

Rheology of complex fluids measured by dynamic light scattering¹

T.G. Mason², Hu Gang, D.A. Weitz*

Exxon Research and Engineering Co., Rt. 22E, Annandale, NJ 08801, USA

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Abstract

We introduce a method for using dynamic light scattering to measure the frequency-dependent linear viscoelastic moduli of complex fluids. The technique exploits the fluctuation dissipation theorem, which relates the relaxation of thermal excitations of a probe particle to the viscoelastic properties of the surrounding medium. The relaxation of the thermal excitations of probe particles are determined by measuring the time evolution of the mean square displacement using dynamic light scattering. A Langevin equation with a time-dependent damping term is used to relate this mean square displacement to the dynamic shear modulus of the medium. This method probes the linear viscoelastic moduli over a much larger frequency range than traditional mechanical means, and in particular, easily extends their measurement to much higher frequencies.

Keywords: Light scattering; Complex fluids; Rheology

1. Introduction

Complex fluids are typically distinguished by larger scale structures within the fluid, including, for example, colloidal particles, polymer molecules, or self-assembled surfactant structures. It is the presence of these larger structures that gives a complex fluid its unique properties and leads to the interesting physics of these materials. As a consequence, scattering methods, which probe these larger scale structures, play a critical role in the

study of complex fluids. Most often these scattering methods are used to study the structures within the fluid; thus, neutron, X-ray, and static light scattering have all been used extensively in the study of complex fluids. Each of these techniques has its own particular advantages. Both neutrons and X-rays are particularly suitable for probing smaller structures, as the wavelengths of the probes are relatively small (of the order of a few angstroms). By contrast, the wavelength of light is significantly longer, making it a more suitable probe of larger scale structures. However, there is an additional advantage enjoyed by light scattering. This is the use of laser sources, which provide a collimated, coherent source, with a much greater brightness than any neutron or X-ray source. Of the many advantages that this increase in brightness brings, perhaps the most significant is for the study of dynamics. Indeed, this increased brightness has

* Corresponding author. New address: Dept. of Physics and Astronomy, University of Pennsylvania, 209 S33rd St., Philadelphia, PA 19104, USA.

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² Present address: Dept. Chemical Engineering, John Hopkins University, Baltimore, MD 21218, USA.

led directly to the development of a distinct, and widely applied technique, dynamic light scattering [1]. Dynamic light scattering (DLS) is the analysis of the intensity fluctuations of the scattered light; these can be related directly to the dynamics of the scattering medium. The simplest application of DLS is to the measurement of the diffusion coefficient of colloidal particles. Provided there are no complicating interparticle interactions, the diffusion coefficient is inversely proportional to the particle size, making DLS a powerful, and widely applied, particle-sizing technique. However, the dynamics of complex fluid systems are much more complicated, and much richer, than those reflected by the diffusion of dilute particles, and DLS has also been applied extensively to probe some of these more complex dynamics [2].

In addition to the dynamics which reflect the diffusional motion of their constituents, complex fluids are also characterized by a different class of dynamics which reflect their response to shear, and determine their rheological behavior. These dynamics are typically parameterized by the complex dynamic shear modulus, $G^*(\omega)$, which is a function of frequency ω . The real part of the modulus, $G'(\omega)$, determines the magnitude of the in-phase response of the medium to an applied oscillatory shear, and thus reflects the elasticity or energy stored by the material. By contrast, the imaginary part of the modulus, $G''(\omega)$, determines the magnitude of the out-of-phase response of the medium to an applied oscillatory shear, and thus reflects the energy dissipated, or viscous loss of the material. The shear modulus of a complex fluid is critical in determining its mechanical properties; these are the properties that most directly affect the appearance and fundamental nature of the material. However, because the elastic modulus directly reflects the response of the material to a shear excitation, and because light scattering directly probes the response of the material to a longitudinal excitation, there has traditionally been a complete separation between the two properties. Light scattering has probed the dynamics of the material which reflect the diffusional motion of the constituents, while their rheological properties are probed using mechanical methods that entail the direct application of a

shear strain and the measurement of the resultant shear stress, or through the application of a shear stress and the measurement of the resultant shear strain. The connection of these mechanical properties with those measured with light scattering has traditionally been tenuous at best. However, in principle, one might expect a rather more direct relationship as both forms of excitation (longitudinal and transverse) are probing the response of the same material. In this paper, we show that there is a direct connection between these two excitations. In addition, we introduce a technique by which DLS can be used to probe directly the shear rheology of a complex fluid.

