce the hydrodynamic thickness of the adsorbed polymer layers as $\epsilon_H = R_d (l - 1)/l$, this force can be recast in the form of a Reynolds lubrication force as

$$F = -6\pi R^2 \eta \frac{h}{h_0} - 2\epsilon_H$$

(18)

The friction of the solvent on the adsorbed polymer is thus equivalent to an effective reduction of the distance $h_0$ between the sphere and the plane by the hydrodynamic thickness of the adsorbed layers. This is in agreement with the result of de Gennes for the flow along a wall coated with adsorbed polymer.13

B. Periodic Compression. We now study the periodic compression of the surface force apparatus when the two polymer layers are nonoverlapping at low frequency. The two adsorbed polymer layers constitute only a small perturbation, and the complex modulus is dominated by the loss modulus which has a value close to that of the pure solvent $G''(\omega) = \omega \eta$. The storage modulus $G'(\omega)$ is a correction of higher order in $\omega$.

It is convenient from now on to use dimensionless units $\tilde{z} = z/h(r), \tilde{u} = u_z/h(r)$ and $\tilde{t} = t/\tau(h)$ where we use the local thickness $h(r)$ as the unit length and the Zimm relaxation time of a loop of size $h(r), \tau(h) = \eta h^3(r)/\kappa k_B T$ as the unit time. The pressure gradient is normalized as $B(h) = \partial_r P(h(r)) h(r) = \partial_r P h^4(r)/\kappa k_B T$.

For an oscillation of pulsation $\omega$, we obtain the following equations of motion.

In the pure solvent ($R_f = R_d h(r) < \tilde{z} < 1/2$):

$$\partial_z^2 \tilde{u} = B(h)$$

(19)

In the polymer layers ($0 < \tilde{z} < R_d$)

$$\partial_z^2 \tilde{u} - \frac{l(l - 1)}{2} \partial_z \tilde{u} - B(h) = 0$$

(20)

and

$$\partial_z \left( \frac{1}{2} \partial_z \tilde{u} \right) + \frac{l(l - 1)}{2} \partial_z \tilde{u} - B(h) = 0$$

(21)

On the solid surfaces, the solvent velocity vanishes due to the no-slip boundary condition, and the polymer network is not deformed so that $v(z = 0) = \tilde{u}(\tilde{z} = 0) = 0$. At the edge of the adsorbed polymer layers, there is no stress on the polymer network and the elastic stress vanishes $\partial u_{\partial r} = 0$; the velocity and the transverse viscous stress are continuous. At the midplane, for symmetry reasons, the transverse stress vanishes $\partial u_{\partial r} = 0$.

The velocity field is now found by perturbatively solving eqs 19–21 in powers of $\omega$; the lowest order allows the calculation of the loss modulus $G''$ and the first correction that of the storage modulus $G'$.

Up to first order in $\omega$, eq 20 reads

$$\partial_z^2 \tilde{u}^{(1)} = \frac{l(l - 1)}{2} \tilde{u}^{(1)} + B^{(1)}$$

(22)

This allows the determination of the velocity profile in the adsorbed layers:

$$\tilde{u}^{(1)} = \frac{B^{(1)}}{l(l + 1)(2 - l)} \left\{ \frac{2}{l} + \frac{(l - 1) R_f^2}{(l + 1)(l - 1)} \right\}$$

(23)

In the free solvent region the velocity is

$$\tilde{u}^{(1)} = \frac{B^{(1)}}{l(l + 1)(2 - l)} \left\{ \frac{2}{l} - \frac{l - 1}{2(l + 1)} R_f^2 + \frac{l - 1}{2l} R_f \right\}$$

(24)

These equations show an apparent singularity when $l = 2$. There is in fact no singularity, but logarithmic corrections appear in this limit.

