XXI ICTAM, 15–21 August 2004, Warsaw, Poland

SINGLE PARTICLE MOTION IN COLLOIDAL DISPERSIONS

Ileana C. Carpen*, Todd M. Squires**, & John F. Brady*
*California Institute of Technology, Division of Chemistry and Chemical Engineering, Pasadena, CA 91125, United States
**California Institute of Technology, Depts. of Applied and Computational Mathematics and Physics, Pasadena, CA 91125, United States

Summary Microrheology uses the motion of tracer particles to infer the properties of a surrounding medium. Most applications have limited themselves to examining motion due to thermal fluctuations, with minimal impact upon the structure of that medium. We investigate the forced motion of a particle through a colloidal suspension, which is affected by both the viscous drag and the force resulting from the microstructural deformation, and thus study the departure of the system from the linear viscoelastic regime.

BACKGROUND

In the last decade microrheology has burst onto the scene as a novel experimental technique to study the properties of materials at the microscopic scale, and is particularly well-suited for examining the properties of soft, heterogeneous materials, especially biological materials. Among the collection of techniques known as microrheology, most involve tracking the movement of a colloidal particle or set of particles in order to determine the properties of the surrounding environment [1]. There are two main types of particle-tracking microrheology: passive—tracking the random motion due to thermal fluctuations—and active—applying a constant or oscillatory force to the particles, for example by using optical tweezers or magnetic fields. Due to the small length scales involved, microrheology became most practical after recent improvements in imaging technology. Unlike conventional rheometry, which measures bulk properties, microrheology allows the measurement of local viscoelastic properties and needs much smaller material samples, a particular bonus for scarce biomaterials and small systems such as individual cells; for gels, microrheology also avoids the problem of slip at the walls, common for rheometers. Microrheological techniques have been used to study a diverse set of systems: cells, actin networks, gelatin, DNA and polyethylene oxide solutions, and the behavior of colloids near the glass transition, as well as fundamental interactions between pairs of colloidal spheres and entropic forces in binary colloids. Microrheology has also been proposed as a tool for fundamental physics or for high-throughput material screening.

A cornerstone of particle-tracking microrheology is the application of the Stokes-Einstein relation for a sphere in a homogeneous, incompressible fluid. For single particle tracking experiments, this takes the form (after a Laplace transform):

$$\tilde{r}^2(s) = \frac{kT}{\pi s a \tilde{G}(s)}, \tag{1}$$

where s is the Laplace frequency, $\tilde{r}^2(s)$ is the mean-squared-displacement of the particle, $\tilde{G}(s)$ is a frequency-dependent modulus (Stokes-Einstein generalized for a viscoelastic medium), k is Boltzmann's constant, T is the absolute temperature, and a is the particle radius. A similar equation applies for two-point microrheology, for which the correlated motion of pairs of particles is used instead of the single-particle mean-squared-displacement [2]. The Stokes-Einstein relation translates the microrheological measurement (mean-squared-displacement) into the macroscopic measurement (viscosity or complex modulus), and is therefore crucial to any type of micro-macro comparison. Most applications of microrheology have been in the 'passive' regime where the tracked particle's motion is induced by the thermal fluctuations in the medium and the applicability (or lack thereof) of the generalized Stokes-Einstein equation (1) has been examined in detail [2]. By contrast, much less work has been done on 'active' microrheology, where the tracked particle is driven by an external force. By its very nature the passive regime is limited to the *linear* viscoelastic behavior of the material, while the active regime can be used to drive the system out of equilibrium and investigate the material's *nonlinear* response. The purpose of this work has been to study analytically and numerically the 'active' system, and its transition from linear to nonlinear behavior.

ANALYSIS

In experiments, particle movement can be induced through the use of magnetic fields or optical tweezers, or alternatively, by having one heavy particle suspended amidst neutrally-buoyant particles. The basic problem reduces to examining the motion of a single particle under the action of an imposed external force and how this motion is affected by the response of the medium. We have chosen to investigate (analytically and numerically) the motion of a particle through a colloidal dispersion. Colloids are ubiquitous and can serve as an example of non-Newtonian media.