Our light scattering technique is based on measuring the time evolution of the mean square displacement, $\langle \Delta r^2(t) \rangle$, of a probe scattering particle in the complex fluid. In a complex medium, $\langle \Delta r^2(t) \rangle$ will reflect directly the response of the system, both the dissipation of energy due to a viscous response and the storage of energy due to an elastic response. Two limiting cases which illustrate this response can be understood simply. If the fluid is purely viscous, the probe particle will diffuse, and $\langle \Delta r^2(t) \rangle$ will increase linearly with time. The diffusion coefficient can then be determined from the light scattering, allowing the viscosity of the fluid to be measured. By contrast, if the medium is strongly elastic, the probe particle will undergo thermally induced, overdamped vibrations. In this case $\langle \Delta r^2(t) \rangle$ will reach some maximum plateau value $\langle \Delta r_{\max}^2(t) \rangle$ and will not decrease further. This maximum value is set by the elastic modulus of the medium, as can be determined from an energy balance argument. The thermal energy density of the particle is roughly $k_B T/a^3$, where k_B is Boltzmann's constant, T is the temperature, and a is the particle radius. This thermal energy is balanced by the elastic energy of the particle, which is roughly $G' \langle \Delta r_{\max}^2(t) \rangle / a^2$. Equating these two terms allows the determination of the static, or low frequency modulus G' , from the measured value of $\langle \Delta r_{\max}^2(t) \rangle$. While this argument is somewhat crude, it illustrates the essential dependence of an elastic contribution on the dynamics probed by light scattering. Indeed, this argument is the basis of the determination of the elastic modulus of gels using light scattering [3]. In the remainder of

this paper, we generalize these simple arguments to show how the full frequency dependence of the viscoelastic moduli of a complex fluid can be determined from the $\langle \Delta r^2(t) \rangle$ of a probe particle measured with light scattering. To test the concept, we compare light scattering and mechanical measurements of the shear modulus made on identical samples. We also show how the light scattering measurements of the modulus provide new information that is not obtainable with traditional mechanical rheometers.

2. Theory

We describe the motion of a single particle by a generalized Langevin equation. The one-dimensional equation of motion describing the forces acting on neutrally buoyant particle is [4,5]

$$m\dot{v}(t) = f_R(t) - \int_0^t dt' \zeta(t-t')v(t') \quad (1)$$

where m and $v(t)$ are the particle mass and velocity. Here we allow for both loss and storage of energy, as is required to describe a viscoelastic medium, by introducing a time-dependent memory function $\zeta(t)$ to describe the viscous damping term. This integral term accounts for the history dependence of the stresses acting on the particle, embodied by $\zeta(t)$, which allows energy stored in the medium to be returned to the particle at a later time. The random force $f_R(t)$ drives the particle motion, and differs from the purely white spectrum of a viscous fluid because it incorporates the instantaneous stochastic Brownian forces as well as the stochastic forces which are stored and later returned to the medium. We assume that the random force is a Gaussian random variable with zero mean, so that

$$\langle f_R(t) f_R(t) \rangle = 0 \quad (2)$$

where the angle brackets denote an ensemble average. Causality guarantees that the distribution of random forces is entirely decoupled from the past distribution of velocities:

$$\langle v(0) f_R(t) \rangle = 0 \quad (3)$$

As the random forces arise from thermal fluctuations, their correlations must also reflect the

capacity of the material to store energy and dissipate it at later times.

