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Rotational diffusion in concentrated platelet systems measured with X-ray photon correlation spectroscopy

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Using X-ray photon correlation spectroscopy we have measured the rotational modes of concentrated charged gibbsite platelets in the isotropic regime. This has been done by analyzing the data qualitatively using available theories for non-interacting systems. The relaxation spectra do not follow the same pattern as for spherical particles at larger wave vectors. It will be shown that this deviation from the behavior of spherical systems arises from the influence of the rotational modes. In addition, in the isotropic state a pre-translational peak in the static q -dependent intensity at large q values is discussed. We suggest that this peak originates from a strong local alignment between platelets before the actual phase transition takes place. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818532>]

INTRODUCTION

Colloidal particles are frequently used in industrial applications as, for example, thickeners, fillers, or stabilizers. One of the more commonly used colloidal particle systems are various types of natural clay¹ due to their specific transport properties and abundant availability. In nature, clays can be found in river, lake, and ocean sediments and their dispersion properties are, therefore, of large interest. In addition, the specific anisotropic nature of clays makes them responsible for many landslides.² In industry, clays can be found in suspensions of paint and drilling fluids and are also used for surface coatings.^{3,4} It is the anisotropic shape and the corresponding anisotropic interaction that is one of the basic reasons for most industrial applications but also for the effects found in nature.⁵ In order to understand the underlying physical processes of clay suspensions, the dynamic properties both in dilute as well as in concentrated suspensions need to be investigated. Unfortunately, natural clays are very complex due to their large polydispersity in size, shape, and composition, which makes them difficult to investigate. Instead plate-like particles, such as gibbsite platelets, can be used in order to mimic clay suspensions. Even with this kind of simplified model system the experimental and theoretical investigations as well as simulations are difficult, in general.⁶ Even more difficult are the investigations of higher concentrated suspensions and of the dynamic properties, in general, in anisotropic systems. Apart from the lack of theoretical framework, experimental difficulties arise from the two very different length scales, due to the anisotropic shape of the particles, and the turbidity of the samples. In dilute systems, many of these problems can be experimentally solved. Theoretical predictions for both dynamic and static properties have been derived

and experimentally tested in dilute systems.^{7,8} For concentrated suspensions of these optically opaque systems, x-ray scattering techniques are a very useful tool due to the high penetration depth of x-rays into the material. Not only are the particles almost unaffected by x-rays, since they are inorganic compounds, but Small Angle X-ray Scattering (SAXS) can also probe a large wave vector, q , range to cover both length scales, i.e., the radius and the thickness, of platelet systems.⁹ Utilizing partially coherent x-rays, X-ray Photon Correlation Spectroscopy (XPCS),^{10,11} the equivalent of dynamic light scattering (DLS), can be used to investigate the dynamics of these systems at high concentrations over a relative large q range. However, such an investigation of the dynamical behavior will have to be mostly phenomenological with comparison to low concentration systems since no theoretical predictions or simulations on the effect on the q or concentration behavior of platelet systems can be found at this time.

In a recent paper a rotational-translational decoupling approximation^{12,13} was used for the analysis of the static q dependent intensity, $I(q)$.⁷ This approximation is based on the assumption that particle shape, orientation, and size polydispersity affect only the form amplitudes^{14–16} which are related to the measurable form factor,⁷ while excluding anisotropic interaction effects. This approximation allows the decoupling of the form and structure factor even though the particles are anisotropic. At higher concentrations, still in the isotropic phase, this model should be less accurate. Even so, due to the simplicity of the model and the possibilities it gives to access the static structure factor, $S(q)$, from the static scattered intensity it can be very useful even at higher concentrations. A similar approach was adapted for the dynamic properties where the platelets were approximated as uniformly charged spheres using a modified version for charged particles of the self-part corrected $\delta\gamma$ approximation of Beenakker and Mazur^{17,18} to access the short-time diffusion function $D(q)$. The input parameter for the otherwise parameter-free $\delta\gamma$ approximation is

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$S(q)$ and it is, therefore, very useful to be able to extract $S(q)$ from the static measurements. The theoretical determination of $S(q)$ and $D(q)$, approximating platelets as spheres, was successfully applied at lower concentrations⁷ and will be used here, with the understanding of its limitation, to get a better insight in the dynamic properties of highly concentrated platelet systems.

