

# X-ray Photon Correlation Spectroscopy Study of the Dynamics of a Hard-Sphere Suspension

L. B. Lurio<sup>1</sup>, D. Lumma<sup>1</sup>, A. R. Sandy<sup>1</sup>, M. A. Borthwick<sup>1</sup>, P. Falus<sup>1</sup>, S. G. J. Mochrie<sup>1</sup>,  
J. F. Pelletier<sup>2</sup>, M. Sutton<sup>2</sup>, Lynne Regan<sup>3</sup>, A. Malik<sup>4</sup> and G. B. Stephenson<sup>4</sup>

<sup>1</sup>Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

<sup>2</sup>Department of Physics, McGill University, Montréal, Québec, H3A 2T8, Canada

<sup>3</sup>Department of Molecular Biophysics and Biochemistry, Yale University, New Haven, CT 06520

<sup>4</sup>Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

## Introduction

After twenty years of research, the dynamics of hard-sphere colloidal suspensions are still not fully understood. Although their static behavior closely resembles that of simple liquids, their dynamics show significant differences: particle motion is diffusive rather than ballistic, and, in addition to direct interactions, the particles experience hydrodynamic coupling to near neighbors via disturbances in the suspending medium. Indeed, the difficulty of fully treating near-field many-body hydrodynamic interactions remains the main obstacle preventing a detailed understanding of the dynamics in concentrated hard-sphere colloidal suspensions.

Recently, Segrè and Pusey [1] found, in hard-sphere dispersions of sterically-stabilized PMMA spheres in decalin/tetralin, that the long-time wavevector-dependent diffusion coefficient ( $D_L$ ) was proportional to the short-time diffusion coefficient ( $D$ ) from  $QR \simeq 1$  to  $QR \simeq 6$ , where  $Q$  is the scattering vector and  $R$  the sphere radius, and that the intermediate scattering function (ISF) itself displayed a certain scaling behavior for  $QR > 2.5$ , offering the hope that a clarification in our understanding ought to be possible. We show here, however, that this scaling is absent for polystyrene (PS) spheres in glycerol, which, insofar as their static structure is concerned, also exhibit behavior indistinguishable from that of hard spheres. Because these suspensions appear milky, as a result of multiple scattering of light, optical studies of the dynamic mode structure would be very difficult. Instead, we have applied the emerging technique of x-ray photon correlation spectroscopy (XPCS) [2].

## Methods and Materials

For the x-ray experiments, the PS-spheres-in-glycerol samples were mounted in an evacuated, temperature-controlled sample chamber and cooled to  $-5^\circ\text{C}$ . We used monochromatic x-rays of energy 7.66 keV with a relative energy bandwidth of  $3 \times 10^{-4}$  full-width-at-half-maximum. Crossed slits, 55 m from the undulator source and 40 cm upstream of the sample, selected a  $20 \mu\text{m}$  horizontal by  $50 \mu\text{m}$  vertical portion of the beam, resulting in a partially coherent flux on the sample of  $\sim 10^{10}$  photons per second. Scattered x-rays were detected 4.85 m further downstream using a CCD detector. Dynamical properties of the suspensions were characterized via autocorrelation of sequences of CCD images, leading to the normalized intensity-intensity autocorrelation function,  $g_2(Q, t)$ ,

which is related to the normalized ISF,  $f(Q, t)$ , via:  $g_2(Q, t) = 1 + B[f(Q, t)]^2$ , where  $t$  is the delay time, and  $B \simeq 0.13$  is a setup-dependent contrast.

## Results

Representative intensity autocorrelations from 30 ms to 300 s, obtained at  $QR = 1.5, 3.5,$  and  $6.0$ , for samples with  $\phi = 0.28$  and  $\phi = 0.52$  are shown in Fig. 1(a) and Fig. 1(b), respectively. For  $\phi = 0.28$ , single exponential fits [lines in Fig. 1(a)], provide a good description of the autocorrelations. Likewise, for samples with  $\phi = 0.027$  and  $0.13$ , single-exponentials describe the data well. (Data not shown.) However, for the higher-volume-fraction samples, the intensity autocorrelations are more complicated. Nevertheless, we find that at both long and short times  $\ln(f)$  varies linearly with  $t$ , so that we may define corresponding short-time and long-time diffusion coefficients:  $D_S = -Q^{-2}d \ln f(Q, 0)/dt$  and  $D_L = -Q^{-2}d \ln f(Q, \infty)/dt$ .

Displayed in Fig. 2 as the open squares is  $D_0/D_S$  versus  $Q$  for each sample, where  $D_0 = k_B T / 6\pi\eta R$  is the Stokes-Einstein diffusion coefficient, with  $\eta$  the viscosity of the suspending medium. The most striking feature of these results is that the inverse of the diffusion coefficient displays a peak that mimics the peak in the static structure factor, informing us that configurations of low free energy are also long-lived. In the absence of hydrodynamic interactions the  $Q$ -dependence of the inverse diffusion coefficient would result entirely from the static structure factor [3]. It is clear from Fig. 2 that  $D_0/D_S$  and  $S(Q)$  are not identical, so that significant hydrodynamic interactions are indicated. Analytic calculations of the  $Q$ -dependence of  $D_0/D$  for hard spheres, have been carried out by Beenakker and Mazur [4]. Their predictions are illustrated as the solid lines in Fig. 2. The good agreement lends strong support to the theory and constitutes further evidence that the interactions between PS particles in glycerol are hard-sphere in character.