The scale of the average instantaneous particle velocity is set by equipartition of thermal energy which sets the value of the average instantaneous square velocity:

$$m\langle v(t)v(t) \rangle = k_B T \quad (4)$$

The dependence of the particle's velocity on the random force can be determined most easily by changing the convolution integral in Eq. (1) to multiplication in the frequency domain, using a Laplace transform. The unilateral Laplace transform of $g(t)$ is [6]:

$$\tilde{g}(s) \equiv L\{g(t)\} \equiv \int_0^\infty g(t') \exp(-st') dt' \quad (5)$$

while the transform of its time-domain derivative, including the initial condition, is

$$L\{\dot{g}(t)\} = s\tilde{g}(s) - g(0) \quad (6)$$

Transforming Eq. (1) and solving for the velocity spectrum yields

$$\tilde{v}(s) = \tilde{\chi}(s)[mv(0) + \tilde{f}_R(s)] \quad (7)$$

where the transfer function

$$\tilde{\chi}(s) = \frac{1}{[ms + \tilde{\zeta}(s)]} \quad (8)$$

represents the complete response of the particle's velocity to an instantaneous force, accounting for inertial effects in addition to the viscoelastic reaction of the medium. Except at very high frequencies, inertial effects can be ignored, and the transfer function is then the reciprocal of the local memory function $\tilde{\zeta}(s)$.

The random nature of the thermal forces decorrelates the average instantaneous particle velocity from its initial velocity, albeit more slowly for a partially elastic fluid than for a purely viscous fluid. To calculate the remaining correlation, we multiply Eq. (7) by $v(0)$ and ensemble average. This is formally equivalent to multiplying Eq. (1) by $v(0)$ and then transforming. Using energy equipartition and the complete decorrelation of the random force with the initial velocity (Eq. (3)) we find

$$\langle v(0)\tilde{v}(s) \rangle = k_B T \tilde{\chi}(s) \quad (9)$$

When the velocity correlation function is known, $\tilde{\zeta}(s)$ can be obtained:

$$\tilde{\zeta}(s) = \frac{k_B T}{\langle v(0)\tilde{v}(s) \rangle} \quad (10)$$

where we have ignored inertial effects. Thus, the spectrum for the memory function is simply proportional to the reciprocal of the velocity autocorrelation spectrum. Its deviation from the frequency-independent Stokes' constant ζ , associated with a purely viscous fluid, indicates that some energy is being stored in the medium.

In an isotropic medium, we can obtain an equivalent expression in terms of the mean square displacement, rather than the one-dimensional velocity autocorrelation function. The one-dimensional velocity autocorrelation function can be obtained from the second time derivative of the mean square displacement:

$$\langle v(0)v(t) \rangle = \frac{1}{6} \left[\frac{\partial^2 \langle \Delta r^2(t) \rangle}{\partial t^2} \right] \quad (11)$$

or in the Laplace domain by its transformation

$$\langle v(0)\tilde{v}(s) \rangle = \frac{s^2 \langle \Delta \tilde{r}^2(s) \rangle}{6} \quad (12)$$

Since the particles are assumed to be at rest at the earliest times, the initial conditions given by the first and second time derivatives of $\langle \Delta r^2(t) \rangle$ at $t = 0$ do not contribute in the transformation. Thus, we have

$$\tilde{\zeta}(s) = \frac{6k_B T}{s^2 \langle \Delta \tilde{r}^2(s) \rangle} \quad (13)$$

We must now relate the linear viscoelasticity of the complex fluid to the memory function. The viscoelastic response is completely described by the stress relaxation modulus $G_r(t)$, which relates the macroscopic stress $\tau(t)$ to the past strain rate $\dot{\gamma}(t)$ [7]:

$$\tau(t) = \int_0^t dt' G_r(t-t') \dot{\gamma}(t') \quad (14)$$

The stress relaxation modulus describes the magnitude and time scales of stress relaxation in the bulk material after an abrupt shear to a fixed strain. For a material in equilibrium, the magnitude of G_r is

given by the thermodynamic derivative of the stress with respect to the strain, and the time scales are set by the decay of the stress autocorrelation function, $\langle \tau(0)\tau(t) \rangle$. From the Laplace transform of Eq. (14), $\tilde{\tau}(s) = s\tilde{G}_r(s)\tilde{\gamma}(s)$, we identify the material's viscoelastic modulus, $\tilde{G}(s) = s\tilde{G}_r(s)$, as the coefficient of linearity between the stress and the strain expressed in the frequency domain [8]. This notation preserves both $G_r(t)$ and $\tilde{G}(s)$ in the appropriate units of a modulus, recognizing that the Laplace transform of $G_r(t)$ by itself yields units of viscosity [7].

