

Rotational Diffusion Microrheology

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Examining the rotational diffusion of a microparticle suspended in a soft material opens up exciting new opportunities for locally probing the frequency-dependent linear viscoelastic shear modulus, $G^*(\omega)$. We study the one-dimensional rotational diffusion of a wax microdisk in an aqueous polymer entanglement network using light streak tracking. By measuring the disk's time-dependent mean square angular displacement, $\langle\Delta\theta^2(t)\rangle$, we predict the polymer solution's $G^*(\omega)$ using a rotational generalized Stokes-Einstein relation. The good agreement of the predicted modulus with mechanical measurements confirms this new microrheological approach.

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At thermodynamic equilibrium, particles suspended in a liquid undergo translational and rotational diffusion due to impulsive forces and torques exerted by liquid molecules [1]. A variety of experimental techniques, most notably optical methods, exist for probing the translational and rotational diffusion of particles and molecules in liquids [2]. Some of these techniques, such as depolarized light scattering [3], absorption spectroscopy [4], and fluorescence anisotropy decay [5], are used to infer the sizes and shapes of particles and molecules from their diffusion using a rotational form of the Stokes-Einstein relation. Although exploiting rotational diffusion to deduce the shapes and sizes of molecules and particles is useful, perhaps an even more interesting application of rotational diffusion exists. This application consists of studying the equilibrium mechanical shear response of viscoelastic soft materials by applying the preceding approach in reverse: introducing probe particles having a known shape and size into a non-Newtonian viscoelastic soft material and measuring their rotational diffusion in order to deduce the viscoelastic shear modulus of that soft material.

Measuring the translational diffusion of probe microspheres suspended in soft materials to deduce the linear viscoelastic shear modulus [6] of these materials has become a cornerstone of the emerging field of microrheology [7–11]. In a viscous liquid, the translational mean square displacement, $\langle\Delta r^2(t)\rangle$, of the microspheres grows linearly with time. However, in a viscoelastic material, $\langle\Delta r^2(t)\rangle$ can be sublinear over certain time scales, reflecting the ability of the material's microstructures to store elastic shear energy. Dynamic light scattering and particle tracking methods can be used to measure $\langle\Delta r^2(t)\rangle$, and a generalized Stokes-Einstein relation (GSER) is used to deduce the frequency-dependent linear viscoelastic shear modulus, $G^*(\omega)$, or, equivalently, the time-dependent creep compliance, $J(t)$. Multiparticle tracking methods have been developed to aid in the exploration of inhomogeneous materials [11–13].

Although significant attention has been given to microrheological methods based on translational diffusion, the use of rotational diffusion to probe the viscoelasticity of soft materials has never been explored. This could be due in part to the predominant use of optically isotropic microspheres in most microrheology experiments; the symmetry of the microsphere precludes the straightforward observation of its rotational diffusion even though this phenomenon is ever present. Likewise, if one's goal is to deduce the dimensions of anisotropic molecules by optically probing rotational diffusion, using a viscoelastic material as a solvent would needlessly complicate the method.

In this Letter, we report the first measurements of the rotational diffusion of an anisotropic microparticle in a viscoelastic soft material. We observe the time-dependent angular displacement, $\theta(t)$, of the symmetry axis of a wax microdisk in an aqueous polyethylene oxide (PEO) entanglement solution using light streak tracking (LST) [14]. We show that the elasticity of the soft material can cause the mean square angular displacement, $\langle\Delta\theta^2(t)\rangle$, of the microparticle to become subdiffusive. We also derive a rotational generalized Stokes-Einstein relation for calculating the frequency-dependent linear viscoelastic complex shear modulus, or, alternatively, the creep compliance, from $\langle\Delta\theta^2(t)\rangle$. The modulus we obtain from $\langle\Delta\theta^2(t)\rangle$ using the rotational GSER is in good agreement with $|G^*(\omega)|$ measured mechanically, confirming the utility of rotational diffusion as a new experimental approach to microrheology.

