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Estimating the viscoelastic moduli of complex fluids using the generalized Stokes–Einstein equation

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Abstract We obtain the linear viscoelastic shear moduli of complex fluids from the time-dependent mean square displacement, $\langle \Delta r^2(t) \rangle$, of thermally-driven colloidal spheres suspended in the fluid using a generalized Stokes–Einstein (GSE) equation. Different representations of the GSE equation can be used to obtain the viscoelastic spectrum, $\tilde{G}(s)$, in the Laplace frequency domain, the complex shear modulus, $G^*(\omega)$, in the Fourier frequency domain, and the stress relaxation modulus, $G_r(t)$, in the time domain. Because trapezoid integration (s domain) or the Fast Fourier Transform (ω domain) of $\langle \Delta r^2(t) \rangle$

known only over a finite temporal interval can lead to errors which result in unphysical behavior of the moduli near the frequency extremes, we estimate the transforms algebraically by describing $\langle \Delta r^2(t) \rangle$ as a local power law. If the logarithmic slope of $\langle \Delta r^2(t) \rangle$ can be accurately determined, these estimates generally perform well at the frequency extremes.

Key words Stokes–Einstein equation · Brownian motion · Complex fluids · Linear viscoelastic moduli · Particle diffusion · Estimation methods

Introduction

The thermally-driven random motion of colloidal spheres suspended in a complex fluid can be very different than the diffusive Brownian motion of similar spheres suspended in a purely viscous fluid. In general, complex fluids contain colloidal structures which partially store and partially dissipate energy when deformed by a perturbative shear; thus they are viscoelastic materials. As the elasticity of the complex fluid becomes significant, spheres suspended within the fluid may exhibit subdiffusive motion or may even be locally bound. For some complex fluids, such as glasses, the colloidal structures giving rise to the elasticity may be able to slowly relax, and the spheres may eventually be able to escape. By establishing the relationship which connects the average microscopic motion of the spheres to the macroscopic viscoelastic response of the complex fluid, one can exploit a variety of experimental techniques for measuring this average motion in order to

obtain the linear shear rheology of the complex fluid. This strategy offers several advantages. First, no external shear must be applied because equilibrium thermal excitations drive the motion of the spheres at all frequencies, so only linear rheological behavior can be probed. Second, because the colloidal spheres are very small, their inertia can usually be neglected, and the viscoelasticity of the complex fluid can be measured at high frequencies.

A phenomenological generalized Stokes–Einstein (GSE) equation has been proposed for obtaining the macroscopic viscoelastic shear moduli of complex fluids from measurements of the ensemble-averaged motion of the spheres (Mason and Weitz 1995, Mason et al. 1997). This GSE equation is based upon the assumption that the complex fluid can be treated as a continuum around a sphere, or equivalently, that the length scales of the colloidal structures giving rise to the elasticity are smaller than the size of the sphere. It also assumes that the Stokes relation for viscous fluids can be extended

to describe the viscoelastic drag on a sphere at all frequencies. This GSE equation has been tested by comparing moduli obtained from Diffusing Wave Spectroscopy (DWS) measurements (Weitz and Pine 1992) of the mean square displacement, $\langle \Delta r^2(t) \rangle$, of spheres within concentrated emulsions, glassy hard sphere suspensions, and polymer solutions (Mason and Weitz 1995), with moduli obtained using mechanical rheometry. These DWS measurements have demonstrated that the moduli can be determined over an extensive frequency range, as many as nine decades, and at frequencies much larger than those typically accessible using mechanical rheometers limited by inertia.

In the original test of the GSE equation, the viscoelastic spectrum, $\tilde{G}(s)$, where s is the Laplace frequency, has been used to represent the frequency-dependent viscoelastic modulus (Mason et al. 1997). Although $\tilde{G}(s)$ is a concise representation, it is not a standard representation, so analytic continuation of a functional form used to fit $\tilde{G}(s)$ has been used to determine the complex shear modulus, $G^*(\omega) = \tilde{G}(i\omega)$ (Bird et al. 1977). For physically motivated forms, this procedure yields $G^*(\omega)$ which agrees well with mechanical measurements. However, this procedure is not theoretically precise because analytic continuation is not stable for all imaginable forms (e.g. to oscillations of the form $\varepsilon \cos ks$ where ε is small and k is large). In particular, the previously used forms have been purposely chosen to avoid such instabilities.

We address this problem by deriving an analytic Fourier-domain representation of the GSE equation for $G^*(\omega)$. In principle, this Fourier-domain representation eliminates the need to analytically continue from the Laplace to the Fourier domain using a fit to a functional form describing $\tilde{G}(s)$. However, in practice, the numerical implementation of the GSE equation to discretely-sampled data for $\langle \Delta r^2(t) \rangle$ known over a limited range of times can introduce significant errors in both $\tilde{G}(s)$ and $G^*(\omega)$ near the frequency extremes. To avoid these errors, we derive algebraic estimates for $\tilde{G}(s)$ and $G^*(\omega)$ based on a local power law expansion of $\langle \Delta r^2(t) \rangle$. We also present a similar method for estimating the time-domain stress relaxation modulus, $G_r(t)$. To demonstrate their utility, we calculate the viscoelastic moduli of a concentrated monodisperse emulsion from a DWS measurement of $\langle \Delta r^2(t) \rangle$ of the droplets and compare these results with mechanical measurements.

