Accounting for inertia effects to access the high-frequency microrheology of viscoelastic fluids

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We study the Brownian motion of microbeads immersed in water and in a viscoelastic wormlike micelles solution by optical trapping and wave spectroscopy. Through the mean-square displacement obtained from both techniques, we deduce the mechanical properties of the fluids at high frequencies by explicitly accounting for inertia effects of the particle and the surrounding fluid at short time scales. For wormlike micelle solutions, we recover the 3/4 scaling exponent for the loss modulus over two decades in frequency as predicted by the theory for semiflexible polymers.

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The quantitative stochastic description of Brownian motion of spherical micro- and nanobeads in a complex fluids has laid the foundations for the invention of tracer microrheology, a powerful, noninvasive method that allows the measurement of mechanical properties over an extended range of frequencies using all optical instrumentation. At very short time-scales, or high frequencies, the stochastic description of Brownian motion fails as pointed out already in the original work of Einstein. At microsecond time scales the influence of inertial effects and hydrodynamic memory becomes sizable. Failing to account for these contributions leads to substantial errors. Removing these effects at high frequencies, the stochastic description of Brownian motion fails as pointed out already in the original work of Einstein. At microsecond time scales the influence of inertial effects and hydrodynamic memory becomes sizable. Failing to account for these contributions leads to substantial errors. Removing these effects at high frequencies, the stochastic description of Brownian motion fails as pointed out already in the original work of Einstein. At microsecond time scales the influence of inertial effects and hydrodynamic memory becomes sizable. Failing to account for these contributions leads to substantial errors.

In this work, we demonstrate how to correct for the influence of inertia in an actual experiment. We study the Brownian motion of microbeads immersed in water and in a viscoelastic wormlike micelle solution by two complementary experimental techniques accessing the MHz frequency range: optical trapping microscopy (OTI) and diffusing wave spectroscopy (DWS). The combined application of these two methods is unique since it covers the most relevant approaches to high frequency microrheology, while other methods, such as particle tracking, are limited to frequencies well below 10 kHz. We account for inertia effects quantitatively using two different approaches: the self-consistent correction of the mean square displacement suggested in and a theoretical expression derived from the recent work of Schieber and collaborators. We find that these two different quantitative methods provide similar results, as shown by a study of the high frequency scaling of the modulus of a viscoelastic wormlike micelle solution. Taking into account inertia effects we find an exponent of , as predicted by the theory for semiflexible polymers. Besides, the proposed methodology allows to extract parameters relevant to the intrinsic properties of the viscoelastic fluid, such as, the bending modulus, the mesh size and the contour length of the molecular components.

In a tracer microrheology experiment, the complex modulus of a bulk material is calculated from the measured mean-square displacements () of microbeads with position . OTI is the more versatile of the two techniques as it acts on individual beads and, therefore, does not rely on averaging over the motion of many beads, as it is the case for DWS. In OTI, the movement of a single microbead is recorded by means of an interferometric position detector. The bead is trapped in the center of a sample chamber using optical tweezers, applying the lowest optical force available, , where is the spring constant of the optical restoring force. DWS is an extension of dynamic light scattering applied to materials with strong multiple scattering and it allows precise measurements of the 3D movement of tracer beads in the complex fluid. The advantages of DWS are its relative ease of use employing standard spectroscopic cuvettes and the minute-scale measurement times with little calibration and post-processing required. DWS also provides access to a large range of experimental parameters and can be applied to viscoelastic fluids and solids with low or high-frequency moduli while covering an extended range of frequencies from to.