Another factor that is of interest in anisotropic systems, which also complicates the analysis, is the rotational contribution to the relaxation spectra when measuring intensity auto-correlation functions, $g_2(q, t)$. If the particles have an anisotropic polarizability, the rotational mode can be reliably determined in a DLS experiment in vertical-horizontal (VH) scattering geometry, where it is possible to still have enough counting statistics. On the other hand, even in non-polarized measurements, the rotational relaxation mode of the anisotropic particles influences $g_2(q, t)$ if q is large enough.⁸ For dilute platelets, the field auto-correlation function, $g_1(q, t)$, was derived in Ref 8. For non-interacting, low concentrated platelet suspensions $g_1(q, t)$ are then related to the experimentally accessible intensity auto-correlation function $g_2(q, t)$ through the Siegert relation. A similar expression for $g_1(q, t)$ has not been derived for interacting, highly concentrated platelet systems. Even so, the rotational modes in this expression for interacting systems should also be present, their amplitudes in the dynamic form factor for platelets, $g_{1,\text{plat}}(q, t)$, should change since the intensity due to the particle orientation no longer can be simply averaged due to interactions. Moreover, the diffusion coefficients are interpreted as “effective diffusion coefficients” which are likewise determined by interactions between platelets. We will, therefore, use this expression in a qualitative way to analyze the dynamic data.

In this paper we will discuss the dynamics probed by XPCS measurements over a large q range in the isotropic regime of two concentrated platelet systems with two different particle radii. We will show by our analysis that the rotational diffusion can be measured with XPCS at higher q . In addition, the corresponding static scattering intensity will add information to the analysis of the system.

EXPERIMENTAL

Two aqueous suspensions, with 10^{-4} M NaCl added, of hexagonal charged colloidal gibbsite [γ -Al(OH)₃] platelets with mean radius $r_A = 110 \pm 20$ nm (sample A) and $r_B = 60 \pm 12$ nm (sample B) and an average thickness $l_A = 10.0 \pm 0.5$ nm and $l_B = 4.5 \pm 0.5$ nm are investigated. Colloidal gibbsite platelets were synthesized according to the standard procedure described by Wierenga *et al.*¹⁹ We have determined the radius and height distributions from transmission electron microscopy (TEM) pictures, and by atomic force microscopy, respectively. An exemplary TEM picture of gibbsite platelets, sample A, used in this study is shown in Fig. 1. The volume fraction of sample A is $\phi_A = 0.092$ and of sample B $\phi_B = 0.062$. Their respective liquid to liquid crystal,^{20,21} L-LC, transition is at $\phi_{A,LLC} = 0.15$ for sample A and at $\phi_{B,LLC} = 0.071$ for sample B.

FIG. 1. TEM picture of gibbsite platelets of sample A with mean radius $r_A = 110$ nm and average thickness $l_A = 10.0$ nm.

The mean aspect ratio of the platelets, $p_{A,B} = l_{A,B}/2r_{A,B} = 0.091$ and 0.075 , respectively, is so small that the ultrathin disk limit ($p \rightarrow 0$) can be applied as a reasonable approximation. In this limit, one obtains the translational diffusion coefficient for the orientationally averaged single-disk:^{22,23}

$$D_t^0 = (D_t^{0,\parallel} + 2D_t^{0,\perp})/3 = k_B T / (12\eta_0 r), \quad (1)$$

and for the (end-over-end tumbling) rotational diffusion coefficient

$$D_r^{0,\perp} = 3k_B T / (32\eta_0 r^3). \quad (2)$$

Here, k_B is the Boltzmann constant, T is the absolute temperature, and η_0 is the solvent shear-viscosity. This gives the translational diffusion coefficient for these systems as $D_{t,A}^0 = 3.1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $D_{t,B}^0 = 5.6 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and rotational diffusion coefficient as $D_{r,A}^0 = 284 \text{ s}^{-1}$ and $D_{r,B}^0 = 1752 \text{ s}^{-1}$. For $p \rightarrow 0$, $D_r^{0,\perp}$ becomes equal to the rotational diffusion coefficient, $D_r^{0,\parallel}$, which characterizes rotation with respect to the platelet rotational symmetry axis. A small but finite value of p lowers somewhat the values of D_t^0 and $D_r^{0,\perp}$, and $D_r^{0,\perp}$ and $D_r^{0,\parallel}$ start to differ from each other. Tirado and García de la Torre^{24,25} provide precise polynomial fits to their simulation data for the diffusion coefficients of cylindrical platelets as a function of p . However, the aspect ratio range, $p > 0.1$, covered by most of these fits, does not include the small aspect ratio of the gibbsite platelets used in this study.

