

Small Angle X-ray Scattering Study of a Hard-Sphere Suspension: Concentrated Polystyrene Latex Spheres in Glycerol

L. B. Lurio¹, D. Lumma¹, A. R. Sandy¹, M. A. Borthwick¹, P. Falus¹, S. G. J. Mochrie¹, J. F. Pelletier², M. Sutton², Lynne Regan³, A. Malik⁴ and G. B. Stephenson⁴

¹Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

²Department of Physics, McGill University, Montréal, Québec, H3A 2T8, Canada

³Department of Molecular Biophysics and Biochemistry, Yale University, New Haven, CT 06520

⁴Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

Introduction

Dispersions of monodisperse spherical particles with effectively hard-sphere interactions are the simplest Complex Fluids. Indeed, one may hope to build understanding of more complicated soft matter on the behavior of hard-sphere colloidal dispersions. Here, we report that suspensions of polystyrene latex spheres in glycerol constitute a hard-sphere system.

In fact, PS spheres in glycerol are a prototypical colloidal system, for which the interactions – so-called Derjaguin-Landau-Verwey-Overbeek (DLVO) interactions, consisting of a screened electrostatic repulsion between charges at the spheres' surfaces plus a longer-ranged, attractive van der Waals component [1, 2] – are representative of a large class of colloids. Nevertheless, colloidal particles interacting via DLVO interactions are frequently taken to have effectively hard sphere interactions [3, 4]. This hypothesis has found recent support in elegant experiments, demonstrating that screened, charged polystyrene colloids behave according to the hard-sphere equation of state [5]. In Ref. [5], to mimic hard spheres, the screening was chosen so that the electrostatic repulsion counterbalances as far as possible the van der Waals attraction. Our SAXS measurements, described below, demonstrate that the interactions between PS spheres in glycerol are indistinguishable from those of hard spheres.

Methods and Materials

To prepare the samples, an aqueous suspension containing PS latex particles with a nominal radius of 71 nm was purchased from Duke Scientific. The relative standard deviation in radius was 0.025. Known weights of the as-received suspension were mixed with known weights of glycerol. Water was then removed by evaporation under vacuum, leaving the PS spheres suspended in glycerol. Samples were manufactured with nominal sphere volume fractions of $\phi = 0.027, 0.13, 0.28, 0.34, 0.49,$ and 0.52 . For the x-ray experiments, samples were mounted in an evacuated, temperature-controlled sample chamber.

The measurements were carried out at the SAXS station at beamline 8-ID at the Advanced Photon Source (APS). We employed x-rays of energy 7.66 keV produced by a 72-pole undulator. A silicon mirror and germanium monochromator selected a relative energy bandwidth of 3×10^{-4} full-width-at-half-maximum. Subsequently, a pair of precision 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. The resulting flux on the sample was $\sim 10^{10}$ photons per second. Scattered x-rays were detected 4.85 m further downstream using a CCD detector.

Results

The time- and circularly-averaged x-ray scattering cross-sections are displayed in Fig. 1 for wavevectors from $QR = 1$ to $QR = 10$ for each sample. At large wavevectors the shape of the scattering appears independent of volume fraction and shows intensity oscillations characteristic of uniform spheres. The solid line in Fig. 1 shows the best fit to the $\phi = 0.027$ -data of a model for the scattering of hard spheres with a volume fraction of 0.027 and a relative polydispersity in radius of 0.025 [6], convoluted with our experimental resolution. The sole fitting parameter was the mean particle radius, resulting in a best-fit value of 66.5 nm, in fair agreement with the manufacturer's value. The model provides a good description of the data for $QR < 3$. However, significant deviations from the theoretical form appear at the scattering minima. We ascribe the discrepancy to small departures of the latex particles from spherical symmetry. Similar behavior was observed in Ref. [7].

A pronounced peak develops near $QR \simeq 3.5$ as the volume fraction increases, corresponding to increasing interparticle correlations. This behavior is highlighted in Fig. 2, which shows as the open circles the structure factors, $S(Q)$, for each sample, obtained by dividing the measured scattering by the particle formfactor, for which we used the measured scattering from the $\phi = 0.027$ sample after applying a small correction for the structure factor. To make clear the behavior at small wavevectors, we illustrate these data on a logarithmic scale.

Discussion

The data of Fig. 2 are analogous to the liquid structure factor of an atomic fluid. The principle peak of the structure factor approaches $QR \simeq 3.5$ at large volume fractions, consistent with what may be expected for hard spheres. By contrast, particles with long-ranged Coulomb repulsions can be expected to exhibit a larger mean separation, so that the first peak of the structure factor occurs at smaller wavevectors, and to exhibit a greater degree of ordering at lower volume fractions. The dashed lines in Fig. 2 correspond to the model hard-sphere structure factor for particles with a mean radius of $R = 66.5$ nm and a polydispersity in radius of 0.025 [6], fitted to the measured structure factor, varying only the volume fraction for each data set.