Representations of the generalized Stokes–Einstein equation

Because there are many ways of representing linear viscoelasticity (Bird et al. 1977) and the average motion of the spheres, there can be many different equivalent expressions of the GSE equation. In this section, we

present several different representations and show how they can be applied to the limiting cases of spheres diffusing in a viscous fluid and harmonically bound Brownian spheres in a viscous fluid.

All representations of linear viscoelasticity for an isotropic material can be recast into a single scalar function, such as $G_r(t)$, the temporal relaxation of the stress due to a small applied step strain after normalizing by the strain amplitude. Equivalently, $\tilde{G}(s)$ can be found from $G_r(t)$: $\tilde{G}(s) = s \mathcal{L}\{G_r(t)\}$, where $\mathcal{L}\{G_r(t)\} \equiv \tilde{G}_r(s) \equiv \int_0^\infty dt G_r(t) e^{-st}$ is the unilateral Laplace transform of $G_r(t)$ (Oppenheim et al. 1983). An alternative frequency-domain representation is: $G^*(\omega) = i\omega \mathcal{F}_u\{G_r(t)\}$, where the unilateral complex Fourier transform of $G_r(t)$ is: $\mathcal{F}_u\{G_r(t)\} \equiv G_r^*(\omega) \equiv \int_0^\infty dt G_r(t) e^{-i\omega t}$ (Bird et al. 1977). The real and imaginary parts of $G^*(\omega) = G'(\omega) + iG''(\omega)$ define the storage modulus and loss modulus, respectively. Because both $G'(\omega)$ and $G''(\omega)$ arise from $G_r(t)$, they are not independent functions but are interconnected through the Kramers-Kronig relations (Chaikin and Lubensky 1996). No additional information about the viscoelasticity is gained by using $G^*(\omega)$ instead of $\tilde{G}(s)$ because both represent $G_r(t)$.

Assuming that the local viscoelastic modulus around a sphere is the same as the macroscopic viscoelastic modulus, then $\tilde{G}(s)$ can be calculated from the unilateral Laplace transform of $\langle \Delta r^2(t) \rangle$ using the GSE equation:

$$\tilde{G}(s) = \frac{k_B T}{\pi a s \langle \Delta \tilde{r}^2(s) \rangle}, \quad (1)$$

where k_B is Boltzmann's constant, T is the temperature, and a is the sphere's radius. Equation (1) has been derived (Mason et al. 1997) by calculating the ensemble-averaged velocity autocorrelation function resulting from a generalized Langevin equation which describes the motion of the sphere in an incompressible isotropic viscoelastic medium using a local memory function, consistent with energy equipartition and the fluctuation-dissipation theorem. Since the solution of the exact flow field for an arbitrary viscoelastic fluid around the sphere is unknown, the Stokes relation for a purely viscous fluid with no-slip boundary conditions at the sphere's surface has been assumed to be valid at all frequencies. The sphere's inertia has also been neglected; this is an excellent approximation for frequencies less than the characteristic inertia-friction frequency of $6\pi a \eta / m$, where η is the fluid viscosity and m is the sphere's mass. For a one-micron sphere in water, this corresponds to about 10^7 Hz.

In the Appendix, we present an equivalent derivation of the GSE equation in the Fourier domain:

$$G^*(\omega) = \frac{k_B T}{\pi a i \omega \mathcal{F}_u\{\langle \Delta r^2(t) \rangle\}}. \quad (2)$$

In retrospect, Eq. (2) could have been found from Eq. (1) by substituting $s = i\omega$ and identifying $G^*(\omega) =$

$\tilde{G}(s = i\omega)$. Physically, Eq. (2) implies that if there are no driving forces acting on the spheres, the logarithmic slope of $\langle \Delta r^2(t) \rangle$ must lie between one, corresponding to diffusive motion, and zero, corresponding to elastic confinement. This implies that $|G^*(\omega)|$ cannot diverge in the limit $\omega \rightarrow 0$. Conversely, as $\omega \rightarrow \infty$, $|G^*(\omega)|$ may grow with a logarithmic slope of at most unity, reflecting a high frequency viscosity.

Alternatively, the time-dependent diffusion coefficient, $D(t) \equiv (1/6)d\langle \Delta r^2(t) \rangle/dt$, can be used to represent the average motion of the spheres. Using $i\omega \mathcal{F}_u\{\langle \Delta r^2(t) \rangle\} = \mathcal{F}_u\{d\langle \Delta r^2(t) \rangle/dt\}$ (the initial condition can be neglected since $\langle \Delta r^2(0) \rangle = 0$), the complex viscoelastic modulus becomes:

$$G^*(\omega) = \frac{k_B T}{6\pi a D^*(\omega)}. \quad (3)$$

Provided $\langle \Delta r^2(t) \rangle$ is sufficiently smooth for the time-derivative to be accurately evaluated, the Fourier transform can be computed. In principle, once $G^*(\omega)$ or $\tilde{G}(s)$ have been found, $G_r(t)$ can be determined through inverse transformation.

