

Optical Measurements of Frequency-Dependent Linear Viscoelastic Moduli of Complex Fluids

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We present a novel experimental method to measure linear viscoelastic moduli of complex fluids using dynamic light scattering. A generalized Langevin equation is used to relate the mean square displacement of a probe particle to the storage and loss moduli of the bulk complex fluid. We confirm the experimental validity of this technique by comparing the light scattering results with mechanical measurements for several complex fluids. This method probes the moduli over a greatly extended frequency range and provides significant new insight into the elastic susceptibility of complex fluids.

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One of the most fundamental properties of any material is its elastic susceptibility, or its response to a shear excitation. For example, the primary difference between a fluid and a solid is their contrasting response to an applied shear strain; solids store mechanical energy and are elastic, whereas fluids dissipate mechanical energy and are viscous. Many materials are viscoelastic; they both store and dissipate energy, with the relative proportions depending on frequency. The elastic susceptibility is parameterized by the complex shear modulus $G^*(\omega)$, which determines the stress induced in a material upon application of an oscillatory shear strain at a frequency ω [1]. The elastic component of the stress is in phase with the applied strain; the ratio of this stress to the strain is the storage modulus $G'(\omega)$, the real part of $G^*(\omega)$. The viscous component of the stress is out of phase with the strain; the ratio of this stress to the strain is the loss modulus $G''(\omega)$, the imaginary part of $G^*(\omega)$. The elastic susceptibility can also be defined in terms of the Fourier transform of the material's response to an impulsive strain [1]; because of causality, $G'(\omega)$ and $G''(\omega)$ are related by the Kramers-Kronig relations [2].

Complex fluids have a rich linear viscoelastic behavior. This is due to the larger length scale of the structures inherent in them; examples include colloidal dispersions and polymer or self-assembled surfactant solutions. These supramolecular structures endow complex fluids with their unique properties, and the interactions between, or within, them govern their dynamics. These dynamics typically possess several characteristic time scales which are reflected in $G^*(\omega)$; moreover, both elastic and viscous components are usually significant, although their relative contributions depend on frequency. However, unlike simple fluids, these frequencies are typically low enough to be experimentally accessible. Traditionally, $G^*(\omega)$ is determined mechanically: For example, a strain is applied and the induced stress is measured. However, because the measurements are mechanical, their frequency range is limited; no single technique can measure $G^*(\omega)$ over an extended range.

In this Letter, we present a novel method for measuring the linear viscoelastic properties of a complex fluid over an extended range of frequencies. We show that the response of the fluid to thermal fluctuations, as probed by the average motion of small particles dispersed within the fluid, provides a close representation of the response of the bulk fluid to an imposed shear strain. The essential physics of this approach is that the bulk mechanical susceptibility of the fluid determines the response of a small particle excited by the thermal stochastic forces which lead to Brownian motion. We use dynamic light scattering to measure the mean square displacement of a probe particle, $\langle \Delta r^2(t) \rangle$, and relate this to $G^*(\omega)$ by describing the motion of the particle with a generalized Langevin equation, incorporating a memory function to account for the viscoelasticity. We compare this $G^*(\omega)$ to that measured by conventional mechanical means. Remarkably good agreement is found. We demonstrate the flexibility of this new technique by measuring the moduli of a variety of complex fluids, and illustrate its potential to determine new behavior.

We describe the motion of a small, neutrally buoyant particle dispersed in a complex fluid by means of generalized Langevin equation [2,3],

$$m\dot{v}(t) = f_R(t) - \int_0^t \zeta(t - \tau)v(\tau)d\tau, \quad (1)$$

where m is the particle mass and $v(t)$ is the particle velocity. This equation expresses the forces on the particle; $f_R(t)$ represents the random forces acting on the particle and includes the contribution from both direct forces between the particles and the stochastic Brownian forces; the integral term represents the viscous damping of the fluid, and incorporates a generalized time-dependent memory function $\zeta(t)$. Energy stored in the medium leads to profound changes in the temporal correlations of the stochastic forces acting on the particle at thermal equilibrium, and the fluctuation-dissipation theorem differs from the commonly encountered delta-function correlation of a purely viscous fluid, becoming [2]

$$\langle f_R(0)f_R(t) \rangle = k_B T \zeta(t), \quad (2)$$

where k_B is Boltzmann's constant and T is the temperature.