The static and dynamic behavior of the colloidal systems has been investigated using x-ray scattering techniques. The static behavior has been measured by SAXS experiments. To be able to probe the dynamics of the colloidal systems as well, the x-ray scattering experiments have been performed using partially coherent x-rays. If coherent photons are scattered by disordered samples, a typical interference (speckle) pattern is created. As changes in the sample lead to changes of the speckle pattern, this allows the analysis of the underlying sample dynamics using XPCS.^{10,11} In an XPCS experiment, the dynamics of a sample is analyzed by means of the normalized intensity autocorrelation function, $g_2(q, t)$, at a given

momentum transfer q :²⁶

$$g_2(q, t) = \frac{\langle I(q, 0)I(q, t) \rangle}{\langle I(q) \rangle^2}, \quad (3)$$

where the brackets, $\langle \rangle$, denote a time average, $I(q, 0)$ denotes the intensity at time zero, and $I(q, t)$ denotes the intensity at a delay time t later. For Gaussian statistics of the scatterers in a homodyne detection scheme $g_2(q, t)$ is related to the field correlation function $g_1(q, t)$ by the Siegert relation $g_2(q, t) = 1 + \beta |g_1(q, t)|^2$, where β is the experimental factor.

The x-ray scattering experiments were performed at the Coherence beamline P10 at PETRA III. The photon energy was set to $E_{ph} = 7.9$ keV, corresponding to a wavelength $\lambda = 1.57$ Å. An x-ray beam of $150 \times 75 \mu\text{m}^2$ (V $\times$ H) was focused by a set of compound refractive lenses to a beamsize of $\sim 5 \times 5 \mu\text{m}^2$ (V $\times$ H) on the sample. The experiments were carried out in Small Angle X-ray Scattering geometry. Two detectors, a Pilatus 300 K detector for the static, time averaged experiments and an avalanche photo diode (APD) for recording fast intensity fluctuations, were placed at a distance of ~ 5 m downstream of the sample position. The incident beam intensity on the sample was monitored using a Cyberstar X2000 scintillation detector, which detects the diffuse scattering of a 25 μm thick polyimide foil (Kapton, DuPont) perpendicular to the beam direction.

To be able to minimize intensity fluctuations arising from the incident beam, a cross-correlation scheme was used where the intensities of the monitor detector and the APD have been cross-correlated.

RESULTS AND DISCUSSION

Static behavior

The static (time-averaged) scattering intensity of the two platelet systems was measured with a 2D-detector. By azimuthally averaging the isotropic 2D-scattering patterns the q dependent scattered intensity, $I(q)$, was extracted which is displayed in Fig. 2(a) for sample A and in Fig. 2(b) for sample B.

No structure peak, related to the average center to center distance in an isotropic solution, is visible at low q 's for any of the samples which would be expected around $q = 0.05 \text{ nm}^{-1}$. Since it was observed in Refs. 21 and 27 for similar systems, this is most likely caused by the present setup which was not optimized for static measurements at low q 's. At higher q 's a clear peak can be seen for sample B. This peak is similar to the one reported in Ref. 21, and is not visible for sample A. The solid lines in Fig. 2 are fits of a polydisperse form factor of randomly orientated platelets with a thickness of 10.0 ± 0.50 nm and 4.5 ± 0.50 nm and a mean radius of 110 ± 20 and 60 ± 12 nm, respectively, for sample A and B. The simple analytic expression for the dimensionless form amplitude of the form factor is given in the literature^{14–16} and the polydispersity was added the same way as in Ref. 7. The decoupling approximation,^{12,13} where the form and structure factor can be decoupled even though the particles are anisotropic, used in previous work⁷ could not be applied here since no structure peak at lower q 's is visible. It is necessary to have

FIG. 2. $I(q)$ as a function of q for (a) sample A and (b) sample B. The solid lines are fits to $P(q)$ of platelets with mean radius $r_A = 110 \pm 20$ nm and thickness $l_A = 10.0 \pm 0.5$ nm for (a) and $r_B = 60 \pm 12$ nm and $l_B = 4.5 \pm 0.5$ nm for (b).

