

# Two-dimensional Interparticle Structure Factor Measurements of Orientationally Ordered Systems

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## Introduction

Submicrometer-size particles of boehmite ( $\gamma$ -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]. In a previous activity report [3], we described the onset of orientational ordering with increasing volume fraction of these rods in glycerol.

In this report, we discuss small-angle x-ray scattering (SAXS) measurements on a series of such suspensions. Specifically, we have used the 2-D scattering information provided by a charged-coupled device (CCD) detector to determine the interparticle structure factor as a function of both the magnitude and direction of the scattering vector simultaneously. This enables directly exploring the connection, if any, between positional and orientational ordering of the rods.

## Methods and Materials

The materials and preparation procedures are detailed in a previous activity report [3]. For this study, samples with volume fractions ranging from 0.2% to 7.5% were prepared.

In any system of identical particles, the measured x-ray scattering intensity can be treated as the product of a single particle's form factor (averaged over the orientations present in the sample) and a structure factor arising from correlations among interparticle separations. The azimuthal dependence of the interparticle structure factor can be obtained immediately from the azimuthal dependence of the scattering, and, from that, the orientational order parameter can be calculated [4-6].

The radial dependence of the structure factor is not so simple, especially for polydisperse rods. However, the assumption that the structure factor in very dilute suspensions is constant vs.  $q$  allows for the use of dilute-suspension scattering as an approximate form factor. Indeed, the magnitude of the measured dilute-suspension scattering agrees with the magnitude of the analytical form factor for monodisperse rods of the size and density of these boehmite rods. Polydispersity effects can be accounted for simply by dividing the measured scattering by the measured dilute-sample scattering rather than an

analytic form factor. This yields the interparticle structure factor in both the radial and azimuthal directions.

## Results

An example of the measured 2-D interparticle structure factor  $S(\mathbf{q})$  is shown in Fig. 1. Insofar as the maximum of  $S$  occurs at approximately the same value of  $q$  for all azimuthal angles, we can treat the azimuthal and radial dependences separately.

The radial dependence  $S(q)$  is shown in Fig. 2. In the absence of a simple analytic form to fit these data, a plot of the peak position in  $q$  versus volume fraction is shown in Fig. 3. The peak position scales as volume fraction to the  $1/3$  power. There is no clear dependence of the peak width with volume fraction.

The azimuthal dependence  $S(\varphi)$  is shown in Fig. 4. Rods oriented along the capillary scatter along  $\varphi = 0$ , and those perpendicular to the capillary scatter along  $\varphi = 90^\circ$ . In some cases, it appears the x-ray beam was probing

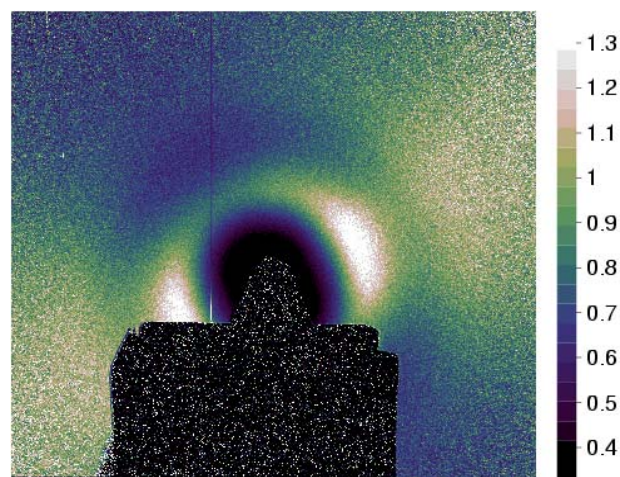


FIG. 1. Measured interparticle structure factor for 2.5% boehmite in glycerol. The 2.5% sample's scattering was divided by the 0.2% sample's scattering to produce this image. Transmitted beam position is near the tip of the beam stop, which is the black region in the lower half of the image.

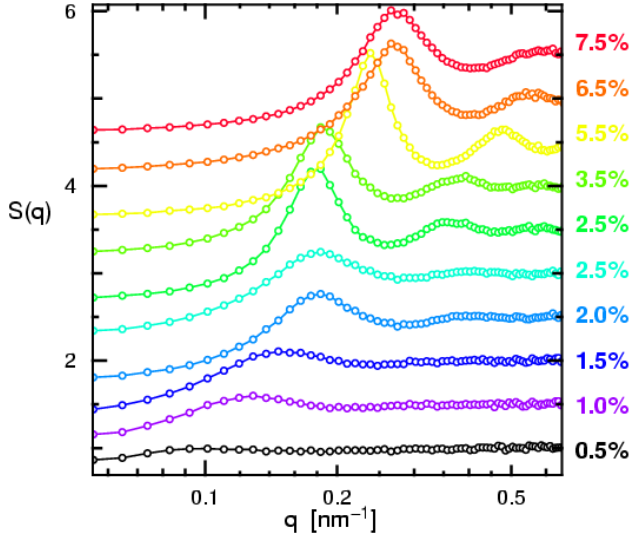


FIG. 2. Radial dependence of interparticle structure factor over a series of volume fractions. In this figure, each  $S(q)$  has been scaled to 1 at large  $q$  and then offset by a constant to minimize overlap. Lines are a guide for the eye.