We suspend anisotropically shaped wax (α -eicosene) microdisks [14] at a very dilute concentration of 10^{-4} in an aqueous PEO entanglement solution (900 k molecular weight at 4% by mass). After sealing the solution between a slide and cover slip, we locate a microdisk (radius $a = 1.5 \pm 0.2 \mu\text{m}$ and aspect ratio of diameter to thickness of $\rho = 5$) using an inverted microscope ($100 \times 1.4 \text{ NA}$ objective). A low-power helium-neon laser tweezer (4 mW) [15] is used to orient the microdisk's

symmetry axis so that it lies in the focal plane about $10 \mu\text{m}$ above the cover slip. Although the disk is birefringent and experiences a restoring optical torque due to the light polarization [14,16,17], this torque is small compared with the average thermal and rotational drag torques, so we can neglect it. The anisotropic shape of the oriented microdisk causes the light scattered from the optical tweezer to form a streak that we can track to a high degree of temporal and angular resolution using a fast digital camera attached to the microscope. The images stored in the digital camera are downloaded to a computer, and the streak intensity in each image is fit to a straight line in order to determine θ using image analysis software. Thus, we measure only the one-dimensional rotational diffusion of the disk's symmetry axis, and we remain insensitive to the disk's rotational diffusion about its symmetry axis.

LST performed at a frame rate of 3 kHz over a 10 s collection time provides a time trace of $\theta(t)$ at a resolution

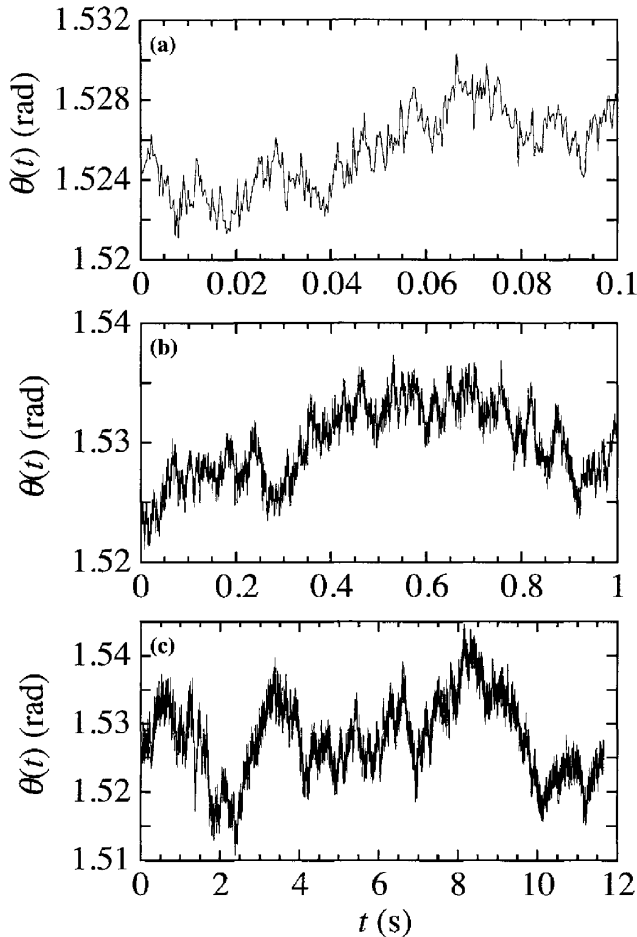


FIG. 1. The time-dependent angular displacement, $\theta(t)$, of a microdisk (radius $a = 1.5 \mu\text{m}$ and aspect ratio $\rho = 5$) in a 4 wt.% 900 k molecular weight PEO solution measured using light streak tracking at 3000 frames/s shown over times ranging up to (a) 0.1 s, (b) 1 s, and (c) 12 s.

of 1 mrad as shown in Fig. 1. Over very short times, the angular fluctuations appear to be bounded, yet at longer times the symmetry axis slowly explores a wider range of angles. We compute $\langle \Delta\theta^2(t) \rangle$ by time averaging the traces for the same microdisk at frame rates of 3 kHz and also 0.5 kHz, as shown in Fig. 2. There is excellent agreement in $\langle \Delta\theta^2(t) \rangle$ for the two frame rates over 3 orders of magnitude in time. At the shortest times, $\langle \Delta\theta^2(t) \rangle$ is subdiffusive, with a slope on the log-log plot less than one, reflecting the entanglement elasticity. Although near our resolution limit, $\langle \Delta\theta^2(t) \rangle$ at short times is not unduly influenced by this limit. For longer times, $\langle \Delta\theta^2(t) \rangle$ approaches a slope of one, reflecting the relaxation of these entanglements.

The one-dimensional rotational diffusion of the symmetry axis of an axisymmetric microparticle in a linear viscoelastic continuum can be described using a Langevin torque equation:

$$I\dot{\nu}(t) = \tau_R(t) - \int_0^t dt' \zeta_R(t-t')\nu(t'), \quad (1)$$

where $\nu = d\theta/dt$ is the angular velocity of the symmetry axis, I is the rotational inertia of the microparticle about a central axis perpendicular to the symmetry axis, τ_R is the random thermal driving torque, and $\zeta_R(t)$ is the rotational memory function which is related to the viscoelasticity of the continuum through a rotational Stokes drag equation. Equation (1) neglects any possible influence of the osmotic compressional modulus on the rotational diffusion.