By taking the unilateral transform [4] of Eq. (1), and using Eq. (2), the viscoelastic memory function can be related to the velocity autocorrelation function, and, hence, to the particle's mean square displacement. We further assume that the microscopic memory function is proportional to the bulk frequency-dependent viscosity of the fluid,

$$\tilde{\eta}(s) = \frac{\tilde{\xi}(s)}{6\pi a}, \quad (3)$$

where s represents the frequency in the Laplace domain. This relationship is exact in the limit of a purely viscous fluid; here we assume the same behavior for viscoelastic fluids at all frequencies, recognizing that this is only an approximation. Then,

$$\tilde{G}(s) = s\tilde{\eta}(s) = \frac{s}{6\pi a} \left[\frac{6k_B T}{s^2 \langle \Delta \tilde{r}^2(s) \rangle} - ms \right]. \quad (4)$$

The first term in the brackets reflects the thermal fluctuation dissipation in the medium. The second term is due to inertia and is negligible except at very high frequencies. If it is neglected, Eq. (4) reflects a generalized, frequency-dependent form of the Stokes-Einstein relation. For a freely diffusing particle, $\langle \Delta \tilde{r}^2(s) \rangle = 6D/s^2$, and the familiar, frequency-independent viscosity is recovered, $\eta_0 = k_B T / 6\pi a D$, where D is the diffusion coefficient.

To compare with mechanical data, we require $G'(\omega)$ and $G''(\omega)$; however, since they obey the Kramers-Kronig relations, they are not two independent functions, and both can be determined from the single, real function $\tilde{G}(s)$. We could, in principle, calculate the inverse unilateral Laplace transform and then Fourier transform it. Instead, we fit $\tilde{G}(s)$ by a functional form in the real variable s , and then obtain the complex function $G^*(\omega)$ using analytic continuation, substituting $i\omega$ for s in the fitted form. We then identify $G'(\omega)$ and $G''(\omega)$ as the real and imaginary parts; this ensures that the Kramers-Kronig relations are satisfied over the frequency range probed. This procedure establishes a general relationship between the mean square displacement of the particles and the bulk rheological properties of the complex fluid.

To test the applicability of this scheme, we apply it to several distinctly different complex fluids. The first system is a suspension of silica particles in ethylene glycol; these particles interact as hard spheres [5]. The particle radius is relatively uniform, $a = 0.21 \mu\text{m}$, and the volume fraction is $\phi \approx 0.56$. To probe the small values of the mean square displacement required, we use diffusing-wave spectroscopy (DWS), an extension of dynamic light scattering (DLS) to the multiple scattering limit [6,7]. The correlation function measured with DWS in the transmission geometry exhibits the behavior characteristic of a concentrated colloidal suspension of hard spheres near the glass transition [8]. There is an initial, rapid decay to a plateau value, followed by a final

decay at longer times. The particles are relatively small, so that DWS is slightly sensitive to collective motion; nevertheless, to a good approximation the correlation function can be inverted to obtain the mean square displacement of the particles [9]. This requires knowledge of the transport mean free path of the light, l^* , which was obtained from static transmission measurements [9]. The measured $\langle \Delta r^2(t) \rangle$ is shown in the inset of Fig. 1. The linear increase at the shortest times reflects the initial diffusive motion of the particles; at longer times their motion is constrained by the local cage structure of their neighbors. The decay in the correlation function at the longest times, which results from the breakup of the cages, cannot be simply interpreted within DWS as a mean square displacement of individual particles, setting the upper limit of the data that can be inverted.

We numerically calculate the Laplace transform of the mean square displacement, and use Eq. (4) to determine $\tilde{G}(s)$. The results are shown by the open circles in Fig. 1. Because of the restricted extent of the data, the accuracy of the Laplace transform is limited at the lowest frequencies. To obtain the real and imaginary parts of the complex modulus, we fit the data by a functional form based on physical intuition about the behavior of a hard sphere colloidal glass, $\tilde{G}(s) = g_1 - g_2 s^{-0.55} + g_3 s^{0.3} + g_4 s^{0.5} + g_5 s$, where the g_i are positive fitting parameters. The first three terms are suggested by mode coupling theories and reflect the cage dynamics [10]; these terms account for the plateau and a low-frequency relaxation. The fourth term accounts for the predicted high-frequency elastic modulus [11,12], while the fifth term reflects the high-frequency viscosity of the suspension. The fit is indistinguishable from the data and is used to determine $G^*(\omega)$. Although our fit is based on intuition, any functional form that fits the data will provide equally good results.

