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Modeling the microrheology of inhomogeneous media

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ABSTRACT

We model the restricted diffusion of small tracer particles near a gel transition by performing Monte Carlo simulations in a site-percolation model. From the mean squared displacement of the particles, we calculate the effective viscous and elastic moduli using the microrheological equations derived from the generalized Stokes–Einstein relation by Mason [T.G. Mason, Rheol. Acta 39 (2000) 371]. The results show a transition from viscous to elastic behavior at a site-filling probability that is different from that at the percolation transition, and that occurs at higher site-filling probability for smaller tracer particles. This behavior is due to confinement of the tracers in the inhomogeneous system, and we discuss the inapplicability of the generalized Stokes–Einstein relation in this case. The simulations are in partial agreement with experimental results obtained for a gelling clay suspension and polymer blends, but there are also differences which suggest the importance of microstructure, and specifically elastic effects in the experimental systems. We discuss the implications of our simulations for the interpretation of microrheological experiments on inhomogeneous media.

1. Introduction

The techniques of microrheology allow determination of the viscous and elastic properties of soft materials on the micrometer length scale from the motion of suspended micron-sized tracer particles [1–3]. The tracer motion can be driven either by an applied force or by thermal fluctuations [2]. In the latter case, the frequency-dependent rheological properties of the material can be calculated from the mean squared displacement of the particles using a generalized Stokes–Einstein equation [4–6,3].

In a purely viscous, Newtonian fluid, a small tracer particle will undergo conventional Brownian motion. Its mean squared displacement $\langle r^2(t)\rangle$ increases linearly with time t, i.e.

$$\langle r^2(t)\rangle = 2dDt, \tag{1}$$

where d is the dimensionality of the motion and D is the usual diffusion coefficient. The Stokes–Einstein relation,

$$D = \frac{k_B T}{6\pi\eta a}, \tag{2}$$

relates D to the viscosity η of the fluid. Here a is the particle radius, k_B the Boltzmann constant, and T the temperature. In a viscoelastic fluid, the diffusion of the tracer particles is restricted because not all of the energy imparted to the particle by the thermal fluctuations is dissipated by viscous drag; some of it is used to elastically deform the material. As a result, $\langle r^2(t)\rangle$ increases sublinearly. The viscous and elastic moduli on the length scale probed by the tracer particle can be calculated by replacing Eq. (2), by a generalized, frequency-dependent version of the Stokes–Einstein relation [4,7,8]. If we define α to be the local logarithmic slope of $\langle r^2(t)\rangle$, i.e.,

$$\alpha(\omega) = \left.\frac{d\ln\langle r^2(t)\rangle}{d\ln t}\right|_{t=1/\omega}, \tag{3}$$

then the magnitude of the frequency-dependent complex modulus $G(\omega)$ can be written as [4,7]

$$|G(\omega)| = \frac{k_B T}{\pi a\langle r^2(1/\omega)\rangle\Gamma(1+\alpha(\omega))}. \tag{4}$$

where Γ is the Gamma function. The elastic and viscous moduli G' and G'' are then

$$G'(\omega) = |G(\omega)|\cos\left(\frac{\pi\alpha(\omega)}{2}\right) \tag{5}$$

and

$$G''(\omega) = |G(\omega)|\sin\left(\frac{\pi\alpha(\omega)}{2}\right) \tag{6}$$

respectively [4,7].

This approach has a sound theoretical basis [8,9] over a range of frequencies, as long as the assumptions inherent in the Stokes–Einstein relation are valid [3]. In the context of the present work, the most important of these is that the material be a continuum as seen by the tracer particle, which requires that the particle be much larger than any structural length scale λ in the material.

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Experiments on homogeneous viscoelastic fluids such as polymer solutions [6,10] have confirmed that as long as $a \gg \lambda$, moduli measured using microrheological techniques agree well with bulk rheological measurements.

On the other hand, many interesting and important complex fluids have microstructure on the scale of microns, and so are heterogeneous on the scale probed by microrheology. In such materials, the mean squared displacement of the diffusing tracers can be restricted by interactions with the microstructure as well as by elasticity. In this case, the assumption of continuity involved in the generalized Stokes–Einstein equation may be questionable, and the interpretation of Eqs. (5) and (6) becomes more difficult. They will no longer give the bulk viscous and elastic moduli, since the motion of the probe particles is affected by the microstructure and they do not sample the bulk material properties. If the material is locally continuous, however, applying Eqs. (5) and (6) to individual particles or groups of particles that sample rheologically similar regions of the material gives local values of the moduli and allows study of the spatial heterogeneity. Microrheology can thus provide information about the microstructure and microscopic properties of complex fluids that is not available from bulk-scale measurements. If the material is not locally continuous, then the generalized Stokes–Einstein relation does not apply and application of these equations to measurements of $\langle r^2(t)\rangle$ is dangerous. Nonetheless, the motion of the tracer particles still contains information about the local environment in which the particles move. It is not legitimate to think in continuum-mechanical terms about a medium that is not a continuum, so the quantities given by Eqs. (5) and (6) can no longer be thought of as elastic and viscous moduli, but they still have something to do with the properties of the material on the scale probed by the particle.

