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Forces on a colloidal particle in a polymer solution: a study using optical tweezers

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Abstract. We report a study of the dynamical behaviour of a polystyrene latex sphere in a telechelic poly(ethylene oxide) solution using optical tweezers. With this new technique, we use a position-sensing detector and a lock-in amplifier to measure the displacement magnitude and phase responses of one latex sphere driven sinusoidally by optical tweezers.

For a single particle in solution, the equation of motion of the particle is simply that of the forced oscillation problem with damping from viscous drag and the restoring force from the elasticity of the solution medium and that of the optical tweezers. Because the system is overdamped, it is not feasible to probe the high-frequency regime. Thus we cannot measure the viscosity and elastic moduli separately from frequency-dependent measurements alone. At low polymer concentration, measurements of the viscosity have been achieved. We compared the measured viscosity with that obtained with other measurements. Key issues for further development of this technique, such as measuring the elastic modulus, are briefly discussed.

1. Introduction and background

Use of laser tweezers, first developed by Ashkin *et al* [1], is a technique based on the fact that dielectric particles tend to fall in a deep potential well produced by the highly localized electric field of a focused laser beam. Recently, Chu's group [2] used a focused laser beam in an optical microscope to manipulate a DNA chain tethered to a micron-sized latex sphere by moving the latex particle in a polymer melt with the laser beam. The technique has also found applications in biological studies [3]. Accurate measurements of small forces and displacements using optical traps have also been documented by several groups [4, 5]. Recently, laser tweezers have also been used to study colloidal interactions [6].

1.1. The principle of optical tweezers

Substantial development in theory has been made for laser tweezers, and calculations have become fairly sophisticated for various geometrical situations [7]. The basic idea of how laser tweezers work, however, is quite simple. For our application, it is sufficient to consider the energy contained in the electric field of the laser beam. If a particle of volume V and higher dielectric constant ε_2 enters the field, the potential energy is lowered by

$$\Delta U = \frac{3\varepsilon_1}{2}\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} V|E^2(r)| \tag{1}$$

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where ε_1 is the dielectric constant of the medium. And the force experienced by the particle is:

$$F = \frac{-3\varepsilon_1}{2}\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} V \nabla_r |E^2(r)|. \tag{2}$$

By tightly focusing the laser beam, and therefore increasing $\nabla_r|E^2(r)|$, we will increase the forces which counteract the random Brownian force or external forces caused by shear flow. It can be estimated that a 100 mW Ar-ion laser beam can produce a force of the order of 100 pN on a polystyrene bead 1 μm in diameter [8]—a force sufficiently large to hold the same particle in a flow of 0.1 cm s^{-1}, or a shear rate about 10^3 l s^{-1}.

1.2. A single-particle trap: the quadratic-potential-well model

Since the laser beam intensity typically has a Gaussian profile in the direction perpendicular to the beam direction, i.e., $I(r) \sim E^2(r) \sim \exp(-r^2)$, it is not unreasonable to model the bottom of the potential well as a quadratic. As long as the particle is kept near the centre of the trap, one can write the potential energy as

$$U(r) = \frac{3\varepsilon_1}{2}\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} V |E^2(r)| \approx \tfrac{1}{2} c r^2. \tag{3}$$

The force experienced by the particle in the trap follows Hooke's law:

$$F = \frac{-3\varepsilon_1}{2}\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} V \nabla |E^2(r)| \approx -cr \tag{4}$$

with a typical spring constant $c = 10^{-3}$ to 10^{-4} dyn cm^{-1}.

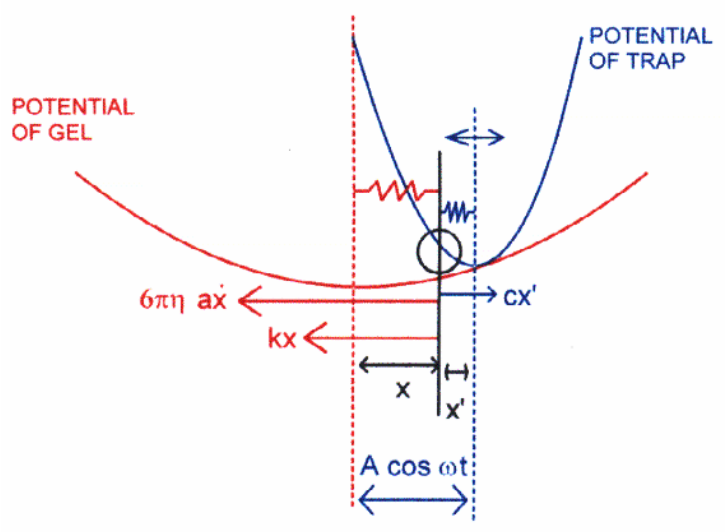

Figure 1. The force diagram of a particle trapped by optical tweezers in a viscoelastic medium.