By directly comparing the results obtained by each of both techniques, we study the Brownian motion of melamine resin microbeads with radii .
1.47 μm, with density $\rho_p = 1570 \text{ kg/m}^3$ at $T = 21^\circ\text{C}$. The sample under study is an aqueous solution at 4 wt % of surfactant cetylpyridinium chloride (CPy$^+$Cl$^-$) and sodium salicylate (Na$^+$Sal$^-$), that self-assemble into a wormlike micelle solution [23]. At sufficiently high frequencies the cylindrical micelles are expected to behave as a solution of semiflexible polymers in the semidilute regime formed by entangled micelles [24]. We measure the steady-state viscosity using a Rheometer MCR502 (Anton Paar, Austria) at 21°C, which yields to $\eta_0 = 360 \text{ mPa} \cdot \text{s}$. In the OTI experiments, a double flow chamber is used: one of the chambers contains water and beads at very low concentration, while the other one encloses the viscoelastic fluid with the same type of beads. After aligning the optical trapping light path to the position detector and adjusting signal amplification, a calibration experiment is performed in the pure water solution. The measurement in the viscoelastic solution is done right afterwards. This procedure allows using the known properties of a Newtonian fluid [25] to extract the volts-to-meter conversion factor, $\beta$, which is then used to calculate the MSD in the viscoelastic medium [26]. For the DWS experiments, we are using a bead concentration of 2 vol.%. Samples are loaded into standard rectangular spectrometer cuvettes with a path length $L = 2 \text{ mm}$ or $L = 5 \text{ mm}$ and a width of 10 mm. Echo Two-Cell DWS experiments in transmission geometry are performed as described in Ref. [27]. The two experimental techniques provide similar MSDs for the bead motion in water, as shown in Figs. (a) and (b). However, for the micelle solution, some differences are observed [Figs. (c) and (d)], in particular for the larger bead size. The optical force in a micelle solution might trap some of the polymeric structure, hindering the Brownian motion and, thereby, slightly incrementing the apparent measured viscosity of the fluid. DWS in turn is sensitive to depletion of the surfactant solution around the beads and a possible onset of depletion-induced bead attraction which can result in enhanced motion and larger MSD-values [28]. To observe the effects of inertia and hydrodynamics in the MSDs, we compare in Fig. (a) and (b) the results obtained for bead motion in pure water with the Chandrasekhar expression for a classic Newtonian fluid [24], given by $\langle \Delta r^2(t) \rangle = 1 - \exp(-kt/\gamma) / 2k_B T / k$ where $\gamma = 6\eta a$. For the case of DWS, there is no optical trap and the classical Stokes-Einstein result $\langle \Delta r^2(t) \rangle = (k_B T / 3\pi\eta a) t$ is recovered in the limit $k \to 0$. In both cases, substantial deviations due to inertial effects are observed at times shorter than $t = 10^{-4} \text{ s}$. For water, the inertia effects in the MSD can be reproduced quantitatively using the classical result according to Hinch [29] [Fig. (a) and (b)].

The standard formalism to convert the measured MSD to the complex elastic modulus $G^*(\omega)$ is the Mason-Weitz (MW) approach based on the Generalized Stokes-Einstein relation (GSER) [22] concurrent with Mason’s approximation [31] to obtain:

\[
Z^*(\omega) = \frac{k_B T}{\imath \omega \pi a \langle \Delta r^2(\omega) \rangle}
\]

where $\langle \Delta r^2(\omega) \rangle$ is the one-side Fourier transform of the MSD. In the absence of inertia effects, $G^*(\omega) \equiv Z^*(\omega)$ for equilibrium Brownian motion in a homogeneous viscoelastic fluid [17]. An alternative methodology to connect the MSDs with the rheological properties of the fluid was reported by Evans, Tassieri et al [32]. Both methods are equivalent, but propagate experimental errors in a slightly different manner [33]. They also have common limitations, such as the omission of optical or external forces, the neglect particle and fluid inertia and the non-consideration of active and heterogeneous materials [34].