Of particular interest for this work are materials that undergo a transition from a primarily viscous fluid to a primarily elastic gel [11–14]. This occurs when the microstructural components of the material become sufficiently interconnected that they form a network which spans the sample. The gel transition is understood as a percolation transition [12,15,16]. For example, consider polymer chains in solution, and let p be the probability that a crosslink forms to connect two chains. As p is increased from 0, clusters of connected chains form and grow in size. The gel transition occurs at a well-defined critical value p_c, at which one cluster becomes large enough that it percolates from one side of the sample to the other. At higher p additional chains join this percolation cluster.

At $p = p_c$, the percolation cluster is a fractal object with structure on all length scales from the sample size down to the scale of the distance between crosslinks [12,15,17]. At the transition, the material also contains smaller clusters with a power-law distribution of sizes that are not linked to the percolation cluster. Similarly, on either side of the transition, the system contains clusters with a range of sizes. Gelling materials are thus heterogeneous, and at the gel transition they are heterogeneous on all scales. This suggests that the interpretation of microrheological data may become problematic close to the gel transition. If the gelation occurs in the presence of microscopic phase separation [11], the material would have additional heterogeneity on the scale of the phase-separated domains.

The rheological signature of the gel transition on the bulk scale is well known [18,19,14]. In the fluid phase the viscous modulus G'' is larger than the elastic modulus G', and as the frequency ω approaches zero $G' \to 0$ while $G''/\omega = \eta$ is constant. In the gel phase, G' approaches a constant at low frequency while $G''/\omega \to \infty$. The system displays critical behavior at the gel point [12], with G'' and G' both showing the same power law scaling in frequency [18].

Several physical and chemical gels have been studied using microrheology [20–35], and indeed the technique has proven useful for locating the gel point and studying the gelation process in weak gels that are difficult to investigate with conventional shear rheometry [26]. In some of these studies, the degree of heterogeneity was examined via the shape of the distribution of particle step sizes [24,22,23,27,28,20,30,32], which is Gaussian for unrestricted diffusion and non-Gaussian in a heterogeneous medium, or by studying subsets of the tracers which display similar behavior [21,23,25,30,35]. In others, some understanding of the heterogeneity is obtained from experiments with different-sized tracer particles [29,21,20,31,34]. Some authors study the mean squared displacement, but do not invoke the generalized Stokes–Einstein relation because the particle size is close to structural length scales [21,33]. In others, the calculated moduli are simply referred to as effective quantities [29,22–25,30] which are not the same as the bulk viscous and elastic moduli.

Our own microrheological measurements on two gel-forming materials provide the primary motivation for the present work. In Ref. [24], Oppong et al. used particle-tracking microrheology to study the gelation over time of a suspension of Laponite, a synthetic clay. Bulk rheological measurements showed a well-defined gel transition as described above. The mean squared displacement determined from the particle trajectories showed an approximate power-law dependence on time, with the logarithmic slope α decreasing from close to one for young samples to zero as the sample aged. Based on the excess kurtosis of the distribution of particle step sizes, the heterogeneity of the suspension was small in the fluid phase but somewhat larger in the gel phase. The moduli calculated from the mean squared displacement using Eqs. (5) and (6) also showed the rheological signature of a gel transition, but with an apparent gel point (determined from the time at which the microrheological moduli were equal and displayed the same power-law dependence on frequency) substantially later than the bulk gel point. This behavior was interpreted by Oppong et al. to be due to continued evolution of the material microstructure after the bulk gel transition had occurred [24]: Although a percolation cluster forms at the gel point, many small regions remain un-gelled and are not incorporated into the percolation cluster until some later time. As time passes, the ungelled regions get smaller. The time at which a tracer particle becomes immobilized by the gel phase thus depends on its size, being later for smaller particles. The dependence on the apparent gel point on tracer size was confirmed by Rich et al., who performed similar experiments on Laponite [29]. Rich et al. found that the immobilization of the tracer particles as the gel evolved was due to elasticity rather than confinement in pores, implying that the material remained locally continuous on the particle scale, even in the gel phase.

Yang et al. [30] used dynamic light scattering to measure $\langle r^2(t)\rangle$ for tracer particles in a concentrated solution of poly(vinyl alcohol) and blends of poly(vinyl alcohol) and poly(ethylene glycol). Gelation occurred over time in the blends, but in tandem with microphase separation. This led to substantial heterogeneity which was visible in the trajectories of tracer particles measured by particle tracking. The mean squared displacement measured by light scattering increased linearly for small t, indicating diffusive motion over short time scales. At intermediate times, $\langle r^2(t)\ \rangle$ displayed a plateau. In fresh samples, the scaling of this plateau with the size of the tracer particle indicated that it reflected localization due to elasticity rather than trapping [1]. At longer t, $\langle r^2(t)\rangle$ again increased approximately linearly with time. The effective microscopic moduli calculated for a blend of 10% PVA and 7% PEG showed a transition from behavior characteristic of an entangled polymer solution at early times to gel-like behavior at late times, with approximately the same power-law dependence on frequency at an age substantially later than the gel time determined from bulk rheological measurements. These results were again interpreted in terms of the evolving properties of the micro-phase separated materials [30].