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One- and two-point micro-rheology of viscoelastic media

L Starrs and P Bartlett

School of Chemistry, University of Bristol, Bristol BS8 1TS, UK

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Abstract

In recent years optical tracer techniques have been developed to determine the micro-rheology of soft viscoelastic materials. Recent theoretical arguments (Levine A J and Lubensky T C 2001 *Phys. Rev.* E **65** 011501) suggest that the correlated fluctuations of a pair of widely separated probe particles should reflect the bulk rheology of the medium that they are embedded in more accurately than the motion of a single particle. We present a experimental test of these arguments. Using optical tweezers techniques (Henderson S, Mitchell S and Bartlett P 2002 *Phys. Rev. Lett.* **88** 088302), we measure at high spatial and temporal resolution the thermal motion of a pair of colloidal particles suspended in a semi-dilute viscoelastic solution of non-adsorbing polystyrene in decalin. From the measured particle trajectories we determine both the one- and two-particle correlations and extract the local and bulk rheology. A comparison of the two measurements shows significant differences which are interpreted in terms of the depletion of polymer molecules from the particle surface.

1. Introduction

A technique that has attracted much attention in colloid science in recent years is optical micro-rheology, first suggested by Mason and Weitz [3]. The thermal motion of a colloidal particle embedded in a viscoelastic medium reflects the rheological properties of that medium. Thus, by measuring the time-dependent position of a colloidal particle, it is possible to infer the rheological properties of its environment. Typically, optical micro-rheology experiments monitor the motion of a colloid by diffusing wave spectroscopy [4], video microscopy [5] or optical interferometry [6]. Here, we have used dual-beam optical tweezers [2] to measure the position with time of one and two colloidal particles suspended in a semi-dilute solution of polystyrene (PS) in decalin. Our micro-rheological analysis is based on that proposed by Crocker *et al* [5] extended to included the effect of a strong trapping potential. In this paper we briefly outline our approach to micro-rheology and present some initial results.

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2. Theory

The optical gradient forces on a high-refractive-index particle within a tightly focused laser beam are well approximated by a harmonic interaction. We, therefore, model our experiments by considering the dynamics of a pair of rigid Brownian particles of radius a, each held in a harmonic potential well, and separated by a distance r within a linear viscoelastic medium. Fluctuations in the positions of the two particles are correlated as a result of the hydrodynamic interactions transmitted through the viscoelastic matrix. The standard Langevin description for the Brownian motion of a pair of neutrally buoyant particle of mass m is readily modified to include the effects of the viscoelasticity of the medium:

$$m\frac{\mathrm{d}u_i(t)}{\mathrm{d}t} = -\int_{-\infty}^{t} \xi_{ii}(t-t')u_i(t')\,\mathrm{d}t' - \int_{-\infty}^{t} \xi_{ij}(t-t')u_j(t')\,\mathrm{d}t' - kx_i(t) + f_i^R(t). \tag{1}$$

Here k is the harmonic force constant of the optical traps (assumed identical), $f_i^R(t)$ denotes the random Brownian forces acting on particle i and the two particles are labelled by the subscripts i and j. The time-dependent frictional coefficient $\xi_{ij}(t)$ in equation (1) is the generalization of the viscoelastic 'memory' to the case of two interacting particles. The self-term $\xi_{ii}(t)$ details the force acting on one sphere when it is moving (and the second sphere is stationary) while the cross-coefficient $\xi_{ij}(t)$ describes the force generated on one sphere by the motion of the second sphere. Equation (1) is simplified by introducing collective and relative normal coordinates and using standard techniques to solve the resulting decoupled equations of motion. An exact expression for the two-particle mean square displacement,

$$d_{ij}(t) = \frac{\langle \Delta x_i(t)\,\Delta x_j(t)\rangle}{\sqrt{\langle \Delta x_i^2\rangle\langle \Delta x_j^2\rangle}}, \tag{2}$$

normalized by the equipartition result, $\langle \Delta x_i^2\rangle = 2k_BT/k$, may be found from equation (1) using standard techniques. In order to derive a simpler result, we make two assumptions. First, we ignore the effects of particle inertia, as the particle's momentum decays on a much faster timescale than those probed by our experiments. Second, we consider only the situation in which the two probe particles are separated by a distance r large in comparison to the radius a. In this limit the friction coefficients depend on the dimensionless sphere separation $\rho = r/a$ [7].