We obtain the macroscopic linear viscoelastic moduli from the microscopic memory function by assuming that the bulk stress relaxations have the same spectrum as the local stress relaxations affecting the particle motion. This motion is determined by the stress of the viscoelastic medium exerted over the particle surface, and the total force can be obtained exactly only if the microscopic flow field around the particle is known. The calculation of the flow field requires knowledge of the frequency dependence of the viscoelastic modulus, which is not known a priori. A proper treatment connecting the memory function of the generalized Langevin equation to the stress relaxation modulus would determine this relationship self-consistently. As this problem is exceedingly difficult [9], we relate them in the limiting case of a dilute suspension of spherical particles in a purely viscous solvent at zero frequency, using Stokes law, and generalize this to all frequencies:

$$\tilde{G}_r(s) = \frac{\tilde{\zeta}(s)}{6\pi a} \quad (15)$$

This relationship is exact for a purely viscous fluid with stick boundary conditions, but we assume the same behavior for viscoelastic fluids, recognizing that this is only an approximation. Eq. (15) represents a mean field assumption, directly connecting macroscopic stress relaxations to microscopic stress relaxations. This effective medium approximation is a critical assumption made in our approach; this is the key to relating the local motion probed by light scattering to the macroscopic shear response of the complex fluid. Combining Eqs. (13) and (15), we obtain the complete relationship describing the macroscopic

viscoelastic modulus in terms of the mean square displacement:

$$\tilde{G}(s) \approx \frac{k_B T}{\pi a s \langle \Delta \tilde{r}^2(s) \rangle} \quad (16)$$

This expression represents a generalized, frequency-dependent form of the Stokes–Einstein relation. It can be recast into a more familiar form using the transform of the time-dependent diffusion coefficient, defined as $D(t) = 1/6 \partial \langle \Delta r^2(t) \rangle / \partial t$ and the complex viscosity spectrum, $\tilde{\eta}(s) = \tilde{G}(s)/s$. When substituted into Eq. (16), the transformed diffusion coefficient takes the familiar form, albeit Laplace transformed,

$$\tilde{D}(s) = \frac{k_B T}{6 \pi a s \tilde{\eta}(s)}$$

This reduces to the simple Stokes–Einstein equation for freely diffusing particles in a purely viscous molecular fluid. In this case, the stress relaxation in the fluid is effectively instantaneous for times much longer than the molecular relaxation, so $G_r(t) = \eta \delta(t)$, implying that $\tilde{G}(s) = \eta s$. Moreover, the Laplace transformed mean square displacement is $\langle \Delta \tilde{r}^2(s) \rangle = 6D/s^2$, and when this is substituted into Eq. (16) the viscosity η can be identified from the coefficient of s in $\tilde{G}(s)$ as $\eta = k_B T / 6 \pi a D$.

All our results were obtained in terms of the Laplace frequency s , which was more convenient because of the integral expression for the memory function in Eq. (1). However, most mechanical measurements of the modulus rely on the application of a sinusoidal excitation and the determination of the in-phase and out-of-phase responses. As a result, they provide data in terms of the real frequency, yielding $G'(\omega)$ and $G''(\omega)$. We can obtain these two real functions from Eq. (16) by applying the Kramers–Kronig relations to the single real function $\tilde{G}(s)$. We first obtain the complex shear modulus, $G^*(\omega)$ from $\tilde{G}(s)$ by using analytic continuation, substituting $i\omega$ for s ; we then take the real and imaginary parts to get $G'(\omega)$ and $G''(\omega)$; this ensures that the Kramers–Kronig relations are satisfied over the frequency range probed. Thus, we use light scattering to measure $\langle \Delta r^2(t) \rangle$, numerically take the Laplace

