

Dynamics of Colloids in Polymers: An X-ray Fluorescence Correlation Spectroscopy Study

J. K. Basu,^{1,2} J. Wang,² S. Narayanan,² Z. Cai,² B. Lai,² J. Lal,³ H. Kim,⁴ S. K. Sinha⁴

¹Materials Research Laboratory, University of Illinois, Urbana-Champaign, IL, U.S.A.

²Advanced Photon Source, Argonne National Laboratory, IL, U.S.A.

³Intense Pulsed Neutron Source, Argonne National Laboratory, IL, U.S.A.

⁴Department of Physics, University of California, San Diego, CA, U.S.A.

Introduction

Complex fluids like polymers have a rich linear viscoelastic behavior [1-3]. Typically, these systems display several time-scale and length-scale regimes for the viscoelastic properties. For a full understanding of the mechanical properties of these systems, it is necessary to measure their viscoelastic properties over large length and time scales. Since the typical length scales of polymers vary from a monomer size (a few Å) to their end-to-end distance (typically a few hundred 100 Å), one can use small probe particles, like colloids, to probe their rheological properties. X-ray fluorescence correlation spectroscopy (XFCS) — a recently developed technique [4] — makes it possible to measure the diffusion coefficient and the mean squared displacement (MSD) of individual particles by using a microfocused x-ray beam to illuminate the colloid-polymer system.

Materials and Methods

XFCS is a new technique used to study the dynamics of particles in solution by measuring the intensity autocorrelation of the fluorescence signal from the probe particle (Fig. 1). The intensity is proportional to the number of particles in the illuminated volume; thus, its fluctuation probes the fluctuation in the average number of particles $\langle N \rangle$ and hence the particle dynamics. Small concentrations of probe particles and a small illuminated volume are required since the fractional rms fluctuation in the number of particles in a given volume, for an assembly of noninteracting particles, is $\langle N \rangle^{-1/2}$. The intensity autocorrelation function $g_f(t)$ of the fluorescence, when a Gaussian incident beam profile is assumed, can be written as follows:

$$\begin{aligned} g_f(\tau) &= \langle I_f(t)I_f(t+\tau) \rangle / \langle I_f(t) \rangle^2 \\ &= 1 + \langle N \rangle^{-1} (1 + \tau/\tau_D) \\ &= 1 + \langle N \rangle^{-1} \{ 1/1 + \Delta r^2[\tau/(6\sigma^2)] \}, \end{aligned}$$

where $I_f(t)$ = fluorescent intensity at time t , $\tau_D = \sigma^2/D_t$, $D_t = K_B T / 6\pi\eta R$, and Δr^2 = the MSD of fluorescing particles. Here D_t = the translational diffusion coefficient, σ = the

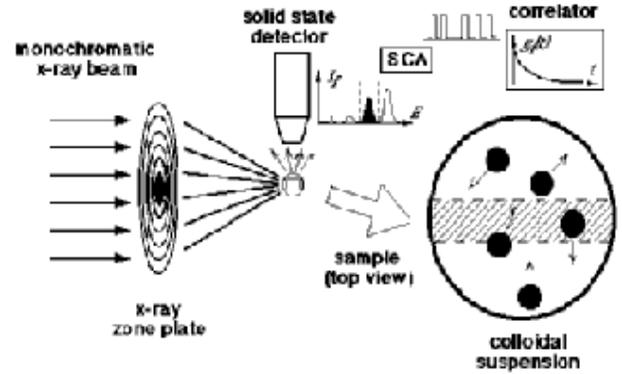


FIG. 1. Schematic of XFCS setup.

half-width, half-maximum (HWHM) beam size, η = the effective viscosity experienced by the particles, and R = the effective hydrodynamic radius of the particles.

The experiments were performed at the APS 2-ID-D beamline. The incident beam was monochromatized to 12.7 keV, and a zone plate with diameter of 150 μm and thickness of 2 μm (outermost zone width = 0.1 μm , focal length = 15 cm) was used to reduce the beam size (2σ) at the sample position to 0.2 μm . Gold $L\alpha = 9.7$ keV fluorescence, from the gold colloidal probe particles, was detected by using an energy-dispersive Ge detector. Colloidal gold with a volume fraction of 10^{-4} and a nominal mean particle diameter of 40 nm was used as purchased from ICN Biomedicals. Also used was 0.09 g/mL of polyethylene oxide (PEO) of mol wt 100K (Sigma-Aldrich). The radius of gyration and entanglement length (ξ) for this mol wt and concentration of PEO are 11 nm and 19 nm, respectively. See Fig. 2.