With these assumptions, we find

$$\left(\frac{s}{k}\right)\tilde{\xi}_{11}(s) = \frac{1}{s\tilde{d}_{11}(s)} - 1, \qquad \left(\frac{s}{k}\right)\tilde{\xi}_{12} = \frac{-\tilde{d}_{12}(s)}{s\tilde{d}_{11}^2(s)}, \tag{3}$$

where the tilde denotes a Laplace transform $\tilde{f}(s) = \int_0^\infty f(t)\mathrm{e}^{-st}\,\mathrm{d}t$ with s the Laplace variable. Thus, measurements of the single-particle fluctuations yield the self-friction $\tilde{\xi}_{11}(s)$, whereas the mutual friction coefficient $\tilde{\xi}_{12}(s)$ is determined from both single- and two-particle fluctuations.

The frequency dependences of the one- and two-particle friction coefficients are determined by the viscoelasticity of the medium. Levine and Lubensky [8] have analysed the general case of a viscoelastic medium and shown that, under typical experimental conditions, the single-particle friction coefficient satisfies the generalized Stokes–Einstein relation:

$$\tilde{\xi}_{11}(s) = \frac{6\pi a\tilde{G}(s)}{s} \tag{4}$$

where $\tilde{G}(s)$ is the Laplace transform of the shear modulus. However, we expect deviations from equation (4) if the local environment of the particle is different from the bulk. Crocker *et al* [5] have suggested that the correlated fluctuations of two, widely spaced particles will,

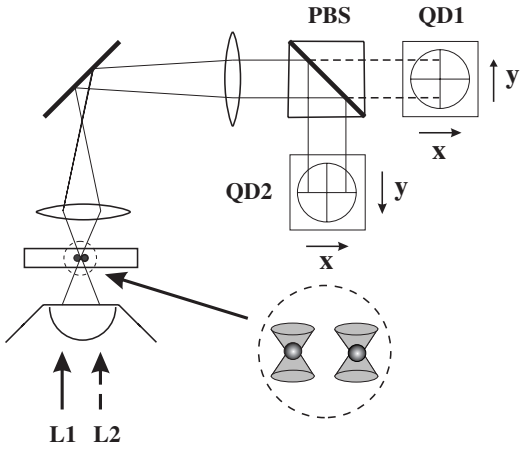

Figure 1. A schematic diagram of dual-trap optical tweezers.

in these situations, more accurately reflect the bulk rheology. In a viscoelastic medium the two-particle friction is, to leading order in $1/\rho$,

$$\tilde{\xi}_{12}(s) = -\frac{9\pi a \tilde{G}(s)}{\rho s}, \tag{5}$$

where no-slip hydrodynamic boundary conditions have been assumed [1].

3. Materials and methods

The thermal motion of colloidal particles was measured with a dual-trap optical tweezers set-up [2] as shown in figure 1. In brief, two spherical colloidal particles were held by optical gradient forces near the focus of a pair of orthogonally polarized laser beams ($\lambda = 1064$ nm). The mean separation r between the probe particles was varied by altering the positions of the trapping lasers with an external computer-controlled mirror. The thermal fluctuations in the position of each probe particle were monitored by recording the interference between the forward-scattered and transmitted infrared beams with a pair of quadrant photodetectors. Custom-built current-to-voltage converters allowed the in-plane positions of both spheres to be recorded with a spatial resolution of $\sim$1 nm at time intervals of 50 μs.

We have made measurements on a viscoelastic semi-dilute solution of PS in a mixed *cis*-decalin and *trans*-decalin solvent (volume fraction of *cis*-decalin 0.48). The PS used had average molecular weight of 10^7 g mol^{-1} and an estimated radius of gyration at 23 °C of $r_g \sim 102$ nm [9]. The overlap concentration c^* was 3.7 mg cm^{-3} and the data presented in this paper were obtained from a sample of concentration $1.7c^*$. Sterically stabilized poly(methyl methacrylate) spheres of radius $a = 643$ nm were added to the polymer solutions at a volume fraction of $\phi \sim 10^{-6}$. The viscous suspensions were loaded into flat, rectangular capillary tubes 170 μm thick which were hermetically sealed with a fast-setting epoxy glue and mounted onto a microscope slide. The samples were left for at least 40 min to allow the particles to settle to the bottom surface before the beginning of an experiment. The trajectories of two spheres were collected at ten roughly evenly spaced pair separations between 3 and 17 μm. 2^{23} data points were collected at each separation at a sampling frequency of 20 kHz. To avoid wall effects, we analysed only spheres at least 15 μm away from the capillary walls. All measurements were performed at room temperature.