To illustrate these equations, we first consider spheres which diffuse in a purely viscous fluid: $\langle \Delta r^2(t) \rangle = 6Dt$, where D is the diffusion coefficient. Using Eq. (3), we find the viscoelastic spectrum rises linearly with s : $\tilde{G}(s) = [k_B T / (6\pi a D)]s$. Alternatively, using Eq. (4), $G^*(\omega)$ is purely imaginary, $G^*(\omega) = i[k_B T / (6\pi a D)]\omega$. Both forms characterize a viscous fluid, $\tilde{G}(s) = \eta s$ or $G^*(\omega) = i\eta\omega$, where η is the macroscopic shear viscosity of the fluid. In either case, the Stokes–Einstein equation is recovered: $\eta = k_B T / (6\pi a D)$. Inverse transformation yields $G_r(t) = \eta\delta(t)$, where $\delta(t)$ is the Dirac delta function, so the stress relaxation modulus exhibits no elastic memory as expected.

Next, we consider a simple viscoelastic material comprised of harmonically bound spheres in a viscous fluid. The thermally-excited spheres may be imagined as being connected to harmonic springs which are unstretched on average. An ensemble-averaged solution of the equation of motion yields:

$$\langle \Delta r^2(t) \rangle = r_0^2 [1 - \exp(-t/t_D)], \quad (4)$$

where r_0^2 is the saturation value of the mean square displacement at long times and $t_D = r_0^2/6D$ is the diffusion time constant of the confined spheres (Xue et al. 1992). Using Eq. (3) and (4), we find $\tilde{G}(s) = (k_B T / \pi a r_0^2)[1 + t_D s]$, or equivalently:

$$G^*(\omega) = (k_B T / \pi a r_0^2)[1 + it_D \omega]. \quad (5)$$

The storage modulus dominates at low frequencies, reflecting the elasticity of the springs, and is independent of frequency: $G'(\omega) = G_0 = k_B T / \pi a r_0^2$. The loss modulus dominates at high frequencies, reflecting the dissipation of the viscous fluid, and rises linearly with

ω : $G''(\omega) = \eta\omega = (k_B T / 6\pi a D)\omega$, with a viscosity which obeys the Stokes–Einstein equation. Inverse transformation yields: $G_r(t) = \eta\delta(t) + G_0$, where the delta function term describes the high frequency viscosity and a constant term describes the low frequency elasticity.

Estimation method for the GSE equation

Because data for $\langle \Delta r^2(t) \rangle$ are generally known at discrete times over a limited temporal range, computations of transforms to the frequency domain may introduce errors in the moduli. For instance, to implement the Laplace transform numerically, it is simple to select a particular frequency s , multiply $\langle \Delta r^2(t) \rangle$ by a decaying exponential, and integrate over time using the trapezoid rule. While this method may be very accurate well inside the frequency extremes, it introduces errors near the frequency extremes due to the truncation of the data set (Marple Jr. 1987). Similar truncation errors near the frequency extremes also occur when the Fast Fourier Transform (FFT) is applied (Marple Jr. 1987).

In contrast to these methods, we estimate the transforms algebraically by expanding $\langle \Delta r^2(t) \rangle$ locally around the frequency of interest, s , using a power law and retaining the leading term:

$$\langle \Delta r^2(t) \rangle \approx \langle \Delta r^2(1/s) \rangle (st)^{\alpha(s)}, \quad (6)$$

where $\langle \Delta r^2(1/s) \rangle$ is the magnitude of $\langle \Delta r^2(t) \rangle$ at $t = 1/s$ and

$$\alpha(s) \equiv \left. \frac{d \ln \langle \Delta r^2(t) \rangle}{d \ln t} \right|_{t=1/s} \quad (7)$$

is the power law exponent describing the logarithmic slope of $\langle \Delta r^2(t) \rangle$ at $t = 1/s$. For thermally-driven spheres, this slope must lie between zero, corresponding to elastic confinement, and one corresponding to viscous diffusion. Evaluation of the Laplace transform of the power law leads to: $s \langle \Delta r^2(s) \rangle \approx \langle \Delta r^2(1/s) \rangle \Gamma[1 + \alpha(s)]$, where Γ is the gamma function. This expression implicitly assumes that contributions to the transform integral from the behavior of $\langle \Delta r^2(t) \rangle$ at times much different (logarithmically) than $1/s$ can be effectively neglected. Substituting into Eq. (1), we find:

$$\tilde{G}(s) \approx \frac{k_B T}{\pi a \langle \Delta r^2(t) \rangle \Gamma[1 + (d \ln \langle \Delta r^2(t) \rangle / d \ln t)]} \Big|_{t=1/s}, \quad (8)$$

where the gamma function is well represented by: $\Gamma[1 + \alpha] \approx 0.457(1 + \alpha)^2 - 1.36(1 + \alpha) + 1.90$ for this range of α and represents at most a 12% correction. Overall, the approximation given by Eq. (8) is worst where the slope of $\langle \Delta r^2(t) \rangle$ varies most rapidly and the power law representation is an oversimplification. However, the maximum deviation for physical $\langle \Delta r^2(t) \rangle$

is small, less than about fifteen percent from the exact result in the worst-case scenario at the knee in $\langle \Delta r^2(t) \rangle$ for an harmonically bound sphere.

