# Microrheology from Rotational Diffusion of Colloidal Particles

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The microrheology of viscoelastic fluids is obtained from rotational diffusion of optically anisotropic spherical colloidal probes, measured by depolarized dynamic light scattering. The storage and loss moduli obtained from the rotational mean squared displacement is in excellent agreement with those obtained from translational diffusion and by mechanical measurements. We also show that this method is applicable to samples with strong light scattering components. This extends the capabilities of the microrheological methods based on the diffusional motion of colloidal probes.

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The diffusive motion of colloidal particles embedded in a complex fluid probes the local mechanical response of the host medium to oscillatory perturbations at frequencies and space scales not attainable by conventional mechanical instruments. This method to determine the mechanical properties, referred to as microrheology [1,2], is currently used to measure the rheology of different soft materials including gels, polymer solutions, and fluids of biological interest such as solutions of filamentous actin and the cytoplasm of living cells [3–7]. The main advantages of microrheology is the possibility to measure the mechanical properties of very small systems (e.g., in living cells with a volume of only a few picoliter) and the accessibility to much higher shear frequencies than those attained mechanically. The basic idea behind this method is the use of a generalization of the Stokes-Einstein relation between the translational motion of the probe particles, described by the mean squared displacement $W(t) = \langle \Delta \boldsymbol{r}^2(t) \rangle / 6$, with $\Delta \boldsymbol{r}^2(t)$ being the particle's displacement at time $t$, and the mechanical properties of the medium described by the stress relaxation modulus $G(t)$ [8]. For noninteracting spherical particles in a simple viscous fluid, the mean squared displacement is a linear function of time, i.e., $W(t) = Dt$. Here $D$ is the free-particle self-diffusion coefficient, related to the shear viscosity $\eta$ of the fluid by the Stokes-Einstein relation, i.e., $\eta = k_B T / 6\pi a D$, with $k_B T$ being the thermal energy and $a$ the particle's radius. In the absence of interactions with neighbor particles and external fields, deviations of $W(t)$ from linearity would reflect a more complex (viscoelastic) local mechanical response of the host medium. This is expressed in the generalized Stokes-Einstein relation, which in the Fourier space reads [1]

$$G^*(\omega) = \frac{k_B T}{i \omega \pi a \langle \Delta \boldsymbol{r}^2(\omega) \rangle}, \tag{1}$$

where $\langle \Delta \boldsymbol{r}^2(\omega) \rangle$ is the Fourier transform of the mean squared displacement, $\omega$ is the frequency of shearing, and $G^*(\omega)$ is the complex shear modulus whose real part $G'(\omega)$ is the elastic or storage modulus and imaginary part $G''(\omega)$ is the viscous or loss modulus. These quantities can be obtained from Eq. (1), using the method devised by Dasgupta *et al.* [9]. In that method, one assumes a local power law for the mean squared displacement, leading to the evaluation of its first and second logarithmic derivatives. The mean squared displacement, the key quantity involved here, can be measured by techniques such as light scattering (single and multiple), and single particle tracking techniques (optical and confocal microscopies). Light scattering techniques have the advantage of measuring directly the ensemble average of the particle's motion, but they require a transparent host. On the other hand, particle tracking techniques are suitable for the study of opaque fluids when fluorescent particles are used as probes [4,7], but they require large probe particles ($\sim 1$ $\mu$m) which reduces the sampling frequency range, and they also need repeated measurements to achieve an adequate ensemble average. Thus, some of these techniques are better suited to be used in samples of some kinds but not in others. Therefore, one needs to develop new techniques, or to make a qualitative improvement of those available, in order to measure $W(t)$ and to extend the use of microrheology to a greater variety of soft materials.

Besides the translational diffusive motion, colloidal particle also rotate due to fluctuating forces exerted on the particle by the medium. In simple viscous fluids both diffusive motions probe the same mechanical property of the medium, namely, its shear viscosity. One may ask the question whether this result has a more general validity. In this Letter we demonstrate, experimentally, that in viscoelastic fluids both diffusive modes probe exactly the same mechanical properties of the host. For this purpose, we introduce the use of spherical probe particles with internal optical anisotropy to determine the microrheology of viscoelastic materials from both rotational and translational diffusion. As we show here, this extends significantly the use of dynamic light scattering, and of the microrheological methods, in two interesting ways: (i) we show that the microrheology can also be extracted from the rotational motion of the probes which, in this case, is measured simultaneously with the translational motion. The use of rotational diffusion can be a very useful tool in cases where the translational motion of the probes is partially quenched as it happens in confined geometries, and (ii) this method is also very useful in applications where the host system also has a considerable light scattering power. The rotational diffusion also probes the material's response in a frequency domain similar to that of the translational diffusion and can be used to characterize that response. The rotational motion is analogous to the translational motion, and can be described for small one-dimensional angular displacement $\Delta\theta(t)$ by the mean squared angular displacement $\Omega(t) \equiv \langle[\Delta\theta(t)]^2\rangle/2$. For freely rotating spherical particles $\Omega(t) = \Theta t$, where $\Theta = k_B T/8\pi\eta a^3$ is the rotational diffusion coefficient [10]. Here too, in the absence of interparticle interactions, deviations of $\Omega(t)$ from linearity would be due to the complex response of the medium. The generalized Stokes-Einstein relation for rotational diffusion of spherical particles, expressed in the Fourier space, is given by [11]