From the velocity field, the pressure field can be calculated:

$$P(r) - P_0 = -6i\omega \eta h \frac{R_1}{h^2(r)} \left[ \frac{1}{2} + \frac{2(l - 1) R_f}{l} + O\left( \frac{R_f}{h_0} \right)^2 \right]$$

(25)

One can then derive the total force on the plane by integration and then the loss modulus

$$G''(\omega) = \omega \eta \left[ 1 + \frac{2(l - 1) R_f}{l} + O\left( \frac{R_f}{h_0} \right)^2 \right]$$

for $\omega \tau_0 < 1$ (26)

This result has a simple interpretation; if $R_f < h_0$, the complex modulus can be expanded in powers of $R_d/h_0$. The zeroth-order term is the modulus of the pure solvent in the absence of polymer. The first-order term is contribution of the polymer, it is proportional to the viscous friction constant $l$, and it vanishes when $l = 1$ in the absence of polymer. The hydrodynamic force is identical to that of the steady compression experiment.

The expansion to second order of eq 21 for $\tilde{u}^{(1)}(z, \omega)$ gives:

$$\tilde{u}^{(1)} = -\int dz \left( 2z \int dz' \frac{l(l - 1)}{2^2} \tilde{u}^{(1)}(z', \omega) \right)$$

(27)

which can be solved combining eq 23 and the boundary conditions.

By injecting the solution of the above equation in the second-order expansion of eq 20,

$$\partial_z^2 \tilde{u}^{(2)} - \frac{l(l - 1)}{2^2} \tilde{u}^{(2)} = -\frac{l(l - 1)}{2} \omega \tau_0 \tilde{u}^{(1)} + B^{(2)}$$

(28)

we find the second-order velocity profile.

In the pure solvent region:

$$\tilde{u}^{(2)} = \frac{B^{(2)}}{2} \left\{ 2z - \frac{l(l - 1)}{2} \frac{R_f}{l(l - 1)} \right\}$$

(29)
In the adsorbed polymer layers:

\[
\eta^{(2)} = \frac{B^{(2)}}{(l + 1)(l - 2)} \left\{ \frac{(l - 1) R_t^2 + (l + 1)(l - 2) R_t^{l - 1}}{2l} \right\}^{1/2} - i \omega \tau^{(1)} \frac{(l - 1)^2}{(l + 1)(l - 2)} \left\{ \frac{(l - 1)(l + 3)(l - 4)}{8(l - 1)(l - 5)} \right\}^{1/2} - \frac{i \omega \tau^{(1)}}{(l + 1)(l - 2)} \left\{ \frac{(l - 2)(l + 6)}{12 + 3(l - 4)} \right\} \frac{R_t^{l - 1}}{l} - \frac{1}{6(l + 1)(l - 5)} \frac{(l - 2)(l + 7)(l - 2)}{2} \frac{R_t^{l - 1}}{l} \left\{ \frac{(l - 1)(l + 1)}{6(l - 1)(l - 1)(l - 3)} \right\}^{1/2} \times \left( \frac{(l - 1)(l + 1)}{2} R_t^{l - 1} - (l - 1) R_t^{l - 1} \right) \right\} \tag{30}
\]

This expression is rather complicated, so we have plotted the second-order velocity profile for various values of the friction parameter \( l \) in Figure 1.

By integration of the velocity profile, the pressure and then the force between the sphere and the plane can be calculated. This force gives the elastic contribution to the complex modulus

\[
G'(\omega) = \frac{\eta \omega^2}{h_0^2} \left( \frac{l - 1}{4(l + 1)(l + 3)} \right) R_t^4 \left( \frac{R_t}{R_0} \right)^6 + \frac{\tau_0}{h_0} \approx \frac{\omega^2 R_t^4}{h_0} \text{ for } \tau_0 < 1 \tag{31}
\]

In this expression, \( \tau_0 = \eta h_0^2/\alpha h_T T \) is the Zimm relaxation time of a polymer solution with a correlation length \( h_T \).

