Azimuthally Asymmetric Scattering from Suspensions of Rod-like Particles

M. A. Borthwick, P. Falus, L. B. Lurio, A. Rühm, D. Lumma, S. G. J. Mochrie*

Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, U.S.A.

**Present Address: Departments of Physics and Applied Physics, Yale University, New Haven, CT 06520.*

Introduction

Submicron-sized particles of boehmite (γ-AlOOH) manufactured with a rodlike shape offer the possibility of studying colloidal suspensions that closely resemble model systems of rigid, cylindrical particles in suspension.[1,2] Assuming the rods interact only via the "excluded volume" effect—the requirement that two rods cannot overlap—a transition from an isotropic phase to an orientationally-ordered nematic phase begins as the volume fraction of rods is increased beyond a certain value. The critical volume fraction, according to Onsager,[1] is given by $\phi=cD/L$, where D is the rod diameter and L its length, and c is found numerically to be 3.340. In the case where the rods possess an electrostatic charge, the equation is modified to $\phi=cD^2/(D_{eff}L)$, with D_{eff} an effective diameter resulting from the rods' mutual repulsion. This phase transition has been reported in aqueous suspensions of boehmite rods.[3]

In this report we describe small-angle x-ray scattering (SAXS) measurements of suspensions of boehmite rods in glycerol. Small-angle x-ray scattering permits observations of the ordering of not only the rods' centers of mass, but also of their axes' orientations. Our results qualitatively resemble those of recent SAXS studies[4] of aqueous suspensions of vanadium pentoxide "ribbons".

Methods and Materials

Aqueous suspensions of boehmite rods were obtained from the Debye Institute at Utrecht University. The rods' average length and diameter were 193.54 nm and 9.11 nm, with standard deviations 52.19 nm and 1.83 nm, respectively. Glycerol was added and the water evaporated to produce suspensions of boehmite in glycerol with nominal volume fractions 0.5%, 1.9%, and 5.6%. Samples of these suspensions were then loaded via syringe into 1-mm-diameter borosilicate glass capillary tubes for SAXS measurements. The measurements were performed at beamline 8-ID at the Advanced Photon Source using the apparatus described in ref. 5.

Results

Time-averaged CCD images of the scattered x-ray intensity are shown in Figs. 1 and 2. The vertical axis of these images runs roughly parallel to the long axis of the capillary as held in the beam. The 0.5% volume fraction sample produced an azimuthally symmetric scattering pattern (Fig. 1), as did the 1.9% sample. In contrast, the scattering from the 5.6% sample (Fig. 2) exhibited a striking asymmetry. The use of an area detector allowed for simultaneous determinations of scattering intensities at different points (angles, φ) around a ring of fixed Q and thus provided a quantitative measure of the asymmetry. Some examples from these data are shown in Fig. 3, where the zero angle was chosen to be along the horizontal axis of the CCD image.

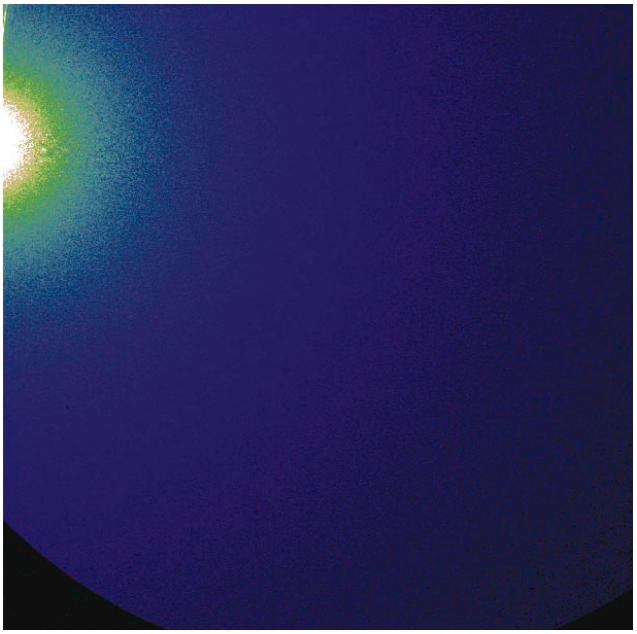

FIG. 1. Time-averaged CCD image of scattering from the 0.5% volume fraction suspension of boehmite in glycerol. The direct beam was located just off the left edge of the image, near the bright spot. Black areas in the image correspond to unilluminated regions of the detector.