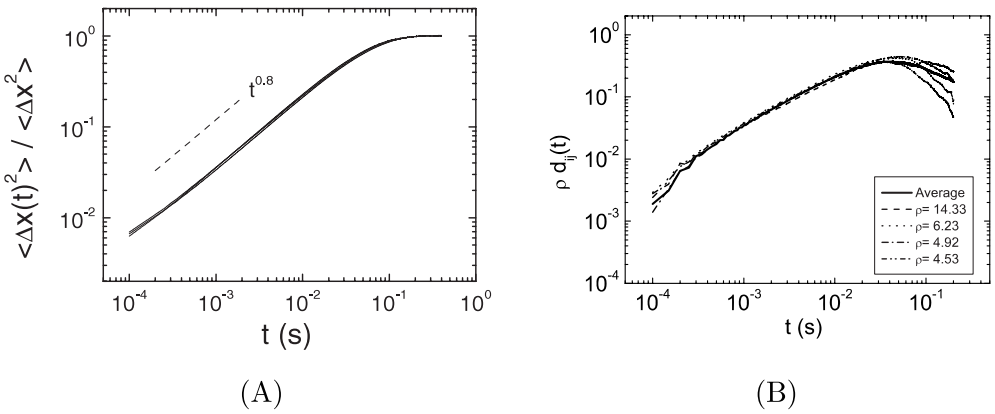

Figure 2. One- and two particle mean square displacements ($C = 1.7c^*$). (A) Three single-particle MSDs are shown for different particle separations between $\rho = 4.53$ and 16.96. (B) Scaled two-particle displacements ρd_{ij} for particle separations $\rho = 14.33$, 6.23, 4.92, 4.53.

4. Results

To characterize the mechanical environment we calculated the mean square x-displacement (MSD), $\langle \Delta x^2(t) \rangle$, from the trajectory of a single particle. Figure 2(A) shows one of the two MSDs, normalized by the plateau displacement, at a number of different pair separations. The data for the second sphere were essentially identical and are not shown. As expected, there is no systematic dependence of the single-particle MSD on the pair separation r, provided that the two spheres remain well separated ($r \gg a$). The measured $\langle \Delta x^2(t) \rangle$ is sensitive only to the local rheological environment around each particle. The MSD increases approximately as $t^{0.8}$ at early times rather than linearly, as expected for diffusion in a purely viscous medium. This is most probably due to the high-frequency elasticity of the polymer solution. At long times, $\langle \Delta x^2(t) \rangle$ reaches the equipartition plateau.

Using the same trajectory data, we have also calculated the two-point correlations. We expect that for widely spaced particles the strength of the correlated positional fluctuations will decay inversely with the particle spacing. Figure 2(B) shows the mutual mean square displacement $d_{ij}(t)$ multiplied by the dimensionless spacing ρ. The data measured for a range of different pair spacings collapse onto a common curve over a wide range of times, although deviations are evident at very long times. The variations seen at long times do not depend systematically on the pair spacing ρ and are probably a reflection of poor statistics or mechanical vibrations. The peak seen in $d_{ij}(t)$ is a consequence of the applied optical potential since for very long times the correlations between the two particles must decay ultimately back to zero.