An analogous procedure in the Fourier domain can be used to obtain an estimate for $G^*(\omega)$. Expanding $\langle \Delta r^2(t) \rangle$ around $t = 1/\omega$ yields: $\langle \Delta r^2(t) \rangle \approx \langle \Delta r^2(1/\omega) \rangle (\omega t)^{\alpha(\omega)}$ with α defined as before. Evaluation of the Fourier transform leads to the relation:

$$i\omega \mathcal{F}_u \{ \langle \Delta r^2(t) \rangle \} \approx \langle \Delta r^2(1/\omega) \rangle \Gamma[1 + \alpha(\omega)] i^{-\alpha(\omega)}. \quad (9)$$

Substitution into Eq. (2) and the use of Euler's equation results in:

$$G'(\omega) = |G^*(\omega)| \cos(\pi\alpha(\omega)/2), \quad (10)$$

$$G''(\omega) = |G^*(\omega)| \sin(\pi\alpha(\omega)/2), \quad (11)$$

where

$$|G^*(\omega)| \approx \frac{k_B T}{\pi a \langle \Delta r^2(1/\omega) \rangle \Gamma[1 + \alpha(\omega)]}. \quad (12)$$

These equations provide a useful physical interpretation of the moduli in terms of $\langle \Delta r^2(t) \rangle$. When the sphere moves diffusively, α approaches one and G'' dominates, whereas when the sphere is confined by the elastic structures of the complex fluid, α approaches zero, and G' dominates. When α approaches zero over a large temporal range, the estimate for the dominant G' will be excellent, whereas the estimate for the weaker G'' will degrade in quality. Conversely, when α approaches one over a large temporal range, the estimate for the dominant G'' will be excellent, whereas the estimate for the weaker G' will degrade. For an harmonically bound sphere, the maximum error in the moduli at ω corresponding to the knee in $\langle \Delta r^2(t) \rangle$ is about 15%.

Given $\tilde{G}(s)$, $G_r(t)$ can also be estimated using local power law expansion: $\tilde{G}(s) \approx \tilde{G}(1/t)(st)^{\beta(t)}$, where $\beta(t)$ is the logarithmic derivative of $\tilde{G}(s)$: $\beta(t) \equiv d \ln \tilde{G}(s) / d \ln s$ at frequency $s = 1/t$. Evaluation of the inverse transform of $\tilde{G}(s)/s$ gives: $G_r(t) \approx \tilde{G}(1/t) / \Gamma[1 - \beta(t)]$, valid only for $\beta < 1$ where convergence is guaranteed. Since viscoelastic fluids may have an asymptotic high frequency viscosity with $\beta = 1$, it is necessary to add a delta function term by hand to completely specify $G_r(t)$:

$$G_r(t) \approx \tilde{G}(1/t) / \Gamma[1 - \beta(t)] + \eta_\infty \delta(t), \quad (13)$$

where $\eta_\infty \equiv \lim_{s \rightarrow \infty} d\tilde{G}(s)/ds$ is the high frequency viscosity. For physical $\tilde{G}(s)$, $0 \leq \beta \leq 1$, over which $1/\Gamma[1 - \beta]$ is well represented by: $1/\Gamma[1 - \beta] \approx 1.033\beta + 0.404\beta^2 - 0.439\beta^3$. Using both Eqs. (8) and (13), $G_r(t)$ can be directly estimated from $\langle \Delta r^2(t) \rangle$.

Application of the estimation method

To demonstrate utility of the new estimation methods, we extract the Laplace and Fourier domain moduli from

$\langle \Delta r^2(t) \rangle$ for a monodisperse concentrated emulsion having $a = 0.53 \mu\text{m}$ at a droplet volume fraction of $\phi = 0.65$, measured using transmission DWS as described in (Mason et al. 1997). At such large ϕ , the droplets pack into a disordered structure and are weakly deformed. Such concentrated emulsions can exhibit a low frequency elastic plateau in the storage modulus due to energy storage by additional deformation of the droplet interfaces by an applied shear. However, when performing DWS, we do not apply a shear because we measure the thermally-driven $\langle \Delta r^2(t) \rangle$ of the droplets (no additional probe spheres have been introduced) and obtain the viscoelastic moduli at equilibrium using the GSE equation.

The data $\langle \Delta r^2(t) \rangle$, shown in Fig. 1, are logarithmically spaced and extend over seven orders of magnitude in time. At the earliest times, $\langle \Delta r^2(t) \rangle$ rises diffusively, then becomes subdiffusive at later times, and eventually saturates to a plateau at long times. For the very longest times, there is a slight rise from the plateau. These trends indicate that, on average, a given droplet diffuses for short times over small length scales, but is prevented from diffusing very far by the cage of neighboring droplets surrounding it. The final upturn suggests that some rearrangement of the colloidal droplet structure is occurring. Since the data are logarithmically spaced and cover a large dynamic range in time, a simple application of the FFT is precluded, so we use the estimation method instead.

