Dynamics of Semidilute Suspensions of Rigid Rods Measured by X-ray Photon Correlation Spectroscopy

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Introduction

Dynamic light scattering (DLS) has been used extensively to study rodlike viruses and polymers in dilute and semidilute suspensions [1-7]. Nevertheless, unresolved issues remain regarding the roles of translational and rotational diffusion in the transport properties of these materials [1, 7]. As the rod concentration increases into the semidilute regime, entanglements between neighboring rods become increasingly important. This tends to strongly hinder diffusion perpendicular to a rod's axis, and a coupling between parallel translation and rotation arises. In semidilute suspensions, techniques such as transient electric birefringence [7], depolarized dynamic light scattering [8], and fluorescence photobleaching recovery [9] together serve to decouple the translational and rotational contributions to diffusion, but none is capable of probing diffusion on the small length scales at which these coupling effects are strongest.

X-ray photon correlation spectroscopy (XPCS), which is the extension of DLS to subnanometer wavelengths [10], is ideally suited for investigations of slow dynamics in colloidal suspensions with length scales well below the colloidal particle size [11]. This report describes XPCS measurements on a semidilute suspension of particles of boehmite (γ-AlOOH) manufactured to be nearly cylindrical in shape [12]. In colloidal suspensions, these particles can be expected to closely resemble model systems of rigid, rodlike particles in suspension. Despite the relatively low x-ray scattering cross sections we have encountered when dealing with dilute and semidilute suspensions, we have been able to easily cover the scattering vectors accessible to typical DLS experiments and further probe to length scales that are shorter by a factor of more than four.

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 of 52.19 nm and 1.83 nm, respectively. Glycerol was added and the water was evaporated to produce a suspension of boehmite in glycerol with 1.5% volume fraction. For XPCS measurements, small quantities of this viscous suspension were placed at the open end of 0.7-mm-diameter borosilicate glass capillary tubes and then centrifuged in order to load the material into the tubes. The open tube end was later sealed via heating. Polarized light microscopy was used to verify that the suspensions exhibited no nematic ordering.

Details of the XPCS apparatus used at beamline 8-ID at the APS are thoroughly outlined in Refs. 11 and 13. For this measurement, a 25×25-μm^2 beam of 1.5×10^9 photons/second at 7.65 keV was incident upon the sample in a transmission geometry. A direct-detection charge-coupled device (CCD) situated 2.8 m downstream of the sample was operated in "kinetics mode" [13], with seven kinetics slices per frame.

The measured quantity in XPCS is the normalized intensity time-autocorrelation function

$$g_2(q, \Delta t) = \frac{\langle I(q,t)I(q,t+\Delta t)\rangle}{\langle I(q,t)\rangle^2},$$

where I is the intensity on a CCD pixel at a given scattering vector q. Use of an area detector allowed us to average together multiple correlation functions from pixels at similar q values, in order to improve the signal-to-noise ratio. To obtain a range of Δt values that was as wide as possible, the results of several sequences of 100-, 300-, and 500-millisecond (ms) exposures were also averaged together.

To further slow the sample dynamics and thereby increase the accessible q-range of the measurement, the samples were held in the beam at a temperature of -5°C.

Results

Some typical examples of correlation functions are shown in Fig. 1. As expected, the data clearly do not exhibit the sort of single-exponential decay expected for the diffusion noninteracting spherical particles. Rather, they are well-described by a double-exponential fit of the form

$$g_2(q, \Delta t) = 1 + \left[S_0(q)e^{-\Gamma_0(q)t} + S_1(q)e^{-\Gamma_1(q)t}\right]^2$$

which includes the two lowest-order terms in a commonly used theory of Pecora [14] for rod diffusion at low to moderate q. The theory stipulates that $\Gamma_0(q) = D_T q^2$ and $\Gamma_1(q) = D_T q^2 + 6D_R$, with D_R being the rotational diffusion coefficient and D_T the isotropically averaged translational diffusion coefficient.
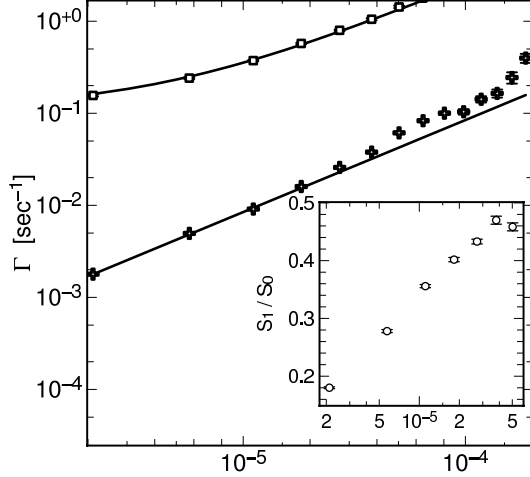
FIG 1. Measured correlation functions for 1.5% boehmite by volume in glycerol, at several representative scattering vectors. Lines are a double-exponential fit to the data.