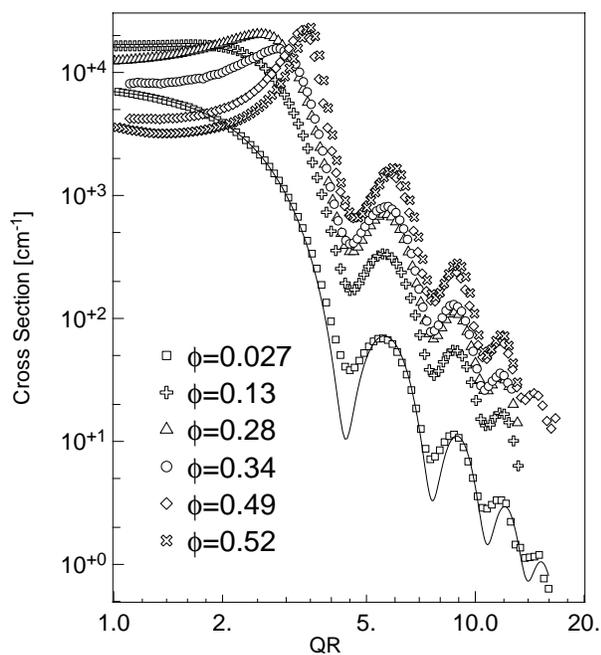


Figure 1: Cross-section for several different volume fractions of PS spheres in glycerol vs. QR .

Evidently, the model provides a good description of the experimental structure factors at all volume fractions, in particular reproducing the position of the principle peak accurately. Gratifyingly, the best-fit values for the volume fractions of the different samples are indistinguishable from the nominal volume fractions. It is, in addition, especially notable that the behavior of the measured structure factor at small wavevectors is reproduced well – within 10% – by the model. This informs us that the osmotic compressibility of PS spheres in glycerol is well described by the hard sphere equation of state [1]. We view the agreement between the model and measured structure factors at small wavevectors, as well as the agreement between the measured and predicted positions of the principal peak in the structure factor, as convincing evidence that PS spheres in glycerol manifest hard-sphere configurations.

Acknowledgements

8-ID was developed with support from the NSF Instrumentation for Materials Research Program (DMR 9312543), from the DOE Facilities Initiative Program (DE-FG02-96ER45593), and from NSERC. Work at MIT was also supported by the NSF MRSEC Program (DMR 9808941). D. L. acknowledges the JSEP for support. The APS is supported by the DOE under contract No. W-31-109-Eng-38. We thank Harold Gibson for his invaluable assistance.

References

[1] P. N. Pusey, *Liquids, freezing and the glass transition* (North-Holland, Amsterdam, 1991).

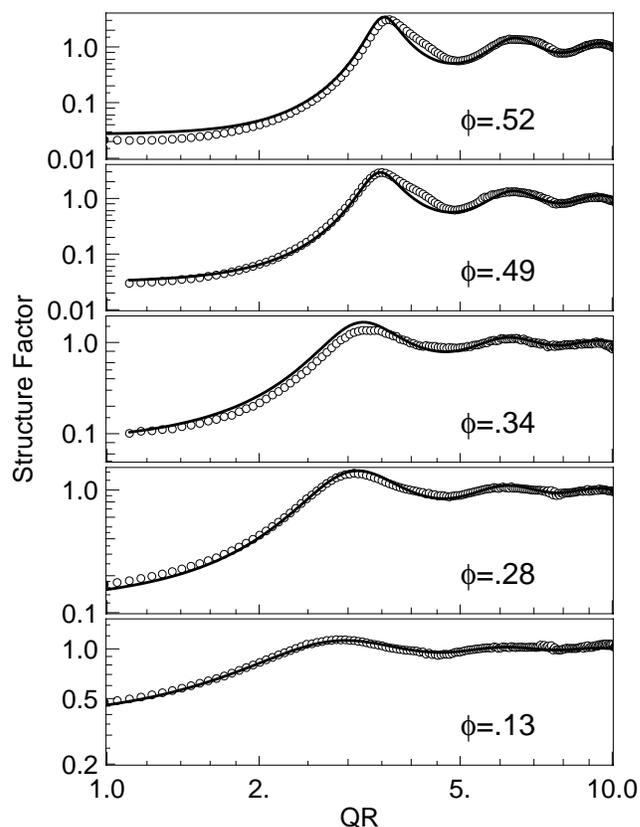


Figure 2: Measured and model structure factors, $S(Q)$, (circles and dashed lines, respectively) vs. QR for PS spheres in glycerol.

- [2] W. C. K. Poon and P. N. Pusey, in *Observation, Prediction, and Simulation of Phase Transitions in Complex Fluids*, edited by M. Baus (Kluwer, Dordrecht, 1995).
- [3] M. H. Kao, A. G. Yodh, and D. J. Pine, *Phys. Rev. Lett.* **70**, 242 (1993).
- [4] T. G. Mason and D. A. Weitz, *Phys. Rev. Lett.* **75**, 2770 (1995).
- [5] M. A. Rutgers, J. H. Dunsmuir, Z.-X. Xue, W. B. Russel, and P. M. Chaikin, *Phys. Rev. B* **53**, 5043 (1996).
- [6] W. L. Griffith, R. Triolo, and A. L. Compere, *Phys. Rev. A* **35**, 2200 (1987).
- [7] B. Chu, Y. Li, P. J. Harney, and F. Yeh, *Rev. Sci. Instru.* **64**, 1510 (1994).