The frequency dependence of the elastic modulus \( (\sim \omega^2) \) at low frequencies is the standard variation for a Maxwell viscoelastic fluid. An interesting point is the \( R_t^4 \approx N^{12/5} \) dependence of the storage modulus, which could be checked experimentally.

This molecular weight dependence can be obtained via the simple following argument. We consider the solution, in the gap of the surface force apparatus as a Maxwell fluid. In the terminal zone, at low frequency, the real and imaginary parts of the complex modulus are related by

\[
G'(\omega) = G''(\omega) = \omega \tau
\]

where \( \tau \) is the viscoelastic relaxation time. Our result for the polymer contribution to the loss modulus eq 26 is \( G''_{\text{p}} = \omega \eta R_t/h_0 \). This gives a storage modulus \( G' = \omega^2 \eta \tau (R_t/h_0) \). If we now choose as the relaxation time, the relaxation time of the large loops with a size of order \( R_t, \tau (R_t) = \eta R_t^4/k_B T \), we obtain

\[
G'(\omega) = \omega^2 h_0^2 \frac{R_t^4}{k_B T \tau_0} = \omega^2 \frac{R_t^4}{k_B T \tau_0} \tag{32}
\]

which is the same result as eq 31, up to a numerical factor which depends on the friction coefficient \( l \). This simple argument emphasizes the fact that at low frequency, the effect of the polymer on the viscoelasticity of the fluid in the gap of the surface force apparatus is dominated by the large loops of size \( R_t \) as already found for the effective hydrodynamic thickness of the layers.

C. Viscous and Elastic Normal Stresses. So far, we have only considered the contribution to the force between plates due to the pressure gradient. We can now check that the contribution of the normal viscous stress and of the normal elastic stress of the polymer network are negligible. The normal velocity gradient \( \partial_x u_z \) can be calculated from the continuity equation (eq 9); it is independent of the radius of sphere. The normal viscous stress is also independent of the sphere radius and upon integration it gives a contribution to the force between the sphere and the plane proportional to the radius of the sphere. This is much smaller than the dynamic force calculated above which is proportional to the square of the radius. Similarly, the normal strain \( \partial_x u_z \) can be calculated from the \( z \)-component of eq 6. It is independent of the sphere radius and the normal elastic force increases also linearly with \( R \). In the limit of zero frequency, the hydrodynamic force vanishes \( (G'' = 0) \) and the elastic force becomes measurable. In the very low frequency limit the elastic modulus reaches a finite value given by the static forces.

The frequency limit above which static forces can be neglected can be obtained by comparison of the static and dynamic (Reynolds) forces; the order of magnitude of these forces are:

\[
F_{\text{stat}} \sim \int (E(x) \partial_x u_z) 2\pi R dR \sim \frac{h_T T}{h^3} R h \gamma \tag{33}
\]

\[
F_{\text{dny}} \sim \eta R^2 \gamma
\]

The static force is small when

\[
\omega \tau (h) > \frac{h_T T}{h^3} \sim 10^{-8}
\]

which is not very restrictive.

Similarly, we can determine the frequency range where the Poisson ratio can be approximated by zero as done in eq 6. In general, the force per unit volume associated to a deformation of an isotropic body can be written as:

\[
f_i = \partial_i \sigma_{ij} = E \varepsilon_{ij} + \lambda \partial_i \nabla u
\]

where \( \sigma_{ij} \) is the stress tensor and \( E \) and \( \lambda \) are the relevant elastic moduli that for simplicity we consider here as constants (this is sufficient to calculate orders of magnitude). The extra force per unit volume in the radial direction is then

\[
\lambda \partial_r \left( \frac{1}{r} \partial_r (ru_z) + \partial_r u_z \right)
\]

The first term involves a second derivative with respect to the radial coordinate and can be neglected within the framework of the lubrication approximation if the two elastic moduli are of the same order of magnitude. The second term can be compared directly to the Brinkman friction force \( \eta \nabla u \). Using the fact that the deformation is \( \partial_x u_z \sim \gamma \) and that the radial velocity is \( v_z \sim \gamma a \) where \( a = \sqrt{R h} \) is the characteristic radial length, we find that the Poisson ratio can be approximated by zero if the frequency satisfies the same inequality given by eq 34.