$$G^*(\omega) = \frac{k_B T}{i\omega 4\pi a^3 \langle\Delta\theta^2(\omega)\rangle}. \tag{2}$$

In this case too, the microrheological moduli are obtained by applying the method used in dealing with Eq. (1).

The systems studied here consisted of polyacrylamide solutions in which spherical colloidal probe particles with optical anisotropy are dispersed. Depolarized dynamic light scattering is used to measure both the translational and the rotational mean squared displacements of the probe particles. The microrheological properties are obtained, as describe above, and compared with mechanical measurements. Optically anisotropic spherical particles for this work were made by emulsification of a liquid crystal (RM257, Merck) in the nematic phase. The internal structure of the droplets, with hydrodynamic diameter of 340 nm and size polydispersity of 7.25%, is frozen by irradiation with UV light [12,13]. The host matrices were prepared by dissolving polyacrylamide (Sigma), molecular weight $M_W = 5\text{–}6 \times 10^6$ g/mol, in deionized water of 17.0 M$\Omega$ cm of resistivity. Particles are dispersed in the polymeric matrix to achieve a final particle volume fraction of around $10^{-5}$ to avoid interparticle interactions and to make sure that only single scattering from the probes occurs. The experiments were carried out at a constant temperature of 23 °C. Mechanical measurements of the viscoelastic moduli were carried out using the concentric cylinders geometry in a Paar-physica MCR300 rheometer. The mesh size $\xi$ of the polymeric network is estimated as $\xi = R_G(c^*/c)^{3/4}$ [14], where $R_G$ is the radius of gyration, $c$ and $c^*$ are the polymer concentration and its critical value, respectively. The latter was determined as the intercept of the linear and the power law behavior of the low shear viscosity vs $c$. We found $\xi$ to be in the range of 1–9 nm for matrices with polymer concentration in the range of 0.8% to 0.1% w/w studied here. Thus, the mesh size is much smaller than the particle's size.

The sample is placed in a goniometer (Brookhaven) in the center of a optical vat filled with index matching fluid (decalin). A polarized laser beam of wavelength $\lambda = 488$ nm is focused onto the sample cell. The light scattered at an angle $\theta_s$ with respect to the incident beam is collected by a monomode optical fiber located in the scattering plane. A second polarizer (the analyzer) is located before the optical fiber to make sure that only one mode reaches the detector. The scattered light is split and directed to two photon detectors (ALV/SO-SIPD), and the signal is processed by a time correlator (ALV 6010/160) operated in the pseudocross correlation mode. The optically anisotropic particles have a nematiclike internal structure, whose director $\hat{\mathbf{n}}(t)$ changes direction randomly due to fluctuating torques exerted by the solvent molecules. Thus, the time correlation function $g^{(2)}(k,t) \equiv \langle I(k,0)I(k,t)\rangle/\langle I^2(k,0)\rangle$ of the light scattered $I(k,t)$ by the particles can be measured in two different geometries of the polarizers: both vertical ($VV$) and one vertical and the other (the analyzer) horizontal ($VH$). Here $k = (4\pi n_s/\lambda)\sin(\theta_s/2)$ is the magnitude of the scattering wave vector and $n_s$ is the refraction index of the medium. In each polarizer's geometry, the corresponding correlation function $g^{(1)}(k,t)$ of the scattered electric field $\vec{E}(k,t)$, is obtained via the Siegert relation, i.e., $g^{(2)}(k,t) = 1 + b \mid g^{(1)}(k,t) \mid^2$, where $b$ is an experimental constant of order one [15]. Thus, the measured quantities of interest are: $g^{(1)}_{VV}(k,t) = \langle E^*_{VV}(k,0)E_{VV}(k,t)\rangle/\langle|E_{VV}(k,0)|^2\rangle$ and $g^{(1)}_{VH}(k,t) = \langle E^*_{VH}(k,0)E_{VH}(k,t)\rangle/\langle|E_{VH}(k,0)|^2\rangle$. These correlation functions describe the particle's dynamics and can be written as [15]