We compare the viscoelastic spectrum for the concentrated emulsion obtained by direct numerical integration (solid line) and the algebraic estimate of Eq. (8) (solid circles) in Fig. 2. The logarithmic derivative of $\langle \Delta r^2(t) \rangle$ has been evaluated discretely using simple differences and smoothing over two neighboring values to reduce scatter. Overall, the short

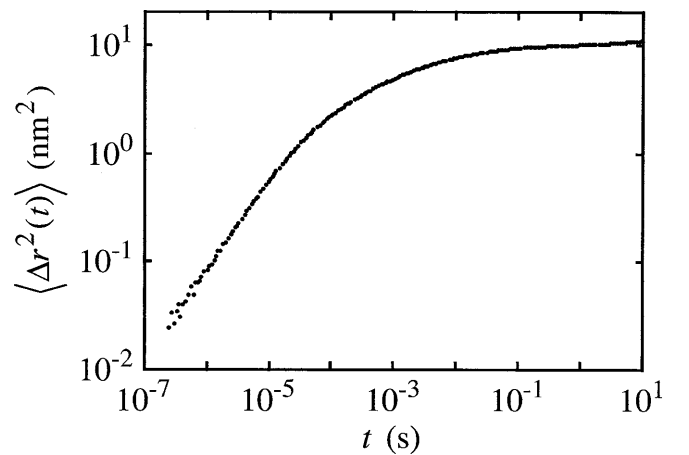


Fig. 1 The measured time-dependent mean square displacement, $\langle \Delta r^2(t) \rangle$, of concentrated monodisperse emulsion droplets having radius $a = 0.53 \mu\text{m}$ at a volume fraction of $\phi = 0.65$

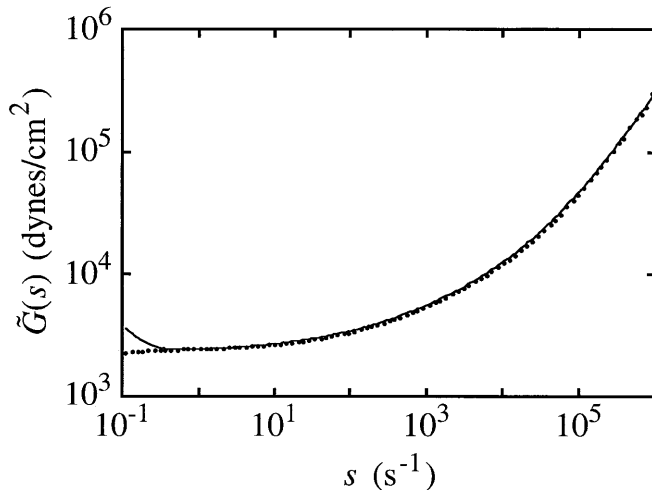


Fig. 2 The frequency-dependent viscoelastic spectrum, $\tilde{G}(s)$, for the concentrated emulsion obtained from $\langle \Delta r^2(t) \rangle$ shown in Fig. 1. The Laplace transform has been computed using numerical integration (solid line) and also the algebraic estimate for the generalized Stokes–Einstein equation given in Eq. (8) (solid circles)

time diffusion leads to a high frequency viscous rise, and the long time saturation leads to a low frequency plateau modulus. However, the truncation errors introduced by the numerical integration are large at low frequencies, whereas the estimate using Eq. (8) provides a reliable result there. Moreover, in the intermediate frequency region, the numerical integration is only slightly more precise than Eq. (8). This example shows that although both analysis procedures introduce errors, overall the algebraic estimate performs better than numerical integration, especially near the frequency extremes.

Moving to the Fourier frequency domain, we plot the storage moduli (solid symbols) and loss moduli (open symbols) obtained using the estimates given in Eqs. (10) and (11) (circles) and measured using a mechanical rheometer at a fixed strain amplitude of $\gamma = 0.02$ (large diamonds) in Fig. 3. At low frequencies, the GSE estimates exhibit a dominant plateau in $G'(\omega)$ and a minimum in $G''(\omega)$. The magnitude of the plateau is in excellent agreement with the mechanical measurements. Although the estimate does qualitatively capture the minimum in G'' , it falls roughly a factor of three lower than the mechanical measurements at the minimum. This difference may result partly from the approximation inherent in Eq. (11) and partly from the finite γ at which the mechanical measurement has been made. In addition to capturing the low frequency behavior, the DWS measurements for the moduli extend to much higher frequencies. The estimated moduli and crossover frequency are also in good agreement with an earlier result of analytic continuation obtained by fitting $\tilde{G}(s)$ to a functional form and taking

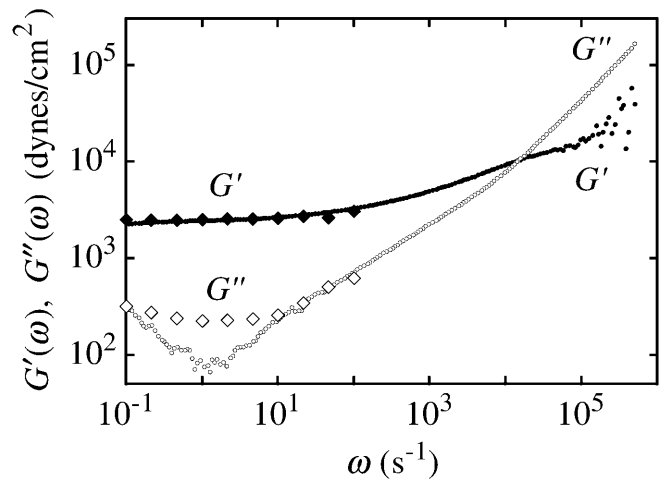


Fig. 3 The frequency-dependent storage modulus, $G'(\omega)$, (solid symbols) and loss modulus, $G''(\omega)$, (open symbols) for the concentrated emulsion obtained from $\langle \Delta r^2(t) \rangle$ in Fig. 1 using the estimates for the generalized Stokes–Einstein equation, Eqs. (10) and (11) (small circles), and by mechanical measurements (large diamonds)

real and imaginary parts respectively (Mason et al. 1997), confirming that previous results have not been biased away from the frequency extremes by the choice of the functional form.