The first systematic approach to account for inertia effects in passive bead microrheology has been described in Ref. [15]. The principal idea is to define an effective viscosity of the medium by $\eta_{eff}(t) = (k_B T / 3\pi \langle \Delta r^2(t) \rangle)$ at and then calculate, for each measured time point $t$, the correction factor $f(t, \eta_{eff}(t)) \geq 1$ for the MSD using the known theoretical result for a Newtonian fluid [31]. The procedure is iterated numerically starting with the measured MSD. The MSD obtained after correction is used for further processing in Eq. (1). The same strategy has been applied in Ref. [33] using the power-spectral density (PSD) [36]. A more fundamental theoretical approach has been more recently derived by Indei, Córdoba,
Schieber and collaborators [14,15]. They study the influence of the bead and medium inertia by means of the inclusion of the Inertial Generalized Stokes Einstein Relationship (IGSER), assuming that the medium is incompressible, finding:

\[
G^*(\omega) = Z^*(\omega) + \frac{m^*\omega^2}{6\pi\rho} + \frac{\rho^2\omega^2}{2} \times \\
\left[ \sqrt{\frac{3\rho^2}{3\pi a^3}} \left( \frac{6\pi a}{\omega^2} Z^*(\omega) + m^* \right) - \rho \right] \quad (2)
\]

where \(m^* = m_{\text{particle}} + 2\pi a^3/3\) is the effective mass of the particle. By calculating \(Z^*(\omega)\) and then using Eq. (2), we obtain the complex modulus without the influence of inertia. It is important to note that other possible corrections to the high frequency bead motion, for example due deviations from the GSER at \(\omega \geq 10^6\) Hz, are not included by these corrections [17]. We apply these correction protocols to the experimental MSDs displayed in Fig. 1 to obtain the complex modulus for the micelle solution. In Fig. 2 we show the results derived from DWS and OTI using a bead size \(a = 0.94\ \mu m\) for OTI and DWS, with and without corrections. The inertia-corrected results for \(G''(\omega)\) calculated using both methods yield to similar results. These results can be compared to the expected behavior at higher frequencies for a solution of semiflexible polymers, which, according to Gittes and MacKintosh [16], is given by:

\[
G_{\text{GMK}}^*(\omega) = i\omega\eta_s + \frac{1}{15} \rho_m \kappa l_p \left( \frac{-2j\xi}{\kappa} \right)^{3/4} \omega^{3/4} \quad (3)
\]

Next, we compare Eq. (3) with the experimental complex modulus for CpyCl/NaSal to study in more detail the accuracy of inertia corrections at high frequencies. To evaluate Eq. (3), we use the standard theory of polymers [38] and the experimental \(G_0\), \(G''_{\text{min}}\), and \(\omega_0\) as input parameters. The quantity \(G_0\) is the value of \(G^*\) at which \(G''^*\) has a local minimum, denoted as \(G''_{\text{min}}\). Both characteristic values can be easily obtained from Fig. 2. The third input parameter is \(\omega_0\), the crossover frequency where the exponent \(\alpha\) of the power-law behavior \(G^* \sim \omega^\alpha\) changes from the Rouse-Zimm behavior to the expected 3/4 at higher frequencies [39]. The persistence length of the polymer-like micelles is then linked to \(\omega_0\) by \(l_p = (kT/8\pi\rho_s \omega_0)^1/3\). The micelle diameter is estimated as \(d_{\text{mic}} = 2.5 \text{ nm}\) [12] and the area density is \(\rho_m = \phi/[(\pi/4)d_{\text{mic}}^2] = 8.2 \times 10^{-15} \text{ m}^{-2}\), where \(\phi\) is the volumetric concentration [28]. Then, we calculate the bending modulus, \(\kappa = kTl_p\), the mesh size, \(\xi = (kT/G_0)^{1/3}\), the lateral drag coefficient, \(\zeta = 4\pi\eta_s / \ln(0.6\lambda/d_{\text{mic}})\) where \(\lambda = \xi\), the contour length between 2 entanglements, \(l_e = \xi^{5/3}/l_p^{2/3}\), and the contour length of the micelles, \(L = l_e G_0 / G''_{\text{min}}\). The results of the calculations for these quantities are summarized in Table I. The different experimental methods (DWS and OTI) as well as the two bead sizes give similar results. The averaged persistence length, \(l_p \sim 33 \pm 6 \text{ nm}\), agrees with previous mechanical measurements for this kind of surfactant solution (29 nm) [13], but the averaged mesh size, \(\xi \sim 42 \text{ nm}\), is slightly lower (52 nm). To quantify the inertia corrections for the viscoelastic fluid at frequencies \(10^4 - 10^6\) Hz, we plot in Fig. 3 the loss modulus obtained from applying the two different correction procedures. The results quantitatively agree with theory, except for some deviations due to the limited accuracy of the experimental methods at higher frequencies. Eq. (11) applied to the inertia-corrected MSDs and to the
TABLE I. Characteristic magnitudes for the wormlike micelle solution obtained from OTI and DWS using Eq. (3). For all data: $d_{mic} = 2.5 \text{ nm}$ and area density $\rho_a = 8.2 \times 10^{15} \text{ m}^{-2}$.