transform of the data, and calculate $\tilde{G}(s)$ using Eq. (16) at each discrete frequency. These data are then fitted to a continuous functional form in the real variable s . Finally, we substitute $s = i\omega$ and take the real and imaginary parts to obtain the desired $G'(\omega)$ and $G''(\omega)$. Provided the functional form properly fits the data for $\tilde{G}(s)$, no additional error in $G'(\omega)$ or $G''(\omega)$ is introduced by analytic continuation. Moreover, the particular functional form chosen for $\tilde{G}(s)$ does not influence $G'(\omega)$ and $G''(\omega)$, provided the parameters in the form can be properly adjusted so that they fit the data correctly over the measured range. Instead, the main error is introduced by the numerical Laplace transform, because the temporal range of the data for $\langle \Delta r^2(t) \rangle$ is limited. However, this error is most pronounced at the bounds of the data and only affects $\tilde{G}(s)$ within a decade of the highest and lowest frequencies. Moreover, the numerical error at the bounds principally influences the weaker of $G'(\omega)$ and $G''(\omega)$, because the deviation leads to greater uncertainty in the phase of G^* than in its magnitude.

The temporal correlations of the stochastic forces acting on the particle at thermal equilibrium are profoundly altered by the medium's capacity to store energy. The particle's translational thermal energy can be retained by the medium and returned at a later time. Consequently, correlations in the random forces acting on the particle may exist over time scales shorter than those associated with the longest local stress relaxation. This delayed dissipation of the thermal power in the medium requires the temporal correlation of the stochastic forces to be proportional to the local memory function [4]:

$$\langle f_R(0) f_R(t) \rangle = k_B T \zeta(t) \quad (18)$$

This expresses the fluctuation–dissipation theorem for the viscoelastic medium. It differs from the delta-function correlation of a purely viscous fluid, which leads to a white noise spectrum. By measuring the mean square displacement of the suspended particles and using the inverse Laplace transform of Eq. (13) to determine $\zeta(t)$, the magnitude and spectral relaxation of the random forces could also be determined. This provides the key insight into the physics that underlies this

technique; we are using the fluctuation–dissipation theorem to determine the viscoelastic response of the medium. Thus, the probe particle is excited thermally, and the relaxation of this excitation reflects the average response of the medium. We follow the relaxation of this response through the mean square displacement of the particle. The analysis presented above transforms the stochastic response into its individual frequency components, allowing comparison to more traditional mechanical data. The essence of this technique is the extension of the Stokes–Einstein relationship between the particle diffusion coefficient and the fluid viscosity. In its usual form, it is a zero frequency relationship; here we assume its validity at all frequencies.

3. Results

The theory presented in the previous section implicitly makes several critical assumptions, including the extension of the Stokes–Einstein relationship to higher frequencies, and the treatment of the fluid as an effective medium. The validity of these assumptions is best determined by comparing data obtained from light scattering with that obtained from mechanical measurements. In this paper, we restrict ourselves to a single system, which not only provides a test of this technique, but also provides an important example of how the light scattering method can lead to new physical insight by yielding data in frequency ranges that are inaccessible with normal mechanical techniques. Examples of tests of the method using other systems are presented elsewhere [10].

We studied an emulsion of silicone oil droplets in water, stabilized by sodium dodecyl sulfate. The emulsion was purified using a crystallization fractionation technique [11] to yield monodisperse droplets. When the emulsion droplets are concentrated by increasing their volume fraction ϕ above random close packing ($\phi = 0.63$), they can no longer retain their spherical shape. The deformation of their shape causes an increase in energy due to the surface tension, and causes the emulsion to become an elastic solid, albeit a weak solid. However, because the droplets are monodisperse, we

can still use light scattering to measure their mean square displacement. The mismatch in the refractive indices of the oil and the water causes these concentrated emulsions to scatter light very strongly. As a result, we used a multiple light scattering technique, diffusing-wave spectroscopy (DWS) [12,13], rather than the more traditional DLS. Diffusing-wave spectroscopy is an extension of DLS into the strongly multiple scattering regime and the resulting autocorrelation function can be interpreted to provide a measure of the mean square displacement of the scattering particles.