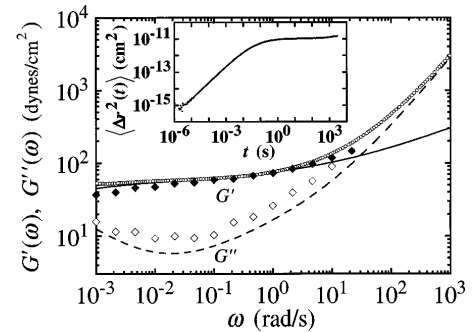


FIG. 1. Frequency-dependent linear viscoelastic moduli for a suspension of hard spheres with $\phi = 0.56$. Data obtained mechanically are shown by diamonds, solid for the storage modulus, and open for the loss modulus. Data obtained optically are shown by lines, solid for the storage modulus, and dashed for the loss modulus. The open circles represent $\tilde{G}(s)$, and are plotted on the same frequency scale. The mean square displacement, measured with DWS, is shown in the inset.

To test this scheme, we determine the moduli directly by an oscillatory mechanical measurement. We employ a controlled strain rheometer using a sample cell with a double-wall Couette geometry. The applied strains are sufficiently low to ensure linearity. In Fig. 1, we compare the measured values of $G'(\omega)$ and $G''(\omega)$, shown by the diamonds, with the predictions from the light scattering, shown by the lines. Excellent agreement is found, particularly with the storage modulus, which is the larger of the two components.

As a second test, we study a polymer solution at a sufficiently high concentration that an entangled network is formed. We use polyethylene oxide with a molecular weight of 4×10^6 dissolved in water at a concentration of 15% by weight. As probe particles, we add polystyrene latex spheres with $a = 0.21 \mu\text{m}$ at $\phi = 2\%$. This ϕ is sufficiently high to ensure multiple scattering from the spheres, but sufficiently low to ensure that the spheres do not contribute appreciably to the viscoelastic behavior. By contrast to the hard sphere suspension, in this case the particles act solely as probes, both for the rheological properties and for the light scattering. We compare the complex moduli obtained from light scattering with those obtained mechanically in Fig. 2; again relatively good overall agreement is obtained. The light scattering data provide a good estimate of the magnitude of the moduli and correctly predict the crossover in the behavior, with $G''(\omega)$ dominating at low frequencies and $G'(\omega)$ dominating at high frequencies. The discrepancy between the two methods is largest at low frequencies; this likely results from the restricted range of the light scattering data, which limits the accuracy of the Laplace transform. Nevertheless, the agreement is remarkably good.

As a third test, we study an emulsion, comprised of uniformly sized oil droplets, with $a = 0.53 \mu\text{m}$, stabilized with a surfactant and suspended in water [13]. The volume fraction is $\phi = 0.62$, resulting in elasticity arising

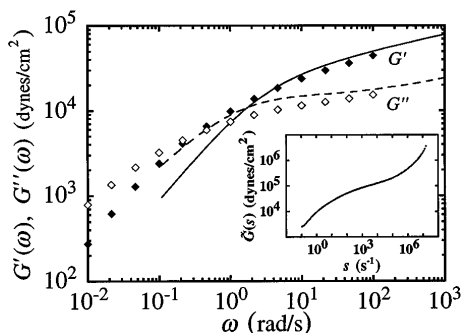


FIG. 2. Frequency-dependent linear viscoelastic moduli for a solution of 4×10^6 molecular weight polyethylene oxide in water at a concentration of 15% by weight. Data obtained mechanically are shown by diamonds, solid for the storage modulus, and open for the loss modulus. Data obtained optically are shown by lines, solid for the storage modulus, and dashed for the loss modulus. The inset shows $\tilde{G}(s)$ over the full frequency range measured.

from the surface tension of the deformed droplets. The strong scattering of the uniformly sized droplets allows DWS to be used to probe their $\langle \Delta r^2(t) \rangle$. The comparison of the light scattering data with the rheological measurements is shown in Fig. 3. Again, very good agreement is obtained; the measurement of $G'(\omega)$ agrees over the whole range of frequencies that overlap, while that of $G''(\omega)$ agrees well at higher frequencies, but does not capture the rise at the lowest frequencies. The accuracy is again restricted by the limited frequency range of the data used for the Laplace transform; the light scattering data decay at longer time, indicating that there is an additional low frequency relaxation, which would result in an increase in $G''(\omega)$ at low frequencies, consistent with the mechanical rheology data.