The scaling behavior discovered by Segre and Pusey [1] is that  $\ln(f)/\Gamma$  is a function solely of time between  $QR = 2.5$  and  $6$ , implying that  $D_S/D_L$  is independent of wavevector. Indeed, they found this to be the case between  $QR = 1.0$  and  $QR = 6.0$ . In comparison, Fig. 3(a) shows our results for the IFS, scaled using  $D_S$  from Fig. 1. The small- $\phi$  data scales to a line with a slope of  $-1$ . By contrast, at  $\phi = 0.49$ , the data deviate from a straight line. More significantly, they do not collapse to a single scaling form.

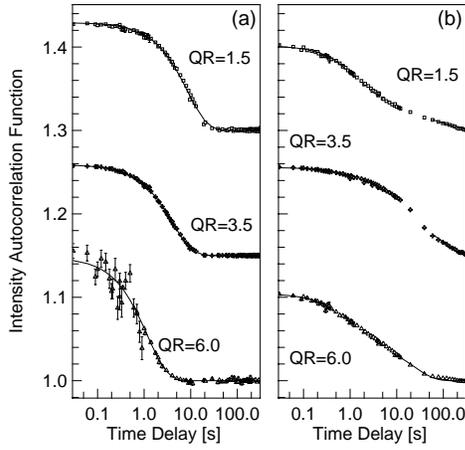


Figure 1: Autocorrelations,  $g_2(Q, t)$ , for (a)  $\phi = 0.28$  and (b)  $\phi = 0.52$  for  $QR = 1.5$  (offset by 0.3), 3.5 (offset by 0.15), and 6.0. Lines correspond to the models described in the text.

The extent to which the scaling behavior is violated for PS spheres in glycerol is quantified in Fig. 3(b), which illustrates  $D_S/D_L$  versus  $Q$  for  $\phi = 0.49$  and  $\phi = 0.13$ . In contrast to what is required by the proposed scaling, this ratio shows a strong  $Q$ -dependence in the vicinity of the peak of the structure factor and a weaker variation at both smaller and larger values of  $Q$ .

### Discussion

We have carried out a detailed XPCS study of diffusion in a concentrated suspension of hard spheres: PS latex spheres in glycerol. We do not find a previously observed proportionality between short- and long-time diffusion constants, nor do we find scaling behavior. The discrepancies between the results of Ref. [1] and our measurements may be an indication that the dynamical behavior of sterically-stabilized systems is distinct from that of charge-stabilized systems, even though differences in the static structure are negligible.

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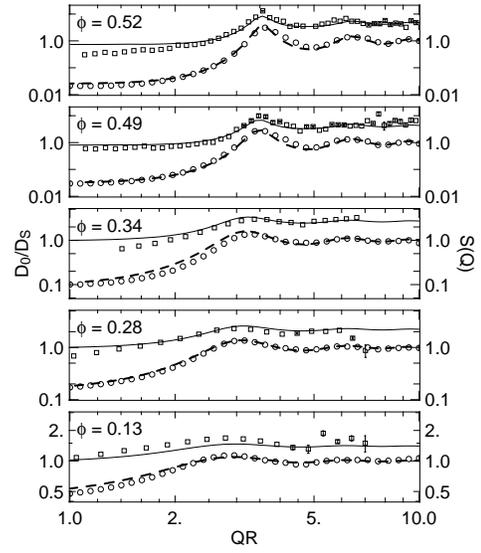


Figure 2: Measured and hard-sphere-model structure factors,  $S(Q)$ , (circles and dashed lines, respectively), and short-time diffusion coefficients relative to the Einstein-Stokes diffusion coefficient,  $D/D_0$ , (squares and solid lines, respectively) vs.  $QR$  for PS spheres in glycerol.

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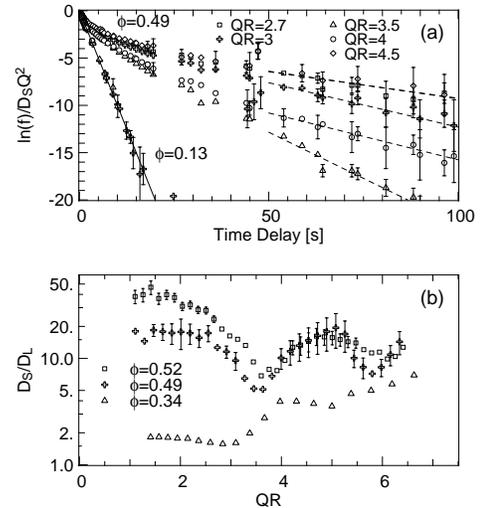


Figure 3: (a) Scaled IFs at several wavevectors for  $\phi = 0.49$ , and 0.13. Symbols are experimental data. The solid line corresponds to a slope of -1. The dashed lines correspond to long-time diffusion. (b) Ratio of short-time to long-time diffusion coefficients.