We have computed the self-and mutual friction coefficients from the one- and two-particle mean square displacements, which are shown in the inset of figure 3. The frequency dependence seen is in sharp contrast to that expected for a purely viscous fluid where $\tilde{\xi}_{ij}$ is independent of frequency. The steady decrease in the particle friction with increasing frequency reflects the viscoelasticity of the polymer solution and in particular its ability to store energy elastically at high frequencies. The connection between the particle friction coefficient and the medium rheology is more easily seen by plotting the scaled functions $(s/k)\tilde{\xi}_{ii}$ and $-(s/k)\rho\tilde{\xi}_{ij}$ as shown in figure 3. In the continuum model of Levine and Lubensky [1] both functions are predicted to be simple multiples of the Laplace-transformed shear modulus $\tilde{G}(s)$, so the ratio $-\rho\tilde{\xi}_{ij}/\tilde{\xi}_{ii}$

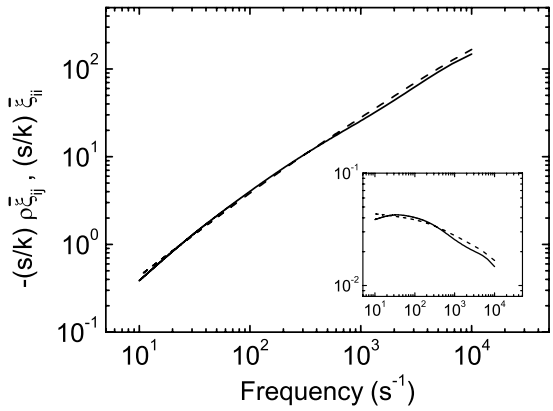

Figure 3. Frequency dependences of the scaled one-particle $(s/k)\tilde{\xi}_{ii}$ (dashed curve) and two-particle $-\rho(s/k)\tilde{\xi}_{ij}$ (solid curve) friction coefficients. Inset: $\tilde{\xi}_{ii}/k$ (dashed curve) and $-(\rho/k)\tilde{\xi}_{ij}$ as a function of frequency.

should be frequency independent and, from equations (4) and (5), equal to 3/2. In partial accord with these predictions, we find that the two scaled friction coefficients do exhibit a very similar functional form. However, the ratio $-\rho\tilde{\xi}_{ij}/\tilde{\xi}_{ii}$ is of order unity.

While we do not have a complete understanding of this discrepancy, one possible explanation is that the nature of the shear coupling between the particle and the medium differs in the one- and two-particle situations. In the immediate vicinity of a probe particle, a depletion zone exists with a reduced polymer segment concentration. While hydrodynamic forces will still couple the motion of the probe particle to the polymer matrix, the depletion zone could modify the nature of the boundary conditions at the particle surface. Cardinaux *et al* [10] have suggested recently that a slip, as opposed to a no-slip, boundary condition might apply in giant-micellar solutions.

The effect of modifying the boundary condition at the surface of a rigid particle in a Newtonian medium has been studied by Jones and Schmitz [11] who have calculated the mobility functions of two identical hard spheres for stick and slip boundary conditions. By inverting the matrix of mobility functions, the ratio of the two- and one-particle friction coefficients in a Newtonian medium are found to be $\xi_{ij}/\xi_{ii} = -3/2\rho + \mathrm{O}(1/\rho)^2$ for stick boundary conditions and $\xi_{ij}/\xi_{ii} = -1/\rho + \mathrm{O}(1/\rho)^5$ for slip. The case of a viscoelastic medium is more complicated; however, an analogous argument may explain our findings. Assuming the depletion of polymer changes the boundary condition to one of slip, then we should identify $\tilde{\xi}_{ii}(s)$ with $4\pi a\tilde{G}(s)/s$ rather than equation (4). By analogy with the Newtonian case [11], the two-particle friction coefficient with slip boundary conditions may then be given by $-\rho\xi_{ij} = 4\pi a\tilde{G}(s)/s$. In this case the ratio $-\rho\xi_{ij}/\xi_{ii}$ is 1.0 which is in close agreement with the value observed in experiment.

5. Conclusions

We have presented a method for obtaining the micro-rheological properties of viscoelastic media from dual-beam optical tweezers measurements. Our method allows the determination of viscoelastic properties of soft-matter systems over an extended frequency range not accessible to conventional rheology. By accounting for the presence of a harmonic potential due to the optical traps, we are able to use a more intense laser beam than in previous studies.

This provides an advantage in increasing the signal-to-noise ratio in our data, thus reducing statistical errors. To test our approach we have measured the time-resolved position of one and two colloidal particles embedded in a semi-dilute solution of PS in a mixed-decalin solvent. The results of our preliminary study are consistent with the model presented and further investigation of the effects of polymer concentration and molecular weight are currently under way to confirm our findings.

Acknowledgments

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