4. Weakly Overlapping Polymer Layers

We now study the case where the two polymer layers overlap around the center of the surface force apparatus. Even in this central region, we assume that the overlap is weak enough that the concentration profile is not perturbed and is still given by the self-similar law on each plate. The case of strongly overlapping layers is well described by the constant concentration model studied by Fredrickson and Pincus.

The geometry is sketched in Figure 2. There are two different regions: in the central part \( r < r_l \), the adsorbed layers overlap and \( h(r) < h_l = 2R_t \). In the outer region \( r > r_l \), the two layers do not overlap and there is a free solvent layer in the middle of the gap.

In the outer region, the boundary conditions for the flow are the same as in section 3. In the central region the
boundary conditions at $z = R_f$ are replaced by boundary conditions at the midplane imposed by the symmetry $\partial_z u_{1/2} = \partial_z u_{1/2} = 0$. In the following, the variables in the central region are indexed by $<$ and the variables in the outer region by $>$. We first calculate the loss modulus $G''$ by perturbatively solving eqs 5 and 6 to lowest order in $\omega$; the storage modulus $G'$ is then obtained from the next order.

A. Loss Modulus. At lowest order in $\omega$, the velocity profile in the central region $(h(r) < h_i = 2R_f)$ is given by

$$u_{1/2}^C = \frac{B_{1/2}^C}{(l + 1)(2 - l)} \left( z^2 - \frac{z^2 - 1}{l} \right) \tag{37}$$

The pressure gradient can be calculated from the incompressibility condition (eq 9):

$$\partial_r P_{1/2}^C = i \omega \eta h_0 \frac{r}{h(r)^3} \frac{6l(l + 1)^2}{l + 3} \tag{38}$$

In the outer region the pressure gradient is the same as that obtained in section 3 for nonoverlapping layers:

$$\partial_r P_{1/2}^O = 6i \omega \gamma h_0 \frac{r}{h(r)^3} \left[ 1 + a \left( \frac{R_f}{h(r)} \right) + b \left( \frac{R_f}{h(r)} \right)^2 + c \left( \frac{R_f}{h(r)} \right)^3 \right] \tag{39}$$

where $a$, $b$, and $c$ are functions of the friction parameter $l$

$$a = \frac{6(l - 1)}{l} \quad b = \frac{12(l - 1)}{(l + 1)} \quad c = \frac{8l(l - 1)}{(l + 1)^2} \tag{40}$$

The hydrodynamic force can be split into two components coming from the central and outer regions, respectively.

$$F_{1/2}^O = F_{1/2}^C + F_{1/2}^O \tag{41}$$

The pressure at very large radius is equal to the atmospheric pressure, so the pressure field in the outer region is directly obtained by integration of the pressure gradient. A further integration gives the contribution to the force from the central region is

$$F_{1/2}^C = -12\pi i \omega \gamma h_0 \frac{R_t^2}{R_f} \int d(l) \tag{42}$$

where $f(l)$ is a dimensionless number depending only on the friction parameter $l$:

$$f(l) = \int_0^\infty \frac{x - 2}{x^3 + ax^2 + bx + c} \, dx \tag{43}$$

In the central region, the pressure is calculated from the pressure gradient by imposing its continuity as $r = r_i$; the contribution to the force from the central region is

$$F_{1/2}^C = -12\pi i \omega \gamma h_0 \frac{R_t^2}{R_f} \int d(l) \tag{44}$$

where

$$g(l) = \int_0^\infty \frac{dx}{x^3 + ax^2 + bx + c} \tag{45}$$

Summing these two contributions, we obtain the viscous dissipation modulus:

$$G''(\omega) = \omega \eta \left\{ \frac{(l + 1)^2}{l + 3} + \alpha(l) + \beta(l) \right\} \tag{46}$$

where

$$\alpha(l) = 4g(l) - \frac{l(l + 1)^2}{l + 3} + 2f(l), \quad \beta(l) = \frac{l(l + 1)^2}{4(l + 3)} - 2g(l) \tag{47}$$