From the estimated viscoelastic spectrum shown in Fig. 2, we employ Eq. (13) to calculate $G_r(t)$ for the concentrated emulsion. The results for $t > 0$ are shown in Fig. 4, where the high frequency viscous contribution, $\eta_\infty \delta(t)$, where $\eta_\infty = 0.33$ P, is not shown in the

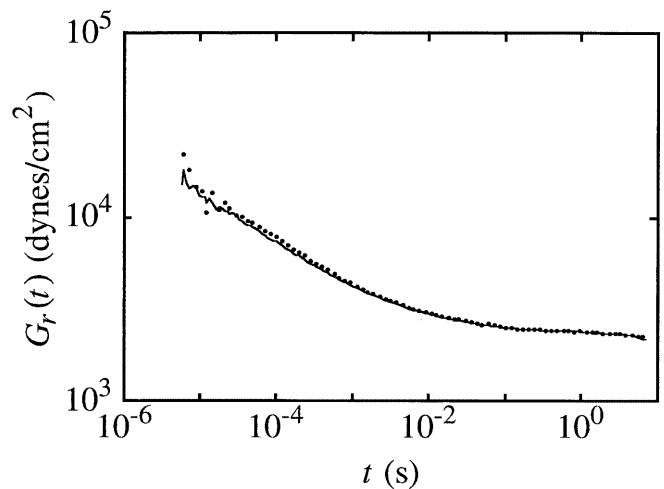


Fig. 4 The time-dependent stress relaxation modulus, $G_r(t)$, for the concentrated emulsion estimated from $\tilde{G}(s)$ in Fig. 2 using Eq. (13) (points). Using this estimate as an initial guess, the exact $G_r(t)$ is found by iteratively forward transforming, comparing with $\tilde{G}(s)$, and correcting $G_r(t)$ (solid line). Not shown is the short time contribution given by $\eta_\infty \delta(t)$, where $\eta_\infty = 0.33$ P is the high frequency viscosity

plot. At the earliest times, $G_r(t)$ decays until it reaches a plateau, reflecting the saturation in $\langle \Delta r^2(t) \rangle$. The early-time scatter in $G_r(t)$ is due to the imprecision in the difference between the high frequency logarithmic slope of $\tilde{G}(s)$ and the perfectly viscous rise $\eta_\infty s$. By forward transforming the estimated $G_r(t)$, comparing this with $\tilde{G}(s)$ obtained by trapezoid integration away from the frequency extremes, and updating $G_r(t)$ using the error, we have developed an iterative method which converges to a precise $G_r(t)$ (solid line). It differs only slightly from the algebraic estimate, demonstrating its good accuracy even when the corrective procedure is not applied.

Discussion

The GSE equation provides a powerful way to determine the linear viscoelasticity of a complex fluid from the equilibrium motion of colloidal spheres suspended within the fluid. It can be recast in many different equivalent representations, all of which are consistent with energy equipartition and the fluctuation-dissipation theorem. However, the essential physics underlying the GSE equation remains the same, regardless of whether the motion is represented by the mean square displacement, the time-dependent diffusion coefficient, or the autocorrelation function of position, and whether the viscoelasticity is represented by the viscoelastic spectrum, the complex shear modulus, the creep compliance, or the complex shear viscosity. As an additional illustration, we have derived a Nyquist representation for the GSE equation relating the complex shear modulus and the power spectrum of the autocorrelation function of position in the Appendix. This demonstrates the equivalence of the two different approaches for extracting microscopic viscoelasticity from single particle tracking measurements in Gittes et al. (1997) and Mason et al. (1997).

In handling real data over a finite range of time, it can be important to minimize the truncation errors which can lead to unphysical behavior of the moduli at the frequency extremes. The algebraic estimation method, based on a local power law expansion, provides much better values for the moduli at the frequency extremes, at the cost of small errors introduced where the logarithmic slope of $\langle \Delta r^2(t) \rangle$ varies rapidly. It also can be implemented when time-sampled data are logarithmically spaced, as we have demonstrated with the concentrated emulsion. Finally, the estimation method is also faster than the FFT.

Because the Laplace-domain viscoelastic spectrum captures both the elastic storage modulus and dissipative loss modulus in only one function of frequency, it is a compact and useful representation. Indeed, theories of $G_r(t)$ developed from microscopic models could be

Laplace transformed using Eq. (1) in order to make a direct comparison with measurements of $\tilde{G}(s)$. Using $\tilde{G}(s)$ rather than $G_r(t)$ also offers the advantage that the cumbersome delta-function contribution to $G_r(t)$, representing the high frequency viscosity, can be eliminated in favor of the more physical high frequency viscous rise in $\tilde{G}(s)$.