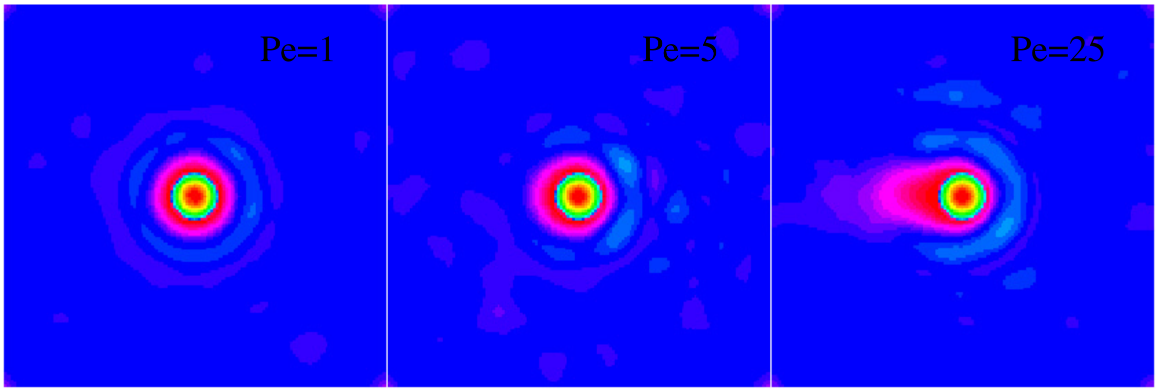

Figure 1. Brownian Dynamics results for the microstructure about a single forced particle in a Brownian suspension at a volume fraction of 35%. The particle generates a discernible wake region as the imposed force is increased beyond O(kT/a) (red regions correspond to low particle density), and a boundary layer of higher density on the 'front' (the direction of the force is left to right). The Péclet numbers based on the applied force, $Pe = Fa/kT$, are 1, 5 and 25, respectively. The total number of particles in the cubic unit cell is $N = 300$.

The particle's translational velocity is determined by a balance between the externally imposed force and the reactive force of the colloidal dispersion, which consists of the familiar viscous Stokes drag and a Brownian force caused by the deformation of the microstructure. For a particle of size a, the Péclet number, $Pe = Fa/kT$, gives the ratio of the external force (F) to the Brownian force (kT/a) and governs the distortion of the microstructure, which is determined from the solution of the Smoluchowski equation. For dilute suspensions in the absence of hydrodynamic interactions a closed form analytical expression can be obtained for all values of the Péclet number. However, consideration of suspensions of appreciable density requires the use of simulations (Brownian Dynamics or, if including hydrodynamics, Accelerated Stokesian Dynamics with Brownian motion (ASDB) [3]). Some results are shown in figure 1.

For small imposed forces (small Pe) the response is found to be viscous, with a linear relation between the imposed force and the velocity of the particle. The system is still in the linear regime for these small Pe (as with 'passive' microrheology) but transitions out of it as the Péclet number is increased. As the force on the particle is increased (increasing the Péclet number) the velocity of the particle decreases with increasing Pe until it reaches a viscous plateau at infinite Pe. This 'shear thinning' of the particle's velocity is reminiscent of the shear thinning of the colloidal dispersion's viscosity and a comparison between the two can be made.

CONCLUSIONS

This research examines the relation between micro and macro-rheology through a combination of theoretical and computational analysis, with an emphasis on the 'active' and nonlinear regime. Most microrheology research and analysis has been performed in the linear regime, with few experiments in the nonlinear regime, despite the great practical interest in the nonlinear problem. The results of this study may be used to both provide insight into currently available results as well as a guide for the design of new experiments.

References

[1] MacKintosh, F. C. & Schmidt, C. F.: Microrheology. *Curr. Op. Colloid Interf. Sci.* **4**:300–307, 1999.
[2] Crocker, J. C., Valentine, M. T., Weeks, E. R., Gisler, T., Kaplan, P. D., Yodh, A. G., & Weitz, D. A.: Two-point microrheology of inhomogeneous soft materials. *Phys. Rev. Lett.* **85**:888–891, 2000.
[3] Banchio, A. J. & Brady, J. F.: Accelerated Stokesian dynamics: Brownian motion. *J. Chem. Phys* **118**:10323–10332, 2003.