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Diffusion of microscopic tracer particles in a yield-stress fluid

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Abstract

The motion of micron-sized fluorescent tracer particles in a gel of Carbopol ETD 2050 is studied using fluorescence microscopy. For a Carbopol concentration at which the material shows yield-stress behavior on the bulk scale, the tracer particles display a range of behavior: Some of the particles show slightly subdiffusive behavior, while others are almost completely immobilized. This indicates that the material is inhomogeneous, with different particles sampling different microrheological environments. From our results we calculate the range of microrheological viscous and elastic moduli of the material, which we compare with bulk values of the moduli as determined by conventional shear rheometry.

Keywords: Yield-stress fluids; Microrheology

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1. Introduction

Yield-stress fluids behave as soft solids when subjected to a shear stress σ less than their yield stress σ_y, but flow when $\sigma > \sigma_y$. Such materials have important applications in many areas; examples include pastes and concentrated suspensions, fresh concrete, and foams. Like all soft materials, their complex rheological behavior is a result of structure on scales much larger than the molecular scale [1]. The bulk properties and flow behavior of yield-stress fluids have been studied extensively using shear rheometry [2,3] and a variety of flow experiments [4–10], as well as numerically [11,12]. On the other hand, the microscopic structure of some yield-stress materials has been probed with scattering techniques both at rest and under shear [13–16]. There has been rather little effort, however, aimed at investigating the rheology of yield-stress fluids on the microscopic scale and the interplay between small-scale structure and microrheology in these materials [17]. In this paper we present experimental results on the diffusion of small tracer particles in a Carbopol gel. We demonstrate that the gel is inhomogeneous on the length scale probed by our experiments, and we separate our tracer particles into populations depending on the degree to which their motion is restricted by the gel structure. We then determine the microrheological viscous and elastic moduli for each population, and contrast our results with bulk rheological measurements.

Various techniques designed to probe the microrheology – that is, the viscoelastic response of complex fluids on the microscopic scale – have been developed over the last decade [18–22]. Microrheological methods typically involve measurements of the motion of small (sub-micron diameter) particles suspended in the material of interest. Passive microrheology is based on the determination of viscoelastic parameters from measurements of the mean squared displacement $\langle r^2(\tau)\rangle$ of the particles as a function of a lag time τ. $\langle r^2(\tau)\rangle$ can be measured with light scattering techniques [23–26] or by directly tracking the trajectories of the tracer particles using video microscopic techniques [27–31]. Active microrheology, on the other hand, involves measurement of the response of a small particle to an external force [35–39].

Microrheological methods in general require a much smaller sample than needed for conventional shear rheometry, so they are useful for characterizing materials which are expensive or which cannot be obtained in large quantities, such as some biological fluids. In these applications, one typically wants the microscopic measurements to give the bulk viscoelastic properties, which requires that the fluid under study be homogeneous on the length scales probed by the experiments. This has been shown to be the case for several complex fluids, including solutions of poly(ethylene oxide), an uncross-linked linear chain polymer [23,24,30]; a suspension of hard-sphere silica particles in ethylene glycol [24]; an oil-in-water emulsion [24,25]; and cross-linked polyacrylamide sols and gels [34].

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In contrast, if the size of the suspended particles is smaller than the size of local inhomogeneities in the material properties, then individual particles will experience different local microrheological environments. In such cases, microrheology provides a tool that can be used to investigate structure and rheology on these small scales. The microrheology of networks of F-actin, a protein which is a major structural component of cell membranes, has been studied in some detail [26,27,29–31,33] using light scattering as well as particle-tracking and two-particle correlation measurements. It has been found that microrheological measurements agree well with bulk measurements if the suspended particles are larger than the mesh size of the actin network. When the particle size is comparable to the mesh size, however, the rheology becomes dependent on the length scale sampled by the tracer particles as they diffuse [27,32,33].