In this paper, we have focused on estimating the various representations for the *moduli* of materials probed by the thermally-excited motion of spheres. Alternatively, one may consider the various representations of the GSE equation in terms of a material's compliance, J . The linear creep compliance, $J(t)$, is a representation of viscoelasticity that contains the same information as the previously discussed moduli. Since the Laplace transform of the creep compliance is $\tilde{J} = (s\tilde{G})^{-1}$ (Bird et al. 1977), then Eq. (1) also implies that $J(t)$ can be obtained directly from the mean square displacement without either estimation or transformation (Petka et al. 1998): $J(t) = (\pi a^2 \langle \Delta r^2(t) \rangle) / (k_B T)$. If the complex frequency-dependent creep compliance is desired, it can be obtained by Fourier transforming this expression for $J(t)$.

Since the mean square displacement of thermally-driven spheres can be obtained from many different types of experiments, numerous applications of the GSE equation and estimation methods can be imagined. In principle, the moduli could also be obtained from real-space microscopic measurements of the motion of colloidal spheres in complex fluids. Alternatively, at a molecular level, it may be possible for NMR techniques to provide the $\langle \Delta r^2(t) \rangle$ of probe molecules from which the viscoelastic moduli may be obtained. Although the validity of the continuum approximation is not certain if the probe molecules are the same size as the others, as the example of the concentrated emulsion has shown, the GSE equation can yield surprisingly good results even when the droplets function both as the probe spheres and the caging structures which give rise to the elasticity.

While the GSE equation has proven to be very useful for probing the viscoelastic properties of complex fluids, it is based upon several approximations. Exploring how the continuum approximation breaks down when the particle size becomes smaller than the characteristic length scales giving rise to the elasticity of the complex fluid is an interesting future direction at both theoretical and experimental levels. Considering how spatial anisotropies in the viscoelastic moduli around the sphere could affect its motion in three-dimensions may provide a basis for obtaining the moduli of ordered or shear-oriented complex fluids. An additional theoretical challenge is understanding how the flow field of a viscoelastic complex fluid around a sphere deviates from Stokes flow over a wide range of frequencies. The solution to this problem could lead to a refinement of the GSE equation.

Conclusion

The linear macroscopic viscoelastic moduli of a complex fluid can be determined from the microscopic motion of colloidal spheres suspended within the fluid using a frequency-dependent generalization of the classic Stokes–Einstein equation. Many equivalent representations for the GSE equation exist, but all can be ultimately recast into the forms presented in this paper. Because a naive numerical application of the GSE equation to discretely sampled data for $\langle \Delta r^2(t) \rangle$ over a finite range of times can lead to artifacts in the reported moduli, we have introduced algebraic expressions for estimating the linear moduli in frequency and time domains based on a local power law approximation of $\langle \Delta r^2(t) \rangle$. These estimates are simple to implement, fast, perform well at the frequency extremes, and can be applied to $\langle \Delta r^2(t) \rangle$ sampled logarithmically over many decades in time. Overall, they may be preferable to discrete transform methods which can introduce truncation errors in the moduli at the frequency extremes.

In the future, it may be possible to introduce correction terms to this estimation method that depend upon higher order logarithmic derivatives of $\langle \Delta r^2(t) \rangle$, by analogy to the discussion contained in Ferry (1980). For example, we anticipate that the error in the estimates where the slope of $\langle \Delta r^2(t) \rangle$ changes most rapidly could be corrected using a more complicated formula for the estimate that includes the logarithmic curvature of $\langle \Delta r^2(t) \rangle$.

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Appendix

We present an abbreviated derivation of the generalized Stokes–Einstein equation in the Fourier frequency domain which follows an earlier derivation in the Laplace frequency domain. The reader may consult Mason et al. (1997) for a detailed discussion. Using this result, the GSE equation can be alternatively re-expressed as a Nyquist formula that has been recently proposed by Gittes et al. (1997) to interpret particle tracking experiments.

The motion of a single neutrally-bouyant sphere in one dimension can be described using a generalized Langevin equation (Hansen and McDonald 1986):

$$m\dot{v}(t) = f_R(t) - \int_0^t dt' \zeta(t-t')v(t'), \quad (14)$$

where m and $v(t)$ are the sphere's mass and velocity, the dot denotes the time derivative, and $\zeta(t)$ is a causal memory function which describes the local viscoelastic

response of the isotropic, incompressible complex fluid. The convolution integral allows for energy stored in the fluid to be returned to the sphere at a later time. The Gaussian random force, $f_R(t)$, incorporates both instantaneous and reactive stochastic forces, and therefore differs from the white spectrum of a viscous fluid. Causality guarantees that the distribution of random forces is entirely decoupled from the past distribution of velocities:

$$\langle v(0)f_R(t) \rangle = 0, \quad (15)$$

where the angle brackets denote an ensemble average. Equipartition of thermal energy sets the value of the instantaneous average square velocity:

$$m\langle v(t)v(t) \rangle = k_B T. \quad (16)$$

The relationship between the velocity of the sphere and the local memory function is most conveniently expressed in the frequency domain. Because $\zeta(t)$ is causal, meaning $\zeta(t) = 0$ for $t < 0+$, the limits of integration for the convolution term can be changed from $(0, t)$ to $(0, \infty)$. Unilateral Fourier transformation and the convolution theorem then imply:

$$v^*(\omega) = \frac{f_R^*(\omega) + mv(0)}{\zeta^*(\omega) + i\omega m}, \quad (17)$$

where initial conditions for the velocity have been retained. To calculate the transform of the velocity autocorrelation function, we multiply Eq. (17) by $v(0)$ and ensemble average:

$$\langle v(0)v^*(\omega) \rangle = k_B T / [\zeta^*(\omega) + i\omega m]. \quad (18)$$