Now, if the particle is forced to oscillate by an externally controlled oscillating laser-beam-steering mirror, the particle in a polymer solution will experience forces, in the direction x perpendicular to the laser propagation direction, from several origins: (1) the laser tweezers exert a spring-like force $-cx$, (2) the viscous force $-6\pi\eta a v$, and (3) the

elastic restoring force $-kx$, due to the viscoelastic nature of the polymer solution shown in figure 1. We can write down the equation of motion for the particle as

$$m\ddot{x} + 6\pi\eta a\dot{x} + (k+c)x = cA\cos(\omega t) \tag{5}$$

where m and a are the mass and radius, respectively, of the colloidal particle, η is the viscosity of the solution, and A the amplitude of the displacement of the oscillating trap. The spring constant k associated with the elastic media can be written as $k = 2(4\mu + 2\kappa)a$, where μ is the shear modulus and κ the bulk modulus of the polymer solution. The above equation has the steady-state solution

$$x(t) = D\cos(\omega t - \delta) \tag{6}$$

where the amplitude D and the phase shift δ of the response are

$$D = \frac{c}{m}\frac{A}{\sqrt{(\omega_0^2 - \omega^2)^2 + 4\omega^2\beta^2}} \tag{7}$$

$$\delta(\omega) = \tan^{-1}\frac{2\omega\beta}{\omega_0^2 - \omega^2} \tag{8}$$

where β is $3\pi\eta a/m$ and ω_0^2 is $(k+c)/m$. We estimate the characteristic frequencies of the oscillation as: $\omega_0 = 10^5$ or 10^6 s^{-1} and $\beta = 10^7$ s^{-1}. With these numbers we conclude that: (1) the quality factor $Q = \omega_0/2\beta$ is very small compared to one and the system is highly overdamped and (2) both δ and D vary appreciably over the range $0 < \omega < 10^3$.

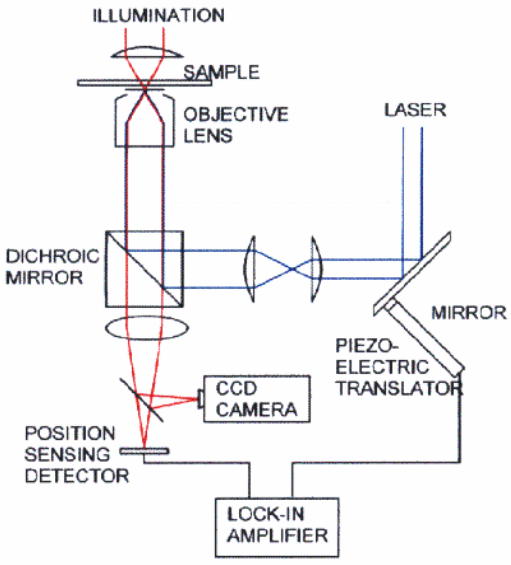

Figure 2. A schematic diagram of the optical tweezers and PSD detection set-up.

2. Experimental details

While the oscillating latex sphere in the trap can be viewed directly using an optical microscope with a CCD camera, quantitative measurements of both D and δ can be best achieved by imaging the particle onto a position-sensitive detector (PSD) [9]. A schematic

diagram is shown in figure 2. With the current techniques available for PSD, particle displacements in solution of the order of 10 nm can be measured. To achieve such sensitivity, however, the imaging of the particle onto the PSD becomes crucial. For our measurement of the dynamic response of a particle in solution, much better sensitivity can be accomplished by measuring the phase shift δ instead.

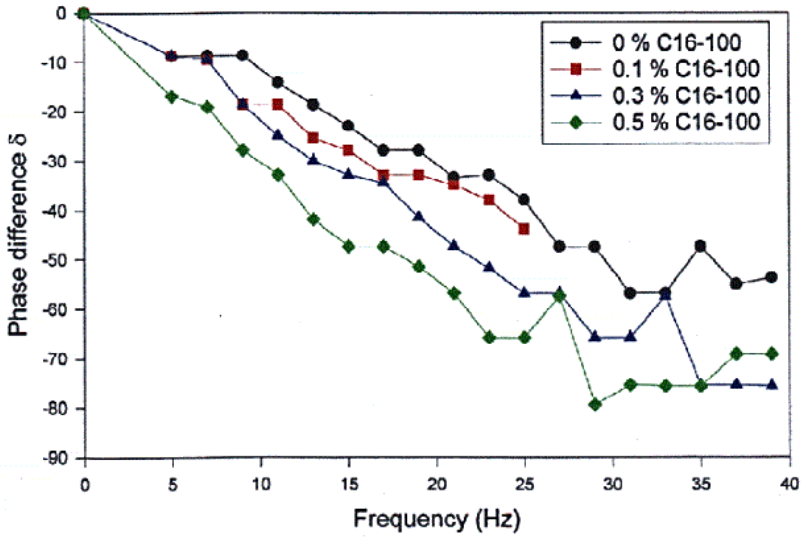

Figure 3. The phase shift as a function of frequency for different polymer concentrations.