The solution of Eq. (1) is completely analogous to that for the Langevin force equation in the case of translational diffusion [8]. By taking the unilateral Laplace transform of this equation into the s -frequency domain, retaining initial conditions, multiplying by the initial angular frequency, and ensemble averaging, one obtains

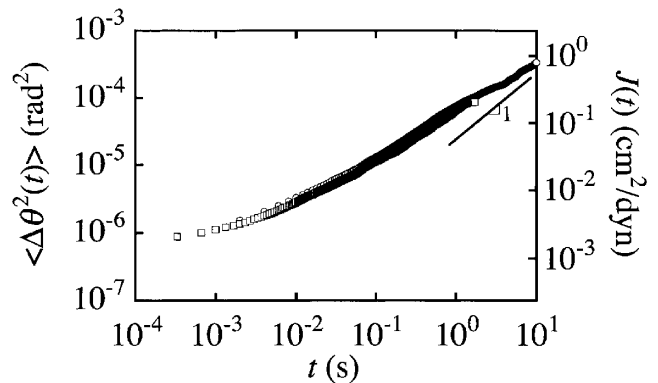


FIG. 2. The time-dependent mean square angular displacement, $\langle \Delta\theta^2(t) \rangle$, of a microdisk in a PEO solution obtained by time averaging the data in Fig. 1. Two different frame rates are shown: 3000 frames/s (squares) and 500 frames/s (circles). The creep compliance, $J(t)$, of the PEO solution calculated using the rotational GSER is shown on the right axis. For reference, a line of slope 1 is shown at long times.

the Laplace transform of the angular velocity autocorrelation function, $\langle \tilde{\nu}(0)\tilde{\nu}(s) \rangle$, describing the average rotational diffusion of many such microparticles. Application of causality and thermal energy equipartition of $k_B T/2$ per single rotational degree of freedom leads to $\langle \tilde{\nu}(0)\tilde{\nu}(s) \rangle = k_B T / (\tilde{\zeta}_R(s) + Is)$, where T is the temperature and k_B is Boltzmann's constant. In order to solve this equation for the viscoelasticity of the continuum in terms of the particle's rotational dynamics, we must know the particle's shape and the boundary conditions (stick or slip) in the expression for the rotational Stokes drag. For spheres of radius a with stick boundary conditions, we assume the rotational memory function to be $\tilde{\zeta}_R(s) = 8\pi a^3 \tilde{\eta}(s)$, where $\tilde{\eta}(s)$ is the frequency-dependent viscosity. We then neglect the rotational inertia, use the identity, $\langle \tilde{\nu}(0)\tilde{\nu}(s) \rangle = s^2 \langle \Delta \theta^2(s) \rangle / 2$, and solve for the viscoelastic modulus, yielding the following rotational GSER for a sphere:

$$\tilde{G}(s) = s \tilde{\eta}(s) = \frac{k_B T}{4\pi a^3 s \langle \Delta \theta^2(s) \rangle}. \quad (2)$$

Reverse Laplace transformation into the time domain gives a creep compliance that is directly proportional to $\langle \Delta \theta^2(t) \rangle$: $J(t) = 4\pi a^3 \langle \Delta \theta^2(t) \rangle / (k_B T)$.

For nonspherical particles, such as microdisks, Eq. (2) must be corrected by a factor proportional to the rotational diffusion coefficient, Θ , of the particle divided by that of a sphere of equal radius. This rotational diffusion coefficient has not yet been calculated theoretically for disks, although the translational coefficient has [18]. Perrin's calculation of Θ for the symmetry axis of oblate ellipsoids [2,19] reveals that, for $\rho = 5$, Θ is 0.4 times that of a sphere with the same a . Thus, to estimate the disk's modulus, we multiply the result of Eq. (2) by 0.4.