The agreement of the light scattering measurements of the elastic moduli with the mechanical ones is excellent. We emphasize, however, that these results are purely experimental; the underlying origin of this agreement is not clear. Formally, the motion of a single particle in a complex fluid can be described with a memory-function equation similar in form to Eq. (1) using projection operator techniques; the shear modulus can also be represented by a memory-function equation of the same form [14]. However, the memory function for a single particle motion represents a longitudinal density autocorrelation function; by contrast, the memory function for the shear modulus represents an autocorrelation function of nondiagonal, or transverse, elements of the stress tensor. The two memory functions are not equivalent. Heretofore, DLS has only been used to measure a longitudinal modulus [15]. Our experiments show that it can be used to measure the transverse modulus as well. It is conceivable that a single relaxation mode dominates both the longitudinal density and transverse stress correlation functions so that they exhibit the same behavior. For example, such equivalence is expected from mode coupling theory near a glass transition [16], and this may account for the data for both the hard spheres and the emulsion. Moreover, the mean

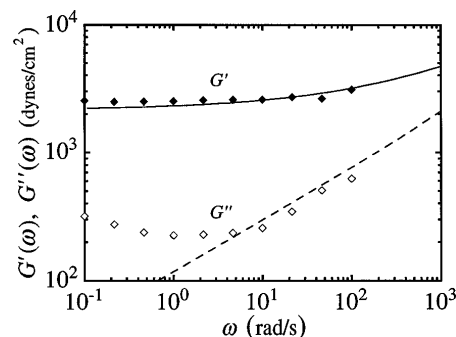


FIG. 3. Frequency-dependent linear viscoelastic moduli for a monodisperse emulsion with $\phi = 0.62$. Data obtained mechanically are shown by diamonds, solid for the storage modulus, and open for the loss modulus. Data obtained optically are shown by lines, solid for the storage modulus, and dashed for the loss modulus.

square displacement does couple to shear modes; this is certainly true in the limit of a simple viscous fluid, where the shear viscosity determines the particle's diffusive motion. Thus, by analogy, we expect the shear elasticity of a complex fluid to determine the mean square displacement of a probe particle. However, the motion of a probe particle, as determined by light scattering, normally reflects the behavior at wave vectors q , which are large compared to a^{-1} . By contrast, the elastic modulus of a material reflects the response in the limit of $q \rightarrow 0$. However, if the probe particle is large enough, its response to thermal fluctuations will presumably reflect the long wavelength limit and thus the bulk moduli of the material. Moreover, the flow pattern of a viscoelastic fluid around the particle is nonuniform, and may differ from that of a simple fluid. This will modify the coefficient in Eq. (3), and may even make it frequency dependent. Thus, the light scattering may not provide a quantitatively exact measure of the elastic moduli; nevertheless, as our results show, the overall trends are correctly captured, and the agreement is very good.

The underlying value and utility of this technique derives from the extended range of the results obtained. For example, combining DWS and traditional DLS allows the measurement of mean square displacements ranging from several angstroms to several microns; by also varying the radius of the probe particles, elastic moduli ranging from 10^{-2} to 10^7 dyn/cm² are accessible. Similarly, the light scattering allows a much greater frequency range to be probed in a single experiment; in particular, the moduli can be measured to much higher frequencies than is possible by mechanical techniques. This range should provide new insights into the underlying physics of the elastic susceptibility of complex fluids. For example, in the inset in Fig. 2, we show the full range of $\tilde{G}(s)$ obtained from the light scattering data for the polymer solution. It contains information about the low-frequency relaxations, where entanglements dominate, as well as the high-frequency relaxations where the glassy behavior dominates. Thus, it reflects the full relaxation spectrum of the polymer solution. Relaxation spectra are typically measured with a rheometer, and the limited frequency range is overcome using the technique of time-temperature superposition [17]. Our data suggest that light scattering can measure the complex modulus over the whole frequency range in a single experiment, without the need for changing temperature. This may be of particular potential importance in the study of polymers that crystallize, where time-temperature superposition is precluded. The light scattering data also provide convincing evidence that, for hard spheres, $G'(\omega) \approx \omega^{0.5}$ at high frequencies, consistent with theoretical predictions which ignore lubrication effects [11,12]. This result is evident from the behavior of $\tilde{G}(s)$ when the high-frequency term proportional to s is subtracted; the remainder clearly exhibits an $s^{0.5}$ dependence.

Dynamic light scattering measurements have long been used to measure viscosity; they also probe the elastic moduli of gels [18]. Our results provide the framework to generalize the use of dynamic light scattering to measure the full frequency dependence of the linear viscoelastic moduli of complex fluids. They clearly illustrate the generality of this method. The complex fluids studied here represent three completely different materials: a colloidal suspension, where the probe particles themselves lead to the rheological properties of the suspension; a polymer network, where the particle merely probe the viscoelasticity of the solution; and an emulsion, where the elasticity results from the surface tension and the deformation of the probe particles. In all cases, the optical measurements of the viscoelastic moduli are in excellent agreement with mechanical measurements. We expect this technique to apply very generally to other complex fluids, although further experiments are clearly required to explore the full range of validity, and further theoretical work is clearly required to determine the underlying physics of this surprising agreement.

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