We show in Fig. 1 the mean square displacement, measured using DWS, for a concentrated emulsion with $\phi \approx 0.65$, and composed of droplets with a radius of $a \approx 0.53 \mu\text{m}$, as determined from DLS from a dilute mixture. The actual volume fraction of oil is $\phi = 0.62$, but the stabilizing screened electrostatic repulsion between the droplets, due to the ionic surfactant coating their surfaces, gives rise to an effective packing volume fraction of 0.65 [14], which just exceeds random close packing of monodisperse spheres. Nevertheless, the scattering from the emulsion at this volume fraction can still be interpreted in terms of a form factor of the spheres and a liquid-like structure factor [15], allowing an unambiguous interpretation of the DWS data in terms of $\langle \Delta r^2(t) \rangle$. As can be seen from Fig. 1, the measured $\langle \Delta r^2(t) \rangle$ initially increases with time, but then slowly saturates at longer times. These data were numerically Laplace transformed, and $\tilde{G}(s)$ calculated using Eq. (13); the results are plotted as the solid symbols in Fig. 2. The long time saturation in

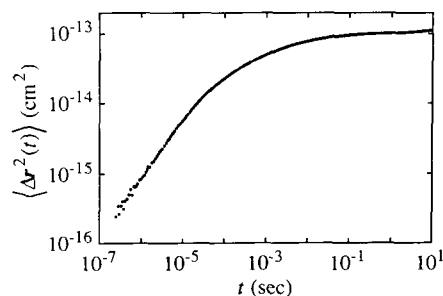


Fig. 1. The temporal dependence of the mean square displacement (\bullet) of uniform emulsion droplets with $a = 0.53 \mu\text{m}$ at $\phi = 0.65$ measured using DWS.

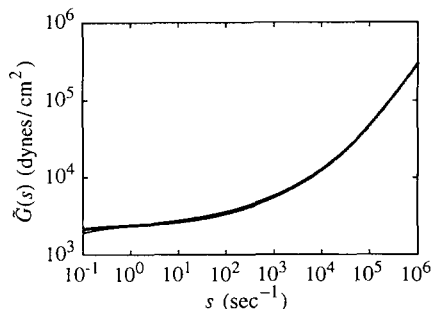


Fig. 2. The frequency dependence of the viscoelastic modulus $\tilde{G}(s)$ (●) for the concentrated emulsion obtained by numerically Laplace transforming the data for $\langle \Delta r^2(t) \rangle$ shown in Fig. 1, and using Eq. (16). The solid line is a fit to the data, and is indistinguishable from the data.

$\langle \Delta r^2(t) \rangle$ leads to a low frequency plateau in $\tilde{G}(s)$, while the early time rise in $\langle \Delta r^2(t) \rangle$ leads to a high frequency rise in $\tilde{G}(s)$. To obtain the frequency-dependent modulus, we fitted the data for $\tilde{G}(s)$ using a functional form which was first developed to describe the data for hard spheres [10,16,17]. It has several different terms to describe the complex frequency dependence. At low frequencies, the plateau behavior is described using an expression derived with mode coupling theory [16]. To describe the higher frequency behavior, two terms are required: one that is proportional to frequency, and a second which proportional to $s^{3/2}$. The fit to the data is shown by the solid line in Fig. 2, and clearly exhibits very good agreement with the data. We emphasize that, while this functional form was derived from physical intuition about the behavior

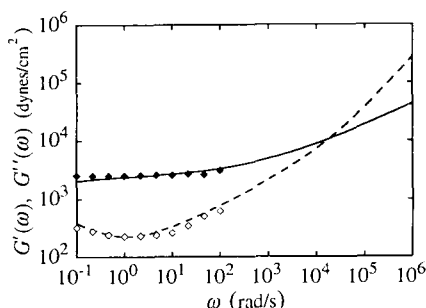


Fig. 3. The frequency dependence of the storage modulus $G'(\omega)$ (—) and $G''(\omega)$ (---) obtained by analytic continuation of the fit of $\tilde{G}(s)$ for the concentrated emulsion shown in Fig. 2. The optically measured moduli are in excellent agreement with $G'(\omega)$ (●) and $G''(\omega)$ (◊) measured mechanically.

of the data, any functional form which describes the data is equally suitable for the purposes of determining the frequency-dependent moduli. Analytic continuation is used to calculate $G'(\omega)$ and $G''(\omega)$, and the results are shown by the solid and dashed lines, respectively, in Fig. 3.