$$g^{(1)}_{VV}(k,t) = [A + Bf_R(t)]f(k,t) \tag{3}$$

and

$$g^{(1)}_{VH}(k,t) = f_R(t)f(k,t), \tag{4}$$

where $f_R(t)$ and $f(k,t)$ are the dynamic correlation functions describing single particle rotational and translational motion in the host matrix, respectively. $A$ and $B$ are constants depending only on the components of the particle's polarizability tensor, which are intrinsic particle properties, and can be measured in a known host fluid. In this work, those constants are determined by light scattering from particles dispersed in water [13]. Although the rotational and translational dynamics are mixed up in the field correlation functions, one can see from Eqs. (3) and (4) that the dynamic correlation functions can be obtained either by measuring both $g^{(1)}_{VV}(k,t)$ and $g^{(1)}_{VH}(k,t)$ at the same scattering angle, or by measuring $g^{(1)}_{VH}(k,t)$ at two different scattering angles. As we show below, both possibilities can be realized and lead to the same results at low polymer concentrations when the light scattered by the polymer matrix is not more than a few percent of the light scattered by the probe particles. For more concentrated polymeric matrices, with higher scattering power, the second option provides a method to block the light scattered from the polymeric matrix from reaching the detector. The mean squared displacements, rotational and translational, can be obtained from the dynamic correlation functions by using the Gaussian approximation, i.e., by assuming $f(k, t) = \exp(-k^2 W(t))$ and $f_R(t) = \exp(-6\Omega(t))$.

Figure 1 shows representative light intensity correlation functions measured in a system with a polyacrylamide concentration of 0.5% w/w (symbols). In this figure one can appreciate some characteristic features of those correlation functions. For instance, the correlation measured in the $VH$ geometry decays faster than that measured in the $VV$ geometry, measured both at the same scattering angle ($\theta_s = 20\,°$). On the other hand, the $VH$ correlation decays faster for larger scattering angles. One of the $VH$ correlation functions for particles in water is also shown for comparison (solid line). As one can see here, the presence of the polymer slows down the diffusive motion of the particles by more than 1 order of magnitude. Nevertheless, the motion of the particles is not quenched and the correlation function $g^{(2)}(k, t)$ reaches its asymptotic value of 1. Then, applying the Siegert relation, together with Eqs. (3) and (4), and the Gaussian approximation, one can get both mean squared displacements from depolarized dynamic light scattering experiments. Figure 2 shows the translational and rotational mean squared displacements corresponding to the system in Fig. 1, measured using both procedures mentioned above. Open symbols represent the mean squared displacements extracted from measurements in the $VH$ optical configuration at two different scattering angles, whereas the closed symbols correspond to measurements in the $VV$ and in the $VH$ configurations at the same scattering angle. As one can see here, both procedures lead to identical results for most of the time window accessible to the experiment. Furthermore, curves for the rotational motion are pretty similar to those corresponding to the translational motion. In fact, if we normalize $\langle \Delta \mathbf{r}^2(t) \rangle$ with $4a^2$, the curve superimposes on the curve of $\langle \Delta \theta^2(t) \rangle$. This indicates already that the microrheology obtained from rotational diffusion will coincide with that from translational motion; see Eqs. (1) and (2).

The excellent agreement between measurements from both optical setups has limitations. For low polymer concentrations, lower than 0.5% w/w, the match between the results from both procedures is excellent. However, for higher polymer concentrations the agreement deteriorates and can lead to very different results. This is due to the fact that the light scattered from the polymer increases as its concentration increases, affecting the measurements done in the $VV$ configuration. For instance, at $c = 0.8\%$ w/w, the light scattered by the matrix is already 18% of the total light reaching the detector. Thus, in such a case the (apparent) mean squared displacement obtained by light scattering contains an spurious contribution from the matrix. On the other hand, in the $VH$ configuration, the light scattered by the matrix is filtered out by the analyzer and the light reaching the detector is only that scattered by the probes. Thus, the use of depolarized light scattering in the $VH$ geometry and optically anisotropic particles, provide a way to measure the actual mean squared displacements and, therefore, to extend the microrheology method to study the local mechanical properties of fluids with a

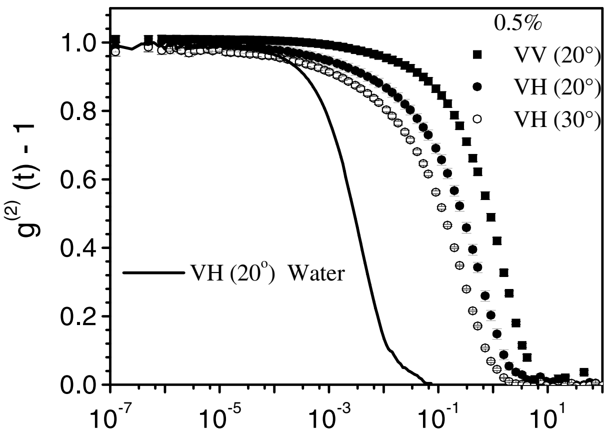

FIG. 1. Time correlation function of the light scattered from optically anisotropic spherical particles dispersed in water (line) and in an aqueous solutions of polyacrylamide at a concentration of 0.5% w/w (symbols). Error bars are within symbol size as shown here.