2.1. The lock-in amplification technique

We feed the oscillating electrical signal provided by the PSD into a lock-in amplifier and a reference signal from the function generator that drives the steering mirror. The lock-in amplifier measures the magnitude and phase of the particle displacement. The results of the phase shift for a polystyrene latex particle 1.1 μm in diameter in solutions of C16-100 PEO chains ($M_w = 100$ kg m^{-1}) terminated on both ends by $C_{16}H_{33}$ hydrophobes are shown in figure 3.

2.2. Determining the viscosity from the dependence of the phase shift on frequency

For frequencies low compared to ω_0, the slope of the tangent of the phase shift versus frequency is equal to $2\beta/\omega_0^2$. We can calculate β for pure water, and use that value to determine ω_0 and the spring constant of the particle trap. Since the spring constant of the particle trap does not change significantly with added polymer, we can determine the viscosity of the polymer solution at various concentrations as shown in figure 4. In carrying out the calculation of the viscosity we have used the corrected particle radius by considering the adsorption of polymer on the latex sphere which makes the effective radius larger than that of a bare particle.

The focused laser beam and the strong illuminating light raise the temperature over the region near the particle trap and thus reduce the viscosity. Without a direct measurement of temperature, we cannot determine precisely the viscosity of pure water. Therefore, we can

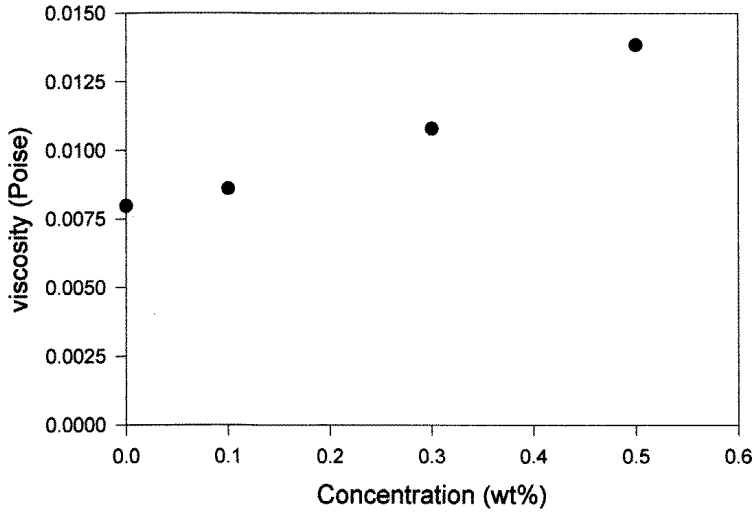

Figure 4. The viscosity (in poise) as a function of polymer concentrations of C16-100 in water.

only determine the spring constant of the particle trap by assuming a local temperature. We compared the intrinsic viscosity obtained by our method (0.79) to that obtained by Jenkins [10] and found that the values correspond to a local temperature of 50–60 °C. We are currently developing a flow cell which also allows for a direct temperature measurement to resolve this problem.

In order to decouple the damping factor β from ω_0 by frequency-dependent measurements, the particle must be driven at frequencies near ω_0. This system is highly overdamped, however, so it is not practical to drive the particle at such high frequencies, i.e. we can only obtain, through frequency-dependent measurements, the value β/ω_0^2. In order to make this technique useful, one must be able to determine the viscosity and elastic moduli independently. Alternatively, the viscous term, β, can be decoupled from ω_0 by varying the laser intensity, which will change the particle trap spring constant. We are currently exploring the possibility of this approach.

3. Conclusions

We are developing a new technique using optical tweezers to study the dynamics of a particle in a polymer solution. In a forced oscillation system, using the combination of phase-sensitive detection and PSD measurements, we are able to measure the viscous response of a particle in dilute aqueous polymer solutions of telechelic PEO. From the phase-shift measurement as a function of frequency in pure water, at a known temperature, we can precisely determine the spring constant of the particle trap. Since the elastic moduli are negligible in these solutions, we can obtain a quantitative measurement of the viscosity by measuring the phase lag as a function of frequency for different polymer concentrations. The intrinsic viscosity compared well with that obtained by other methods.

Several important issues, however, need to be addressed in order to develop this technique further. First, one needs to find a reliable way to decouple β from ω_0 so that one can investigate the full viscoelastic response of the system. Second, a precise local temperature measurement or a flow cell with temperature control is necessary in order to

calibrate the spring constant by a known viscosity. Third, absolute measurement of the displacement by this technique can only be achieved with very good control of image quality, which will be discussed in a separate paper [11].

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