FIG 2. Fitted autocorrelation decay coefficients versus scattering vector squared. The slower mode (Γ_0, crosses) is fitted to $D_T q^2$ at low q, while the faster mode (Γ_1, squares) is fitted to the form $D_T q^2 + 6D_R$. The inset shows the amplitude of the fast mode relative to the slow mode at Γ_0(q) values where both could be measured.

Least-squares fits to $\Gamma_1(q)$ and $\Gamma_0(q)$ in the double-exponential form are shown in Fig. 2, along with the amplitude ratio, S_1/S_0. Fitted values for the diffusion coefficients were as follows: from $\Gamma_0(q)$, $D_T = 8.4$ nm^2/s; and from $\Gamma_1(q)$, $D_T = 240$ nm^2/s and $D_R = 0.018$ s^{-1}. In general, the modes tended to merge as the scattering vector was increased, and thus the overall decay profile became more like a single exponential at high q.

Discussion

A far more complicated but more generally applicable theory of rod diffusion was developed by Maeda [15]. It combines the Pecora formalism with Doi, Shimada, and Okano's [16] mean-field, random-phase treatment of rod-rod interactions. Maeda's theory is better suited for use at high q, since it includes a computationally efficient treatment of the higher-order decay modes expected to dominate at shorter length scales. A fit to Maeda's form yielded $D_T = 10.3$ nm^2/s and $D_R = 0.023$ s^{-1}.

The two analysis techniques above agreed well, except for the translational diffusion coefficient as determined from the faster of the two modes in the double-exponential fits. Its value should theoretically be identical to that found for the slow mode. One possibility is that the slowest two modes effectively merge at high q, becoming indistinguishable. Then, what appears to be an increase in $\Gamma_1(q)$ with q would instead indicate the appearance of a third, still faster decay mode, $\Gamma_2(q)$. Indeed, the Pecora theory predicts that S_1/S_0 displays a maximum at approximately $qL = 9$ [17], while the fitted S_1/S_0 (Fig. 2 inset) seems to increase steadily through $qL = 12$.

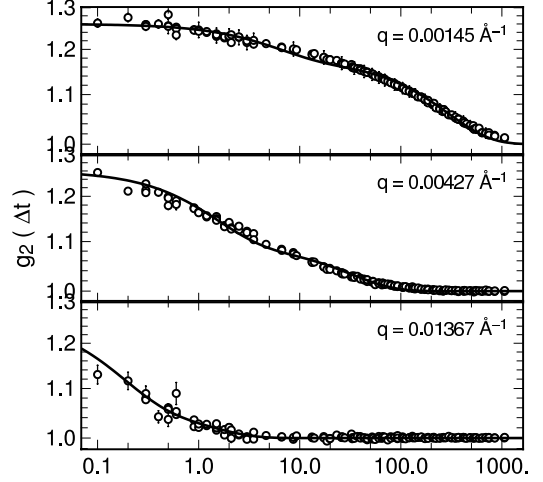Another interesting feature of the double-exponential fit results is the departure of $\Gamma_0(q)$ from a q^2 dependence at higher scattering vectors. Deviations of this sort have been seen with DLS in a wide variety of systems [4, 6, 7, 8, 18]. At volume fractions comparable to those of our samples, rotation is not entirely hindered by entanglement, and the deviation tends to be positive [1]. Typically these deviations are seen in first cumulant decay rates, which for the results above, are qualitatively similar to the slow mode in Fig. 2. Recently, Phalakornkul et al. [7] developed an expansion of $\Gamma(q)$ that includes q^4 and q^6 terms. The high-q data shown in Fig. 2 demonstrate not one but two inflection points in $\Gamma_0(q)$, indicating that perhaps even an eighth-order expansion is necessary to accurately model diffusion at large scattering vectors.

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