The functions $\alpha(l)$ and $\beta(l)$ are plotted as a function of $l$ in Figure 3. The figure also displays the variation of the effective viscosity $G''(\omega, l)/\omega$. The coefficients $\alpha$ and $\beta$ vanish when $l = 1$ in the absence of polymer and the loss
modulus \( G'' \) is equal to the pure solvent value given by Reynolds lubrication theory eq 1. \( G'' \) also increases with \( l \), i.e., when the friction between polymer and solvent increases. The dominant contribution to the hydrodynamic force comes from the central region where the two adsorbed polymer regions overlap.

**B. Storage Modulus.** The storage modulus is obtained from an expansion to second order in \( \omega \). In the outer region where the two polymer layers do not overlap \( (h(r) > h_i) \), the velocity profile is the same as the one derived in section 3 (eqs 29 and 30). In the central region, where the two layers overlap, the velocity profile is found by substituting \( l/2 \) to \( R_l \) in eq 30, which corresponds to a change in the boundary conditions. After integration of the velocity, we obtain the pressure gradient using the incompressibility condition eq 9:

In the inner region \( h(r) > h_i \):

\[
\partial_r P^{(2)} = -6\phi \left( l, h(r), \frac{R_l}{R_i} \right) \omega^2 \eta \gamma \frac{\tau_0}{h_0^2} (48)
\]

In the outer region: \( h(r) < h_i \):

\[
\partial_r P^{(2)} = -6\phi(\theta) \omega^2 \eta \gamma \frac{\tau_0}{h_0^2} (49)
\]

where \( \phi(l, x) \) and \( \Theta(l) \) are rather complicated functions of the friction parameter \( l \), and of the dimensionless variable \( x = h(r)/R_i \) that will not be displayed explicitly.

The elastic modulus is then obtained following the same procedure as in the previous section:

\[
G'(\omega) = 2\omega^2 \eta \tau_0 \left[ \frac{R_l^2}{h_0^2} [2\Theta(l) + 2\Phi(l) + \Psi(l)] - \frac{R_l}{h_0} \left[ 2\Theta(l) + \Phi(l) + \frac{1}{2} \Theta(l) \right] \right] (50)
\]

where \( \Theta(l) \), \( \Phi(l) \), and \( \Psi(l) \) are two \( l \)-dependent functions defined by the integrals:

\[
\Theta(l) = \int_2^\infty \phi(l, x)dx \quad \Phi(l) = \int_2^\infty (x-2)\phi(l, x)dx \quad \Psi(l) = \int_2^\infty x\phi(l, x)dx (51)
\]

These integrations were performed numerically and the results are shown in Figure 4. As expected, all the \( l \)-dependent factors in the expression of \( G' \) increase monotonically and vanish for \( l = 1 \), in the absence of polymers between the surfaces. The adsorbed polymer in this case also has a purely elastic response and the storage modulus is proportional to \( \omega^2 \). The important result is the variation with molecular weight: \( G' \) is proportional to \( R_l^2 \) or to \( N^{5/3} \). As for the dissipative response, we can see in Figure 4 that \( G' \) is dominated by the central region (represented by \( \Theta(l) \)).

**5. Periodic Compression at High Frequency**

In the low frequency limit, the adsorbed polymer chains act as an elastic porous medium that has been described by the Brinkman approximation. At higher frequency, the internal modes of the loops forming the adsorbed layers are excited and the Brinkman approximation is not valid. This high frequency limit is now discussed briefly.
In the center of the gap there is no polymer and the velocity profile is governed by the usual Stokes equation.