To verify the light scattering data, we also measured the elastic moduli using traditional mechanical means. We used a strain-controlled rheometer with the sample contained in a double-walled Couette cell. The frequency dependent moduli are shown by the symbols in Fig. 3: the solid symbols represent the storage modulus $G'(\omega)$, and the open symbols represent the loss modulus $G''(\omega)$. The agreement between the two techniques is excellent. This validates our light scattering technique, at least as applied to these emulsion systems. Other measurements have also validated this method for measuring the moduli of colloidal suspensions and polymer solutions [10].

One of the greatest advantages of the light scattering technique is the large range of frequencies that it covers. This is immediately apparent in Fig. 3. The traditional mechanical techniques are limited to relatively low frequencies, in our case to $\omega \leq 10^2 \text{ s}^{-1}$. This results from the limitations of mechanically oscillating the relatively large mass of the rheometer cell at high frequencies, due to its inertia. By contrast, the probe particle for the light scattering has colloidal dimensions, and thus inertial effects are avoided until much higher frequencies. As a result, the light scattering data extends to $\omega \approx 10^6 \text{ s}^{-1}$.

The rheological behavior at these much higher frequencies can provide new insight into the properties of complex fluids. As an illustration of this, we consider the behavior of these compressed emulsions. To isolate the behavior at high frequencies we consider the modulus in Laplace frequency $\tilde{G}(s)$. The limiting form of its behavior at high frequency must be purely viscous, reflecting the fluid nature of the emulsions, and thus it must increase as s at the highest frequencies. By contrast, at low frequencies the behavior is dominantly elastic, and thus $\tilde{G}(s)$ should be constant. To isolate the behavior between these two asymptotic limits, we subtract from the measured $\tilde{G}(s)$ a constant and a term linear in s . We illustrate this in Fig. 4, which

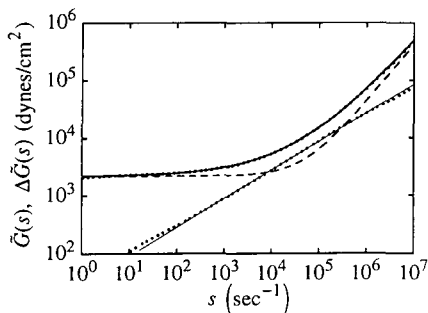


Fig. 4. The dynamic shear modulus $\tilde{G}(s)$, measured with light scattering (\diamond) as a function of the Laplace frequency s for the emulsion with $\phi \approx 0.67$. (---) The asymptotic contributions of an elastic component at low frequencies and a viscous component at high frequencies. The difference (\bullet) represents the additional contribution to the modulus, and exhibits an $s^{1/2}$ frequency dependence (—).

shows a plot of $\tilde{G}(s)$ values for an emulsion with $\phi \approx 0.67$ (solid squares). The dashed line shows the sum of the constant and the term linear in frequency. Their magnitudes have been adjusted to match the values of $\tilde{G}(s)$ at low and high frequencies, respectively. The difference $\Delta\tilde{G}(s)$ between the data and the asymptotic dependence is shown by the open symbols; it has a clear $s^{1/2}$ dependence, as illustrated by solid line through the data.

A similar behavior is observed for emulsions at all volume fractions. We show examples of this for representative volume fractions of the same emulsion in Fig. 5. These data were obtained in the same fashion; $\tilde{G}(s)$ was determined using light scattering and the asymptotic low and high frequency contributions, represented by a constant and a term

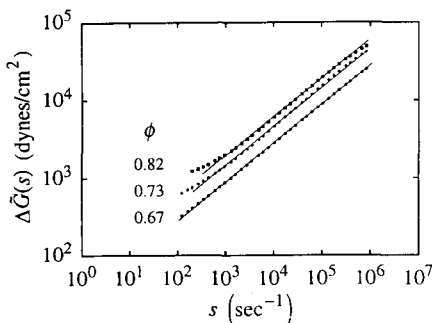


Fig. 5. The $s^{1/2}$ contribution to the dynamic shear modulus for the same emulsion at three different volume fractions.