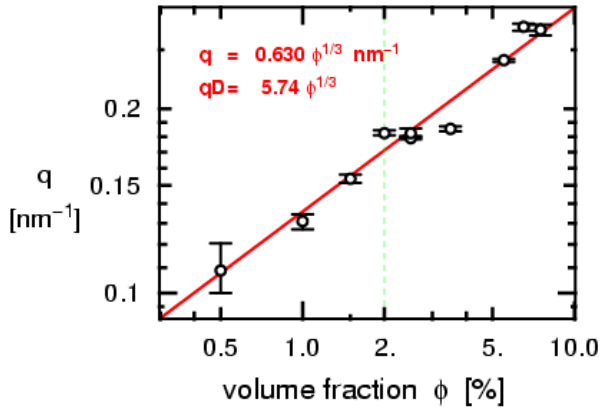


FIG. 3. Volume fraction dependence of the  $q$ -value of the first peak in  $S(q)$ . Error bars represent the variation of the peak position over the full range of azimuthal angles. The green dashed line signifies the transition from isotropic to nematic (see Fig. 4.).

multiple nematic domains in the sample at once, which is not unexpected given that no orienting field was applied during measurement. The rods appear predominantly aligned along the capillary at volume fractions near the isotropic/nematic transition but perpendicular to the capillary at higher volume fractions.

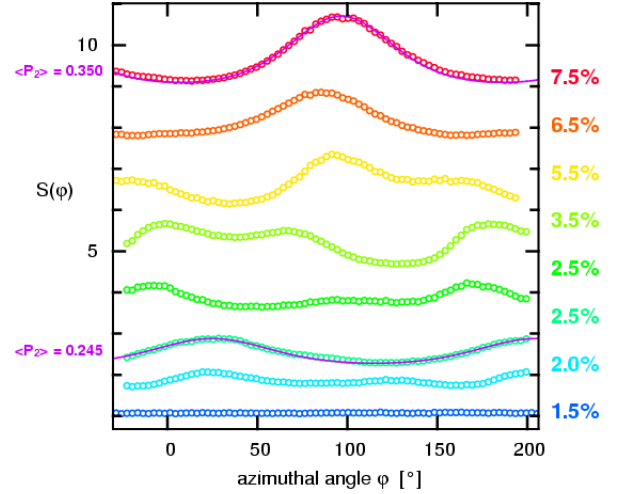


FIG. 4. Azimuthal dependence of interparticle structure factor over a series of volume fractions. In this figure, each  $S(f)$  has been offset by a constant to minimize overlap. Purple lines are a fit using a Maier-Saupe-form orientational distribution function [6], and the orientational order parameter  $\langle P_2 \rangle$  is given alongside.

## Discussion

The above results stand in stark contrast to those found in dilute aqueous suspensions of charged rodlike virus and DNA particles [7-9]. In those studies, all done in the isotropic phase, the  $q$  value of the structure factor peak was seen to vary as  $\phi^{1/3}$  below the overlap concentration  $\phi^*$  ( $\phi^* \approx 0.7\%$  for our rods) and as  $\phi^{1/2}$  above  $\phi^*$ . The structure factor peak exhibited the same dependence [9]. In our samples, the  $1/3$  exponent persists well above the overlap concentration ( $\phi^* \approx 0.7\%$  for our rods) and even into the orientationally ordered phase. We also find no  $\phi^{1/3}$ - or  $\phi^{1/2}$ -dependence of the peak width.

In addition, the coefficient of our peak-position fit is significantly larger than that expected for charged rods. Using the form  $2\pi\beta(\phi/\phi^*)^{1/3}/L$  for the peak position (the rod length  $L$  being 193.5 nm on average in this case) gives results of  $\beta = 3.70$ , much greater than the values of  $\beta = 0.58$  or  $\beta = 0.93$  that would be expected for charged rods in a regularly spaced cubic or hexagonal array, respectively [8].

Alternatively, when compared with the distance of the closest possible approach for two sterically separated rods (the diameter  $D$  being 9.1 nm on average here), our data indicate that the peak position goes as  $2\pi\beta_D\phi^{1/3}/D$ , with  $\beta_D = 0.914$ . From this, we might surmise that these suspensions, unlike those in Ref. 7 and 8, pack similarly to suspensions of ideal point charges at any volume fraction where steric repulsions can be accommodated by rod reorientation.

The onset of rod alignment seems to change the behavior of correlations among the rod positions little, if at all. More likely, the reverse holds; i.e., by maximizing their spacing, the rods' orientational entropy is maximized, especially above  $\phi^*$ . As this maximum spacing varies inversely with the volume fraction, so varies the range of orientations available to the rods.

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