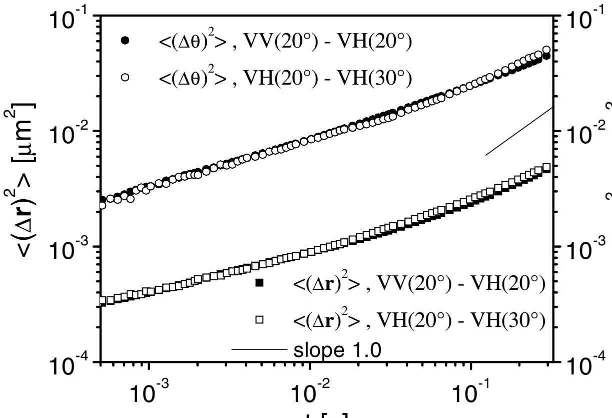

FIG. 2. Translational and rotational mean squared displacements of optically anisotropic particles, measured in the $VV$-$VH$ geometry (closed symbols) and in the $VH$-$VH$ geometry at two different angles (open symbols). As shown here, the slope of both mean squared displacements is lower than one (the slope of the solid line is 1). Thus, the motion of the particles in the polymeric matrix is subdiffusive.

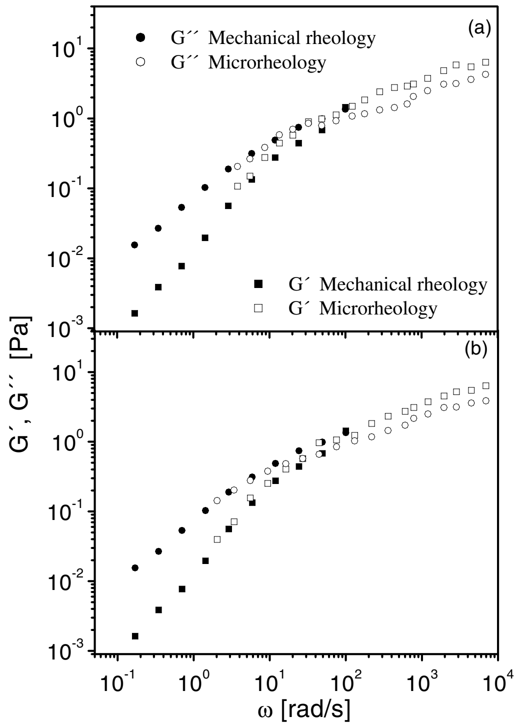

FIG. 3. Comparison of the storage $G'$ and loss $G''$ moduli of the sample in Fig. 1, measured by translational (a) and rotational (b) probe diffusion microrheology and mechanical rheology.

considerable scattering power. We checked this by introducing polystyrene spheres of diameter 1 $\mu$m as scattering inclusions in the sample with 0.5% w/w of polymer. The latex particles at a volume fraction of $10^{-4}$ scatter light about 4 times that from the optically anisotropic particles when measured in the $VV$ configuration. The mean squared displacements of the anisotropic particles measured without the scattering inclusions (Fig. 2) are recovered when measurements in the sample with inclusions are carried out in the $VH$ geometry at two different angles. On the other hand, measurements in the $VV$ and $VH$ at the same angle lead to a complete different results for both mean squared displacements.

Finally, in Fig. 3 we show the storage (open squares) and loss (open circles) moduli for the system in Fig. 1. Closed symbols correspond to mechanical measurements. Figure 3(a) shows microrheology results from translational diffusion, whereas Fig. 3(b) shows those from rotational diffusion. As one can see here, there is an excellent agreement between microrheology from both diffusional motions and mechanical measurements. This nice agreement is observed in the range of polymer concentration studied here, 0.1 to 0.8% w/w. For higher concentrations, the particle's dynamics becomes too slow and the intensity correlation functions do not reach their asymptotic values of one within the time scale of the experiment. Investigations in that concentration regime may require the introduction of a nonergodic treatment to the light scattering data [13].

This Letter presents a methodology to study simultaneously the translational and rotational motion of spherical colloidal probes in viscoelastic fluids. As shown here, both diffusion modes are sensible to the mechanical properties of the host medium and both probe the same properties when the host is a simple viscoelastic fluid. This opens the possibility to study a number of different media where rotational motion can be applied as a novel and useful tool to overcome problems in measuring the translational diffusion. It is also shown here that this method provides a simple way to study the microrheology of soft materials with strong scattering components by light scattering techniques.

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