Impact of the Excluded Volume Effect on the Dynamics of Binary Hard-Sphere Suspensions

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Introduction

X-ray photon correlation spectroscopy (XPCS) enables the range of length scales accessible by dynamic light scattering to be extended to smaller objects and dimensions. Using x-rays also allows one to study opaque materials. In a recent study on a suspension of monodisperse latex spheres of radius 710 Å,[1] which can be treated very well as hard spheres, the technique has been applied to a simple model system. It was found that the scaling behaviour reported in an earlier study on sterically stabilized hard spheres does not apply to charge-stabilized hard spheres and is, thus, not universal.

One of our goals at sector 8-ID is to extend such studies to more complicated systems. In this report we present first results of a study on a binary suspension of (mono-disperse) latex spheres of radii 1000 Å and 300 Å. An interesting aspect in this system is that, due to the excluded volume effect, there should be an attractive interaction between the large spheres, which is mediated by the small spheres. This effect results from an entropic term in the free energy and does not require additional direct interactions between the hard spheres. To the best of our knowledge, the impact of this effect on the dynamics of such a system has not yet been studied.

Methods and Materials

Latex spheres were purchased in form of aqueous suspensions. To slow down the dynamics, the water was replaced by glycerol by means of selective evaporation. Binary suspensions of spheres in glycerol were prepared in boro-silicate glass capillaries at various combinations of volume fractions, ranging from 0 to 30% of large and 20% of small spheres, respectively.

Coherent small-angle scattering experiments were conducted at 8-ID, where a Ge(111) channel-cut and a pair of 20 x 20 micron slits provide a coherent beam of about 109 photons per second. At a detector distance of 3008 mm, the speckle size corresponds to the CCD pixel size of 22.5 microns, and the theoretical scattering contrast on the CCD images was 22%. Scattering images were recorded every 20 ms and analyzed off-line. All experiments were conducted between –20 and –10°C.

Results

Figure 1 shows correlation functions obtained from different samples at various q-values. While the correlation functions of the single-component systems can be fitted well with single exponential decays, some of the binary systems seem to exhibit more than one characteristic times or their correlation functions look stretched.

At a volume fraction of large spheres of 10% and 20%, an increasing volume fraction of small spheres slows down the dynamics. In the first case (10% large spheres), the correlation functions look stretched or like a double-exponential when the volume fraction of small spheres equals the one of the large spheres (see the corresponding curves in Fig. 1). In the second case (20% large spheres), the dynamics in the case of equal volume fractions of large and small spheres was already too slow to be measured. Adding large spheres to any system of small spheres with volume fractions between 0 and 20% slows down the dynamics considerably (not shown here).

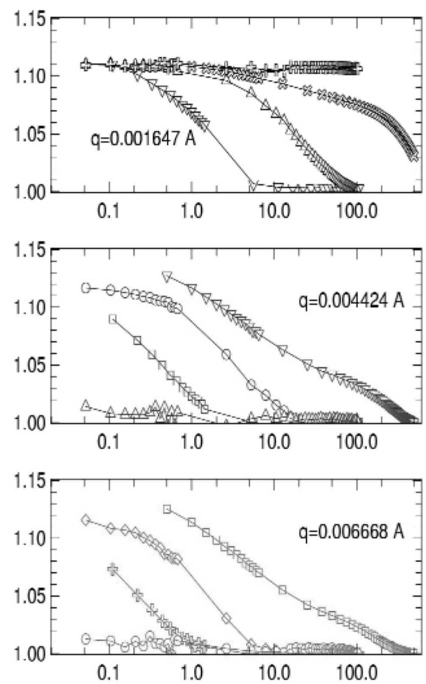

FIG. 1. Correlation functions of different samples at various momentum transfers q. The combinations of volume fractions of large and small spheres are: 0.1/0, 0.1/0.05, 0.1/0.1, and 0.1/0.2, starting from the fastest system.

Discussion

At very high volume-fractions (≥30%), the binary samples tend to become inhomogeneous on larger length scales. Ergodicity assumptions may then no longer be entirely justified in our experiments, which can render repeated measurements of the correlation functions inconsistent with each other. We observed this effect in some of the samples, regardless of whether the measurements were repeated in the same or a fresh region of the sample. However, e.g., in cases where there seem to be two characteristic time constants, mostly the amplitudes of the two signals with different characteristic times seem to change while the time constants are not necessarily altered. At this stage of the data analysis, a definite conclusion in that regard cannot be drawn. Attempts to refine the analysis and to also interpret the more complicated data sets are continuing.

One of the final goals of our studies is to relate the q-dependence of the characteristic times to the static structure factor which we obtained by integrating over all frames of an images time-series. In several cases a peak in $\tau(q)$ seems to mimic a peak in the structure factor (not shown). Further analysis is required to verify this first observation.

Acknowledgments

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 APS was also supported by the NSF MRSEC Program (DMR 9808941). Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. We thank H. Gibson for his valuable technical assistance.

Reference

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