In the steady-state experiment, when the two adsorbed polymer layers overlap \( R_t > \xi_w \), we use the dynamic blob model and eqs 55 and 56. We do not give a complete derivation here but rather use a simple scaling argument. 

We first consider the case where the two adsorbed layers are not overlapping \( h_0 > 2R_F \). In the high frequency limit, the dynamic blob size \( \xi_w \) is smaller than the Flory radius \( R_F \) of the largest loops and we divide the gap between the sphere and the plane into three regions. Close to the adsorbing surface \( z < \xi_w \), the Brinkman equation can be used and the velocity profile is calculated using the two fluids model of section 2. At intermediate distances \( \xi_w < z < R_t \) we use the dynamic blob model and eqs 55 and 56. In the center of the gap there is no polymer and the velocity is governed by the usual Stokes equation.

In the intermediate range, the relative velocity between polymer and solvent satisfies

\[
\dot{u}_z \left( \nabla_r - i\omega \nabla_r \right) = \frac{1}{\xi_w^2} \left( i + \frac{i\omega}{z} \right) \left( \nabla_r - i\omega \nabla_r \right) + \frac{\partial P}{\eta} \tag{57}
\]

This equation can be solved in the limit \( z \gg \xi_w \) and gives the velocity profile in the intermediate region

\[
v_z = \frac{1}{2} B \left( z^2 - z + C \right) - BC' \left( z^3 + \frac{\xi_w}{z^4} \right)
\]

where \( B = \partial P/\eta \) measures the pressure gradient and \( C \) and \( C' \) are integration constants that could be determined from a matching of this velocity with the velocity profile in the inner region. This matching is rather complicated and will not be done explicitly here.

The first term on the right hand side is the same as the velocity profile in the central region where there is no polymer. The second term is due to the friction between polymer and solvent; it decays exponentially over the dynamic blob size \( \xi_w \) and is vanishingly small over much of the intermediate region. In most of the intermediate region, the influence of the polymer is negligible and the mechanical behavior of the surface force apparatus is the same as that of two surfaces coated with polymer layers of thickness \( \xi_w \). It is clear from the representation of the blob model of Figure 5 that the friction is drastically reduced at high frequency; it becomes negligible in eq 56 and the velocity profile is not affected by the polymer in the intermediate region.

The complex modulus is then obtained at the level of scaling laws by replacing \( R_t \) by \( \xi_w \) in eqs 26 and 31. We obtain

\[
G'(\omega) \approx \eta \tau_0^{-1/3} \omega^{2/3}
\]

\[
G''(\omega) \approx \omega \tau_0^{-1/3} \omega^{2/3}
\]

In the case where the two adsorbed polymer layers overlap \( R_t > h_0 \), we use the same kind of scaling argument. If \( h_0 < \xi_w < R_t \) or \( \omega \tau = \tau(R'_{0})^{-1} < \omega < \omega_0 = \tau_0^{-1} \), the two layers of thickness \( \xi_w \) on the sphere and the plane overlap and we find the complex modulus from the results of section 4 (eqs 50 and 46) by replacing \( R_t \) by \( \xi_w \)

\[
G'(\omega) = \eta \tau_0^{-1/3} \omega^{4/3}
\]

\[
G''(\omega) = \omega \eta^{-1/3} + \tau_0^{-1/3} \omega^{4/3}
\]

At even larger frequency (\( \omega > \omega_0 \)) the layers of size \( \xi_w \) on the two surfaces no longer overlap and the complex modulus is given by eq 59. It is easily checked that the modulus is continuous when \( \omega = \omega_0 \) and crosses over smoothly to the low frequency results when \( \omega = \omega_0 \).

6. Discussion

We have analyzed the viscoelastic behavior of adsorbed polymer layers in an idealized surface force apparatus of a sphere and a plane. Two types of experiments have been considered, a steady-state experiment where the distance between the sphere and the plane decreases with a small constant velocity, and a finite frequency experiment where the distance has small amplitude oscillations.