By assuming that the time-averaged $\langle \Delta \theta^2(t) \rangle$ for the single microdisk is equivalent to the ensemble-averaged $\langle \Delta \theta^2(t) \rangle$, we use Eq. (2) and the correction factor to calculate $|G^*(\omega)|$ for the PEO solution [20]. The short-time subdiffusive behavior of $\langle \Delta \theta^2(t) \rangle$ results in a trend in $|G^*(\omega)|$ towards a plateau at higher frequencies. The long-time approach of $\langle \Delta \theta^2(t) \rangle$ to simple diffusion results in a trend in $|G^*(\omega)|$ towards a low frequency viscous relaxation: For comparison, we have measured $|G^*(\omega)|$ of the PEO solution in a controlled strain mechanical rheometer equipped with a concentric cylinder geometry; this $|G^*(\omega)|$ is compared with the calculated $|G^*(\omega)|$ in Fig. 3. The mechanical $|G^*(\omega)|$ lies systematically about a factor of 1.4 lower than the rotational $|G^*(\omega)|$; the frequency dependencies are similar. We attribute this error in the absolute magnitude to two possible sources: the correction factor of a true disk compared to an oblate ellipsoid and the strong propagation of the error in a by $|G^*| \sim a^{-3}$ in the rotational GSER. We believe that this systematic deviation is primarily due to our uncertainty in a because a small 10% error in a propagates into more

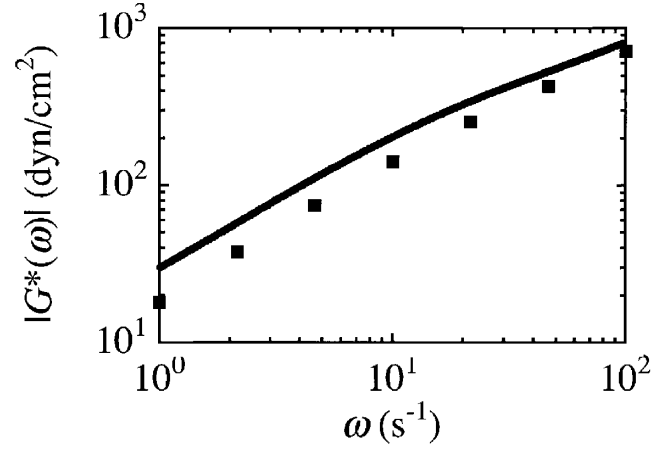


FIG. 3. The magnitude of the frequency-dependent complex shear modulus, $|G^*(\omega)|$, of the PEO solution obtained from the LST measurement of the microdisk using the rotational GSER (solid line) and by mechanical rheometry (squares).

than a 30% error in $|G^*|$. Our rotational $|G^*|$ is in excellent agreement with recent translational microrheology measurements of microspheres in a PEO solution at the same molecular weight and concentration [21]. In Fig. 2 (right axis), we have rescaled the microdisk's $\langle \Delta \theta^2(t) \rangle$ to show $J(t)$ of the PEO solution at short times well below a millisecond.

One of the advantages that rotational diffusion microrheology may offer over translational diffusion microrheology is the possibility of accessing larger moduli. An order of magnitude estimate for the maximum modulus one can obtain using translational diffusion is $G_{\max}^* \approx k_B T / (a_{\min} \Delta r_{\min}^2) \approx 10^6$ dyn/cm² at room temperature for $a_{\min} = 1 \mu\text{m}$ and $\Delta r_{\min} = 1 \text{ \AA}$, measured using the very sensitive technique of diffusing wave spectroscopy [8]. The same type of estimate for rotational diffusion yields a larger modulus: $G_{\max}^* \approx k_B T / (a_{\min}^3 \Delta \theta_{\min}^2) \approx 10^8$ dyn/cm² for $a_{\min} = 1 \mu\text{m}$ and $\Delta \theta_{\min} = 10 \mu\text{rad}$. This 10 μrad angular resolution should be attainable using position sensitive photodiode detection of the light streak angle rather than digital image analysis. Furthermore, the scaling $G_{\max}^* \sim a^{-3}$ suggests that rotational diffusion of smaller particles or molecules may offer access to even larger moduli, provided the continuum approximation and the stick boundary condition remain valid.

Rotational diffusion microrheology can also be used to probe weak materials. If one detects an absolute angle, as we do using LST, and not θ modulo π , then $\langle \Delta \theta^2(t) \rangle$ can grow in an unbounded way and very long-time relaxations of weak materials can be probed. For our LST measurement, the longest time scale is about a decade larger than we have shown and is set by the terminal viscosity of the PEO solution and the small restoring optical torque due to the birefringence of the microdisk. Using an optically isotropic microdisk would actually improve the

measurement since the disk would not experience any optical restoring torques of significance in the θ direction, even at long times. By contrast, rotational diffusion methods that measure the mean dephasing of the orientations of many particles may be restricted to higher frequencies and larger moduli.

In summary, we have established the fundamental principle of rotational diffusion microrheology. This principle consists of measuring the time-dependent mean square angular displacement of a known probe particle in a soft material and deducing that material's viscoelastic compliance or modulus using the rotational GSER. We have demonstrated the validity of this principle in a specific case by performing the first single particle rotational diffusion microrheology experiment using LST of a microdisk in a polymer solution. Our rotational diffusion measurements of the viscoelastic shear modulus of the polymer solution agree well with mechanical measurements. The framework that we have developed may also be appropriate for deducing the viscoelastic moduli of soft materials using other techniques, such as depolarized light scattering, that measure rotational diffusion of many identical probe particles in larger material volumes.