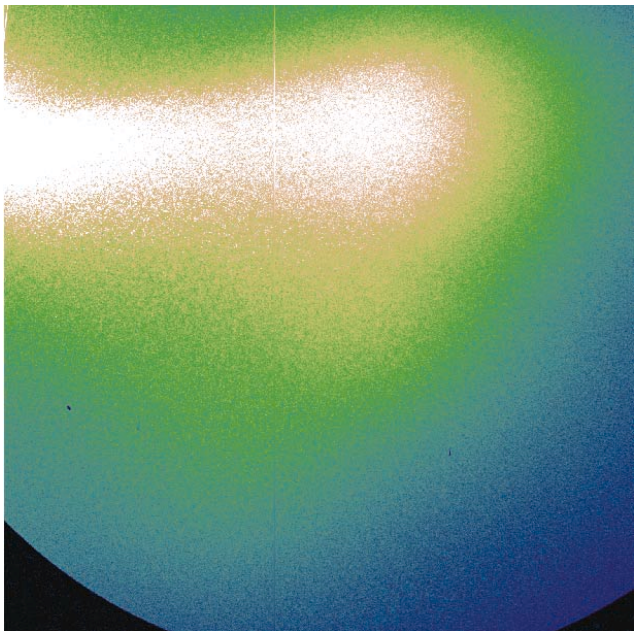

FIG. 2. CCD image of scattering from the 5.6% volume fraction sample.

Radial scattering cross section (Σ(Q)) curves of the sort typically constructed from SAXS data were analyzed as well. The cross sections, normalized by volume fraction, are plotted in Fig. 4. Data along a single φ-value suffice for the two azimuthally uni-

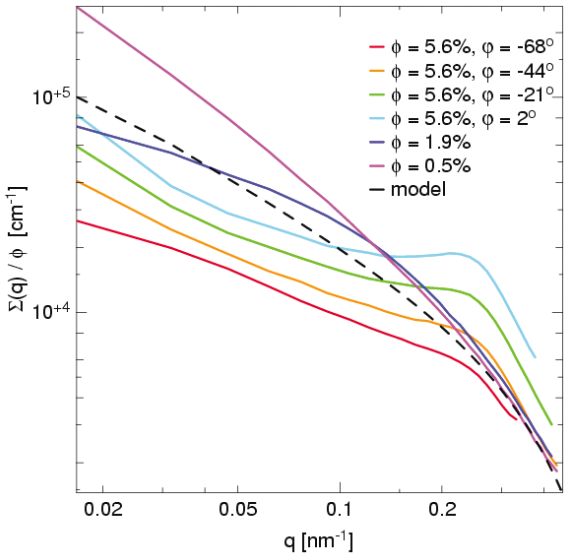

FIG. 3. Azimuthal dependence of the scattering cross section at Q = 0.05 nm^{-1}. The zero of azimuthal angle is along the horizontal in Figs. 1 and 2.

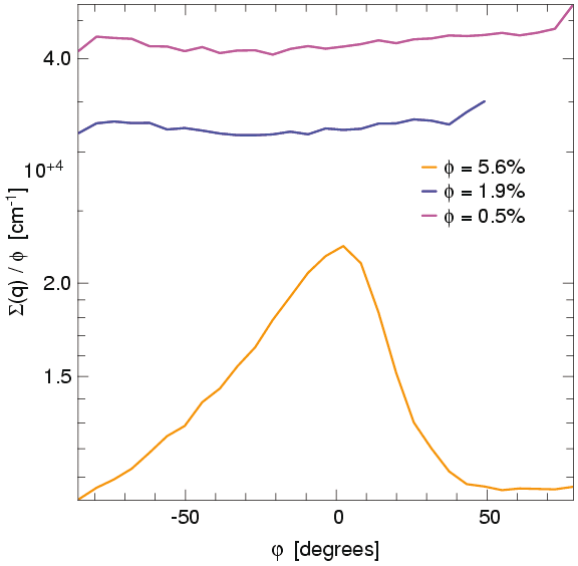

FIG. 4. Scattering along the radial direction for various volume fractions and azimuthal angles. The model curve corresponds to a dilute suspension of noninteracting, monodisperse rods.

form samples, while four such curves are shown for the third sample. These are compared to the predicted scattering from a dilute suspension of randomly-oriented, noninteracting, rigid cylinders[6] of length 193.5 nm and diameter 9.1 nm, given an electron density difference of 1.2 times the electron density of glycerol.

Discussion

The asymmetry in the 5.6% volume fraction sample clearly indicates some orientational ordering of the rods at this concentration. This result is consistent with polarized-light microscopy studies of all three samples, which revealed birefringence in only the 5.6% sample. Since its scattering is most intense along the horizontal direction of the image, we infer that the rods were aligned parallel to the capillary in this sample.

That alignment occured at such a low volume fraction compared to the Onsager value of 15.7% suggests either that (a) the charge on the rods leads to an effective diameter of 25 nm or greater; or that (b) flowing into the capillary oriented the rods and the highly-viscous suspension remained in a nonequilibrium state; or perhaps both of the above. Option (a) is supported by another interesting feature of the scattering: the deviation of all of the normalized Σ(Q) from the model cross section for Q below ~ 0.03 nm^{-1}. This can be contrasted to hard-sphere systems, where the single-particle cross section for spheres agrees with measured Σ(Q) values even at volume fractions above 2%.[7] The convergence of the normalized Σ(Q) at higher Q confirms that the physical diameter of the rods is ~10 nm, and the azimuthal symmetry in the scattering at low volume fractions implies that any longer length-scale ordering at these concentrations is not merely due to excluded volume effects.

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 MIT 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, Office of Science, Office of Basic Energy Sciences under Contract No. W-31-109-ENG-38. We thank Harold Gibson for his invaluable assistance.

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