In the steady-state experiment, when the two adsorbed polymer layers do not overlap, each polymer layer has a hydrodynamic thickness \( \xi_w \) of the order of the size of the largest loops \( R_t \), and the effect of the polymer is equivalent...
to an effective reduction of the gap between the sphere and the plane by 2e− in agreement with a previous result of de Gennes.

In the finite frequency experiment, there is a finite elastic modulus at zero frequency when the two layers overlap. If this plateau value is subtracted off, the complex modulus has at low frequency a Maxwell-like behavior, the real part $G'$ is proportional to $\omega^2$ and the imaginary part $G''$ varies linearly with $\omega$. When the two adsorbed polymer layers do not overlap, the effect of the polymer on the loss modulus is small and the imaginary modulus is small and is proportional to $R_f^2$. This prediction could perhaps be checked experimentally. When the two layers overlap, the contribution of the polymer to the loss modulus due to the friction between polymer and solvent is of the same order as the pure solvent contribution. The elastic modulus is proportional to $R_f^2$. This Maxwell regime is expected until a pulsation $\omega_f$ of the order of the inverse Zimm relaxation time of the chains. At higher frequency we predict a contribution of the polymer to the complex modulus proportional to $(i\omega)^{3/2}$ in the nonoverlapping case. In the overlapping case there are two frequency regimes if $\omega_f < \omega < \omega_0$ where $\omega_0$ is of the order of the inverse relaxation time of a loop with a size $h_0$ (the minimum distance between the sphere and the plane), the contribution of the polymer to the loss modulus is of the same order as the pure solvent contribution and the elastic modulus varies as $\omega^{4/3}$. At higher frequency we find the same result as in the nonoverlapping case.

The hydrodynamic model used to describe the adsorbed polymer layers is the two fluid models. At low frequency we have used the so-called Brinkman approximation to describe the friction between polymer and solvent; at higher frequency we have constructed a blob model. It will be interesting to compare these rather rough models to a hydrodynamic model based on first principles such as the one currently worked out by Wu and Cates. At high frequency, inertial effects of the solvent that govern the diffusion of vorticity also become important; they can, however, be neglected as long as the distance between the sphere and the plane is smaller than $(\eta/\rho\omega_0)^{1/2}$ where $\rho$ is the solvent density. This constraint is always satisfied in the relevant experimental frequency range.

It is interesting to compare our results with those obtained by Fredrickson and Pincus who studied a similar problem for a surface force apparatus where the two surfaces are coated with grafted polymer and not with adsorbed polymer. They studied only the low frequency limit and found a loss modulus varying linearly with frequency but an elastic modulus with an anomalous behavior $G' \approx \omega^{13/11}$. This is due to the fact that for grafted polymer, the flow does not penetrate inside the polymer layer over the whole thickness but only over a very small part of the layer (with a size equal to the blob size).

Experiments have been performed in the geometry studied here by Pelletier et al. with, however, small differences. The polymer is not in a good solvent but in a $\eta$ solvent, the static force between the sphere and the plane is not monotonically repulsive but is attractive at large distances. The solution is not washed and replaced by pure solvent after the adsorption of polymer. In the case where the adsorbed polymer layers do not overlap, the gap does not contain pure solvent but a semidilute polymer solution. Nevertheless it is interesting to compare qualitatively our results with these experiments. At low frequency, a finite elastic modulus is measured only when the two layers overlap. After subtraction of this plateau value, a Maxwell behavior is observed. At higher frequency, the complex modulus increases with a lower power of $\omega$ and seems to depend weakly on $h_0$, but the range of $h_0$ is rather small. The crossover between the low frequency and high frequency regimes occurs at around 10 Hz; this roughly agrees with estimates that can be made of $\omega_f$ or $\omega_0$ ($\approx 100$ Hz). We hope that further experiments will allow a more quantitative comparison with our theoretical results.

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References and Notes