The simple example of rotational diffusion microrheology that we have presented provides a starting point for many fascinating theoretical and experimental research directions. The coupling of the translational and rotational diffusion of an anisotropic microparticle in a complex fluid, and the corresponding impact on the translational and rotational GSER, is an interesting problem that will receive future attention. The rotational motion of anisotropic microparticles may excite osmotic compressional as well as shear modes in the complex fluid; the inclusion of such compressional modes in the rotational GSER may be important for some soft materials. The continuum approximation and stick boundary condition may break down as smaller probe particles or even nanoscale molecules are used; understanding how this occurs may be essential for predicting the largest moduli that can be measured accurately using rotational diffusion microrheology. Experimentally, one can envision translational-rotational versions of two-particle or multiparticle microrheology experiments and corresponding extensions of the single particle rotational GSER into the multiparticle framework. Because many subcellular biological structures, such as organelles and viruses, are anisotropic in shape, the use of rotational diffusion to study viscoelasticity in biomaterials should provide a useful counterpart to translational diffusion approaches. Using faster optical devices to detect the scattered light streak may permit the exploration of long-time tails found in simple rotational diffusion [22] and how these tails may affect microrheology.

We eagerly anticipate further tests and applications of rotational diffusion microrheology using a wide variety of techniques for measuring the rotational diffusion of probe particles and molecules in soft viscoelastic materials.

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- [1] A. Einstein, *Investigations on the Theory of the Brownian Movement* (Dover, New York, 1956).
- [2] B. J. Berne and R. Pecora, *Dynamic Light Scattering with Applications to Chemistry, Biology, and Physics* (Dover, New York, 2000).
- [3] D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Am. Chem. Soc.* **96**, 6840 (1974).
- [4] R. L. Fulton, *J. Chem. Phys.* **55**, 1386 (1971).
- [5] T. J. Chuang and K. B. Eisenthal, *J. Chem. Phys.* **57**, 5094 (1972).
- [6] R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids* (John Wiley and Sons, New York, 1977).
- [7] T. G. Mason and D. A. Weitz, *Phys. Rev. Lett.* **74**, 1250 (1995).
- [8] T. G. Mason, G. Hu, and D. A. Weitz, *J. Opt. Soc. Am. A* **14**, 139 (1997).
- [9] F. Gittes, B. Schnurr, P. D. Olmsted, F. C. MacKintosh, and C. F. Schmidt, *Phys. Rev. Lett.* **79**, 3286 (1997).
- [10] T. G. Mason, K. Ganesan, J. H. v. Zanten, D. Wirtz, and S. C. Kuo, *Phys. Rev. Lett.* **79**, 3282 (1997).
- [11] J. C. Crocker *et al.*, *Phys. Rev. Lett.* **85**, 888 (2000).
- [12] A. J. Levine and T. C. Lubensky, *Phys. Rev. Lett.* **85**, 1774 (2000).
- [13] A. J. Levine and T. C. Lubensky, *Phys. Rev. E* **65**, 011501 (2002).
- [14] Z. Cheng, P. M. Chaikin, and T. G. Mason, *Phys. Rev. Lett.* **89**, 108303 (2002); T. G. Mason, *Phys. Rev. E* **66**, 060402(R) (2002).
- [15] M. P. Sheetz, *Laser Tweezers in Cell Biology* (Academic Press, San Diego, 1998).
- [16] M. E. J. Friese, T. A. Nieminen, N. R. Heckenberg, and H. Rubinsztein-Dunlop, *Nature (London)* **394**, 348 (1998).
- [17] E. Higurashi, R. Sawada, and T. Ito, *Phys. Rev. E* **59**, 3676 (1999).
- [18] M. L. Mansfield, J. F. Douglas, and E. J. Garboczi, *Phys. Rev. E* **64**, 061401 (2001).
- [19] F. Perrin, *J. Phys. Radium* **VII**, 1 (1936).
- [20] T. G. Mason, *Rheol. Acta* **39**, 371 (2000).
- [21] B. R. Dasgupta, S.-Y. Tee, J. C. Crocker, B. J. Frisken, and D. A. Weitz, *Phys. Rev. E* **65**, 051505 (2002).
- [22] R. Hocquart and E. J. Hinch, *J. Fluid Mech.* **137**, 217 (1983).