Conclusions

Colloids in polymer solution show three clearly different regimes of diffusive behavior corresponding to the different time-scale and length-scale dependencies of the viscoelastic properties of the polymer. These could be

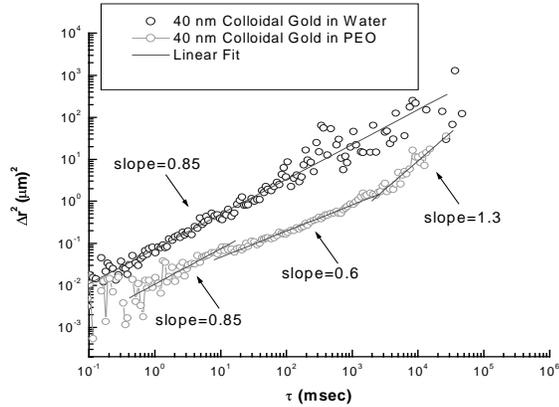


FIG. 2. Fluorescence intensity autocorrelation $g_f(\tau)$ vs. time delay τ for 40 nm of colloidal gold particles in water and 0.09 g/mL PEO solution in water. The solid line is a fit by using the equation in the text.

classified as (1) normal (or Stokes-Einstein) with a slope of ~ 1 in Fig. 3, (2) subdiffusive with a slope much smaller than 1, and (3) superdiffusive with a slope greater than 1. In water, on the other hand, the colloids show mostly normal diffusive behavior over the same range of time scales as those for the colloids in polymers. This clearly shows the length-scale dependence of the viscoelastic behavior of complex fluids like polymers when compared with simple liquids like water. Future work would focus on studying the viscoelastic properties of polymer solutions by varying their concentrations to change the relative size of the mesh and the probe colloidal particles. We also plan to more systematically study the possibility of anomalous diffusion behavior [5] and carry out a Laplace transform scheme on the obtained MSDs to extract detailed frequency (ω) dependent complex shear modulus $G^*(\omega)$ [6].

Acknowledgments

We acknowledge many useful discussions with Professor K. Schweizer at the University of Illinois at Urbana-Champaign and Professor A. Sood at the Indian

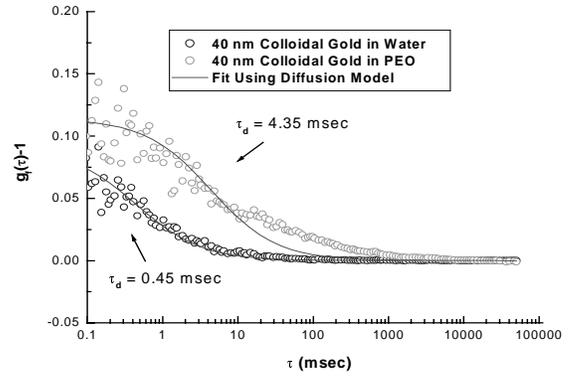


FIG. 3. MSD $\Delta r^2(\tau)$ vs. time delay τ for 40 nm of colloidal gold particles in water and 0.09 g/mL of PEO solution in water. Note that normal Stokes-Einstein diffusion predicts a slope of 1.

Institute of Science, Bangalore, India. J. K. Basu acknowledges support by the U.S. Department of Energy (DOE), Division of Materials Science, under Award No. DEFG02-91ER-45439, through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign. Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

- [1] P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (1979)
- [2] M. Doi and S. F. Edwards, *Introduction to the Theory of Polymer Dynamics* (1988).
- [3] F. Brochard Wyart and P.-G. de Gennes, *Eur. Phys. J. E1*, **93** (2000)
- [4] J. Wang et al., *Phys. Rev. Lett.* **80**, 1110 (1998).
- [5] A. Pekalski and K. Sznajd-Weron (editors), *Anomalous Diffusion: From Basics to Applications* (1999).
- [6] T. G. Mason and D. A. Weitz, *Phys. Rev. Lett.* **74**, 1250 (1995)