linear in s , were subtracted to yield the results for $\Delta\tilde{G}(s)$ shown. In all cases, the frequency dependence of $\Delta\tilde{G}(s)$ is best described by $s^{1/2}$. The origin of this additional contribution to the modulus arises from the nature of the disordered packing of the droplets. As their volume fraction increases, the droplets must deform in order to fit into the restricted volume. This causes them to form flattened facets where two droplets are pressed together, and leads to a repulsive force between the centers of two neighboring droplets. However, for each droplet, the forces due to its neighbors balance, so that the net force on each droplet is zero. These interdroplet forces are only repulsive and act only between the centers of the drops. However, because of the disorder in the packing, there are bound to be some localized regions where the droplets can not respond elastically to a shear in some direction, and instead the droplets slide in this direction, thereby dissipating energy. These regions are randomly situated and randomly oriented throughout the sample. Liu et al. [18] have modeled the response of these slip regions by analogy to a random distribution of smectic layers [19]. The time response of these layers varies with the orientation of their slipping direction compared with the direction of the shear imposed, with the slowest response for those regions with a slip plane nearly perpendicular to the direction of the shear, so that their response is the most nearly elastic. However, if the distribution of slip directions is random, the sum over directions yields a Gaussian form when all the contributions are included. This leads directly to a term which varies as the square root of frequency and which contributes equally to both the real and imaginary parts of the shear modulus [18]. As some of the barriers to the slipping are sufficiently low, some regions will slip spontaneously due to thermal excitations, leading to the observed $s^{1/2}$ behavior in the data. As these regions that slip do not support shear elastically, they result in a weakening of the elastic or storage modulus of the emulsion; indeed, the measured value of $G'(\omega)$ is significantly lower than expected for these emulsions [14]. Because this contribution arises from a viscous dissipation of a small volume, it is most readily apparent at high frequencies, where its contribution is greater than the purely

elastic response of the rest of the emulsion. For this reason, it cannot be detected using normal mechanical measurements; by contrast, the light scattering method discussed here is ideally sensitive to this behavior. Thus, this is an example of new physics that can be studied using this technique.

4. Conclusion

In this paper we have introduced a new method of measuring the viscoelastic properties of complex fluids using DLS. The method exploits the fluctuation–dissipation theorem; it follows the motion of a probe scatterer as it relaxes after thermal excitation. The relaxation of the energy reflects the behavior of the surrounding medium: if it is viscous the particle undergoes diffusive motion; by contrast, if it is elastic the particle stores energy for some period of time and cannot freely diffuse. Although this dissipation of thermal energy is a stochastic process, the individual frequency components can nevertheless be resolved, allowing the full frequency dependent behavior to be determined. The key assumption made in this method is the extension of the Stokes–Einstein relationship to non-zero frequencies. This relation normally relates the diffusion coefficient of a particle to the viscosity of the medium at zero frequency; here we assume that a similar relationship also holds at nonzero frequencies. This allows us to use DLS to measure the time dependent diffusion coefficient, by measuring the time evolution of the mean square displacement of a probe scatterer, and thereby determine the time evolution of the viscosity of the medium. This time dependent viscosity reflects both storage and dissipation of energy, and hence reflects both the viscous loss and the elastic storage moduli. We have shown here that the moduli measured with the dynamic light scattering technique are in excellent agreement with those measured by traditional mechanical means.

All the DLS measurements used in this study employed diffusing-wave spectroscopy, the extension of dynamic light scattering to the strongly multiple scattering regime. This was particularly convenient for the samples studied in this work;

they scattered very strongly and they were quite elastic, so that the total mean square displacements were quite small and thus required the additional sensitivity to small displacements afforded by DWS. However, there is nothing unique about the use of DWS for these new rheological measurements. Traditional DLS can also be used to measure the mean square displacement of probe particles, and therefore can also serve to measure the viscoelastic response of complex fluids.

The prime advantage of this optical technique is the extended frequency range it affords. Since the probe scatterer is very small, its inertia does not affect its response until very high frequencies. Thus this optical method allows the viscoelastic response of a complex fluid to be measured to much higher frequencies than by traditional mechanical means. We have described here an example which illustrates how this leads to new physical insight. We have discussed the behavior of compressed emulsions, which have a contribution to their viscoelastic response that increases as the square root of the frequency. This can only be observed optically as it is apparent only at frequencies that are much higher than those achieved with mechanical rheometers. This is but one example of the power of this technique; many other new physical phenomena in complex fluids can now be studied.

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