| $\alpha$ ($\mu$m) | Tech. | $\omega_0$ ($s^{-1} \times 10^4$) | $G_0$ (Pa) | $G_\infty$ (Pa) | $I_p$ (nm) | $\kappa$ (Jm$^{-1}$) | $\xi$ (nm) | $\zeta$ (Ns/m$^2 \times 10^{-3}$) | $L$ (nm) |
|-------------------|-------|---------------------------------|------------|--------------|----------|----------------|----------|---------------------------------|--------|
| 0.94              | OTI   | 1.7 $\pm$ 0.1                   | 50 $\pm$ 5 | 15 $\pm$ 2   | 31.0 $\pm$ 0.6 | 12.6 $\pm$ 0.3 | 43 $\pm$ 1 | 5.4 $\pm$ 0.2                   | 34 $\pm$ 4 | 180 $\pm$ 50 |
| 0.94              | DWS   | 1.0 $\pm$ 0.1                   | 50 $\pm$ 5 | 15 $\pm$ 2   | 37 $\pm$ 1   | 15.0 $\pm$ 0.5 | 43 $\pm$ 1 | 5.4 $\pm$ 0.2                   | 48 $\pm$ 4 | 160 $\pm$ 50 |
| 1.47              | OTI   | 1.0 $\pm$ 0.1                   | 60 $\pm$ 6 | 30 $\pm$ 3   | 37 $\pm$ 1   | 15.0 $\pm$ 0.5 | 41 $\pm$ 1 | 5.2 $\pm$ 0.2                   | 43 $\pm$ 3 | 90 $\pm$ 20  |
| 1.47              | DWS   | 3.0 $\pm$ 0.1                   | 60 $\pm$ 6 | 30 $\pm$ 3   | 25.7 $\pm$ 0.3 | 10.4 $\pm$ 0.1 | 41 $\pm$ 1 | 5.2 $\pm$ 0.2                   | 69 $\pm$ 3 | 140 $\pm$ 40 |

Indei-Schieber method [Eq. (2)] yield to similar results, matching the theoretical curves and the $\omega^{3/4}$ behavior, especially when using OTI and small beads. Differences between both methods arise when using DWS and bigger beads, where Eq. (2) provides better results.

In conclusion, our experimental data and analysis demonstrate that, when properly accounting for inertia effects, passive microrheology easily provides access to the mechanical properties of viscoelastic fluids up to frequencies in the MHz scale. The correction procedure is simplified by the availability of an analytical expression that can be applied straightforwardly to the experimental data. This procedure extends the range of application of microrheology up to two orders of magnitude, and therefore will enable new experiments in a regime which is fairly inaccessible to traditional mechanical rheometry.

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An equivalent Fig. for \( a = 1.47 \, \mu\text{m} \) is included in Supp. Material.

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For DWS experiments we use \( G_0 \) and \( G''_{\text{min}} \) from OTI. We select \( \omega_0 \) for the experimental \( G^* \) to match \( G^*_{\text{GMK}} \), obtaining \( \omega_0 \sim 10^4 \text{Hz} \), consistent with literature values.