Passive microrheological measurements give the mean squared displacement of small particles moving in a viscoelastic material due to thermal fluctuations. The microscopic viscous and elastic moduli are extracted from the mean squared displacement under the assumption that the Stokes–Einstein relation that is valid for purely viscous Newtonian fluids can be generalized to viscoelastic fluids with frequency-dependent linear viscoelastic moduli [22,24]. It is also assumed that inertial effects on the motion of the probe particles are negligible. The method by which the viscoelastic moduli are calculated has been described by Mason [22]. Briefly, we define $\alpha(\omega)$ to be the frequency-dependent logarithmic slope of the mean squared displacement, evaluated at a frequency ω equal to the reciprocal of the lag time:

$$\alpha(\omega) = \left.\frac{\mathrm{d}\ \ln\langle r^2(\tau)\rangle}{\mathrm{d}\ \ln\tau}\right|_{\tau=1/\omega}. \tag{1}$$

The magnitude of the mechanical modulus $G(\omega)$ is then

$$|G(\omega)| = \frac{k_{\mathrm{B}}T}{\pi a\langle r^2(1/\omega)\rangle\Gamma(1+\alpha(\omega))}. \tag{2}$$

Here k_{B} is the Boltzmann constant, T the temperature, a the radius of the suspended particles, and Γ the Gamma function. The viscous and elastic moduli, G'' and G', respectively, are given by

$$G''(\omega) = |G(\omega)|\sin\left(\frac{\pi\alpha(\omega)}{2}\right) \tag{3}$$

and

$$G'(\omega) = |G(\omega)|\cos\left(\frac{\pi\alpha(\omega)}{2}\right). \tag{4}$$

Here we study the microrheology of a Carbopol gel. When dispersed in water, Carbopol forms a transparent gel whose rheological properties can be tuned by varying the Carbopol concentration and pH. Steric interactions among swollen microgel particles and cross-links between polymer chains in the material give rise to a yield stress [40–45]. The high degree of transparency of Carbopol gels, the relative unimportance of aging [46,47] in these materials, along with the ease with which samples can be prepared, has led to the use of Carbopol gels as model yield-stress fluids [4,8,45].

In a previous paper [17], we presented the results of both particle tracking and dynamic light scattering measurements of the microrheology of Carbopol gels as a function of Carbopol concentration. We showed that the microrheological moduli were several orders of magnitude smaller than the moduli determined from bulk shear rheometry. We also demonstrated that the gels were inhomogeneous on the length scale probed by our measurements, so that individual tracer particles sampled different microscopic rheological environments.

In the present paper we look in more detail at the variations in microrheological environment for a sample with a Carbopol concentration of 0.5 wt.%. This material is a stiff gel on the bulk scale, but we find that while some of the suspended tracer particles are more-or-less completely immobilized by the gel, others diffuse almost freely. We separate our tracer particles into populations depending on their mean squared displacements and study the behavior of each population.

The remainder of this paper is organized as follows. In Section 2 we present the experimental details. Our results are presented in Section 3 and discussed in Section 4. Section 5 is a brief conclusion.

2. Experiment

Our experiments were performed using Carbopol ETD 2050, which consists of polymers based on polyacrylic acid, crosslinked with a polyalkenyl polyether [44]. Samples were prepared in a dust free environment. Fluorescent latex microspheres 0.49 μm in diameter, with density 1.05 g/cm^3 and refractive index 1.59 at 589 nm were obtained as a suspension in water [48]. These microspheres contained a dye which fluoresced in the red when excited with green light. They were sonicated in an ultrasonic bath to disperse any clumps prior to use, then diluted with deionized water to give a sphere volume fraction of typically 5×10^{-5}. Carbopol powder was added slowly to the continuously stirred dilute sphere suspension to a concentration of 1.2 wt.%. The resulting dispersion had a pH of about 3. Sodium hydroxide solution was added to raise the pH to 6. Gel samples of the desired Carbopol concentration c were obtained by diluting this stock solution with additional water/sphere suspension (and readjusting the pH to 6 if necessary); most of the results reported here were obtained with $c = 0.5$ wt.%. Any air bubbles were removed by centrifugation. Samples used for rheological measurements were prepared the same way but without the microspheres.

Our particle-tracking apparatus has been described elsewhere [17]. Samples containing the fluorescent microspheres were loaded into a sample cell 10 mm × 10 mm × 0.75 mm high which was sealed with a silicone-based grease. The cell was mounted on the stage of an Olympus BX50Wi upright epi-illumination fluorescence microscope with an overall magnification of 150× which was focused on the mid-point of the cell, giving a resolution of 0.27 μm/pixel. The samples were allowed to equilibrate for half an hour at room temperature before measurements were made. Typically from 50 to 100 fluorescent spheres were visible in the field of view at any time. Images of the spheres were captured with a 640 pixel × 480 pixel CCD