This is formally equivalent to multiplying Eq. (14) by $v(0)$ and then transforming. Equation (18) has been simplified using energy equipartition (Eq. 16) and the absence of correlation of the random force with the initial velocity (Eq. 15). Solving for the local memory function, we find:

$$\zeta^*(\omega) = k_B T / \langle v(0)v^*(\omega) \rangle, \quad (19)$$

where the initial term has been dropped. For colloidal spheres, this is a good approximation at low ω . Equation (19) can be expressed in terms of the unilateral Fourier transform of the mean square displacement in three dimensions for $\omega > 0$ using the identity:

$$\mathcal{F}_u\{\langle \Delta r^2(t) \rangle\} = [6/(i\omega)^2] \mathcal{F}_u\{\langle v(0)v(t) \rangle\}, \quad (20)$$

so that the memory function becomes:

$$\zeta^*(\omega) = 6k_B T / [(i\omega)^2 \mathcal{F}_u\{\langle \Delta r^2(t) \rangle\}]. \quad (21)$$

This equation is also consistent with the fluctuation-dissipation theorem, which requires that the transform of the autocorrelation function of f_R also be proportional to the local memory function:

$$\mathcal{F}_u\{\langle f_R(0)f_R(t) \rangle\} = k_B T \zeta^*(\omega). \quad (22)$$

To obtain the macroscopic complex modulus, we assume that the complex fluid can be treated as a continuum around the sphere. This is strictly valid when the length scales of the structures giving rise to the elasticity are much smaller than the sphere's radius, a . Since the exact solution of the flow field for an arbitrary complex fluid surrounding a moving sphere is unknown, we assume that the Stokes relation (with stick boundary conditions) for the drag of a purely viscous fluid can be used to determine the complex viscosity, $\eta^*(\omega)$, over all frequencies:

$$\eta^*(\omega) = \zeta^*(\omega)/6\pi a . \quad (23)$$

From this, the complex shear modulus can be calculated using $G^*(\omega) = i\omega\eta^*(\omega)$:

$$G^*(\omega) = \frac{k_B T}{\pi a(i\omega)\mathcal{F}_u\{\langle\Delta r^2(t)\rangle\}} , \quad (24)$$

valid for $\omega > 0$. This equation represents a generalization of the Stokes–Einstein equation in the Fourier domain consistent with the conventions of standard rheology. If $\langle\Delta r^2(t)\rangle$ is known and its complex Fourier transform can be precisely evaluated, then the storage and loss moduli can be directly extracted as the real and imaginary parts of Eq. (24).

An alternative expression for Eq. (24) can also be found using the bilateral Fourier transform (Oppenheim et al. 1983), defined as:

$$\mathcal{F}_b\{\langle\Delta r^2(t)\rangle\} \equiv \int_{-\infty}^{\infty} dt \langle\Delta r^2(t)\rangle e^{-i\omega t} . \quad (25)$$

To make bilateral transformation feasible, we assume $\langle\Delta r^2(t)\rangle$ is even. This implies that the bilateral transform can be decomposed into a sum of conjugate unilateral transforms:

$$\mathcal{F}_b\{\langle\Delta r^2(t)\rangle\} = \mathcal{F}_u\{\langle\Delta r^2(t)\rangle\} + \mathcal{F}_u^\dagger\{\langle\Delta r^2(t)\rangle\} , \quad (26)$$

where the dagger denotes the complex conjugate. By solving Eq. (24) for $\mathcal{F}_u\{\langle\Delta r^2(t)\rangle\}$ and substituting into Eq. (26), we find:

$$\mathcal{F}_b\{\langle\Delta r^2(t)\rangle\} = -\frac{2k_B T}{\pi a \omega} \frac{G''(\omega)}{|G^*(\omega)|^2} , \quad (27)$$

where the minus sign is consistent with our conventions. The Nyquist formula of Eq. (27) is an alternative expression of the GSE equation using a bilateral Fourier transform. For $\omega \neq 0$, the Weiner-Khinchine theorem (Chaikin and Lubensky 1996) implies:

$$\mathcal{F}_b\{\langle x(0)x(t)\rangle\} = \mathcal{F}_b\{\langle\Delta r^2(t)\rangle\} , \quad (28)$$

for the transformed autocorrelation function of position, $\langle x(0)x(t)\rangle$, so neglecting the phase, the power spectrum of position is:

$$|\mathcal{F}_b\{\langle x(0)x(t)\rangle\}| = \frac{2k_B T}{\pi a \omega} \frac{G''(\omega)}{|G^*(\omega)|^2} . \quad (29)$$

This Nyquist representation can be less convenient than Eq. (24) because $G'(\omega)$ and $G''(\omega)$ cannot be directly obtained without the aid of an additional integral equation given by the Kramers–Kronig relations. In fact, by substituting the Kramers–Kronig relations into Eq. (29), and solving for $G'(\omega)$ and $G''(\omega)$, one can obtain Eq. (24).

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