the peak in $S(q)$, $S(q_{\max})$, in the experimental scattering data, otherwise the fit will be arbitrary without additional input parameters since $S(q_{\max})$ is strongly depending on both the concentration and the interaction in the system. In addition, the decoupling approximation should be less accurate at these high platelet concentrations, whereas anisotropic interaction effects are more likely to have a significant influence. We note, however, that the experimental data at these high concentrations are consistent with the decoupling approximation at high q 's in that $I(q) \sim P(q)$. This makes fitting with only the form factor at high q 's a good approximation as is visible in Fig. 2. The peak around $q = 0.17 \text{ nm}^{-1}$ in sample B cannot be accounted for by the form factor or a structure factor assuming an effective spherical shape of the platelets. Still this peak has all the characteristics of a structure peak. To emphasize the nature of this peak, we divide the experimental $I(q)$ by the fitted form factor, the result can be seen in Fig. 3.

In principle, this is not stringent correct, however it helps to visualize the peak. The result resembles strongly a structure factor peak but appears at too large q values to be the center-to-center distance of the particles. Instead, this peak is located at a much smaller length scale of about 36 nm, which

FIG. 3. $I(q)/P(q)$ as a function of q for sample A (red dashed line) and sample B (black solid line).

is very close to the thickness of the platelets plus the Debye screening length, $\kappa^{-1} \approx 24$ nm when including the counterions of the platelets. We interpret this finding as a local pre-ordering in the vicinity of the L-LC transition in the isotropic regime since the 2D-scattering pattern is isotropic and no birefringence between cross polarizers or any non-ergodicity in the XPCS measurements could be seen. In addition, for the more diluted sample A, no such peak is visible (red dashed line in Fig. 3), which strengthens the assumption that this is a pre-transitional effect. By comparing the relative concentration with respect to the L-LC transition, $\phi_{\text{rel}} = \phi/\phi_{\text{LLC}}$, which is for sample A $\phi_{\text{A,rel}} = 0.61$ and for sample B $\phi_{\text{B,rel}} = 0.87$, it is obvious that sample B, which shows a pronounced peak, is much closer to the L-LC transition than sample A. In comparison, ϕ_{rel} is 0.8 in Ref. 21 where a similar peak is found showing that ϕ_{rel} needs to be at least 0.8 for this peak to appear supporting the claim that this is a pre-transitional effect. To our knowledge, no theory or simulations have addressed or shown similar behavior.

Dynamic behavior

In order to investigate the dynamics of these systems and to cover both length scales of the anisotropic colloidal particles, we performed XPCS experiments. Several intensity autocorrelation functions, $g_2(q, t)$, at different q 's are shown in Fig. 4 for sample A.

The correlation functions are truncated at about 4 ms due to the large noise level arising from periodic fluctuations of the beam intensity caused by the periodic bunch spacing of the synchrotron ring. This makes the analysis of the correlation data more difficult at larger q values since the relaxation times are getting faster and the plateau of the auto-correlation function and the primary decay are affected by the noise. Since the decay of the correlation functions is single exponential an analysis with first cumulant, single exponential, or CONTIN will give the same result. Due to the noise and truncation we found that the best approach to analyze $g_2(q, t)$ over all q vec-

FIG. 4. Measured $g_2(q, t)$ for sample A at q -values as indicated in the figure legend. Dashed lines show exponential fits.

tors was using an exponential function as

$$g_2(q, t) = \beta * (\exp(-t/\tau))^2 + 1, \quad (4)$$

where τ is the relaxation time and β is the instrumental amplitude. Since the sample is ergodic and the same point detector was used for all measurements, the data was analyzed using the same amplitude, β , of $g_2(q, t)$ for all q 's. This improves the reliability of the analysis, however, there will be an increasing error of the determined relaxation times at larger q values which was estimated to be no more than 20% at the largest q vector measured. From the obtained relaxation times we can determine the dynamic function, $D(q) = 1/\tau * q^2$, for both measured systems, which are shown in Figs. 5(a) and 5(b).

There is no standard way to analyze the dynamics of highly concentrated platelet systems in the isotropic regime, nor are there any simulations or theoretical predictions available to our knowledge at this time. We, therefore, approach our analysis of the data from the known dilute cases in Refs. 7 and 8. In both of our systems at low q values, $q < 0.075$ nm⁻¹, a typical slowing down of $D(q)$ can be seen. If we model this part of the dynamic function using the well-known combination of modified penetrating-background corrected rescaled mean spherical approximation (MPB-RMSA)^{28,29} and $\delta\gamma$ approximation^{17,18} as was successfully applied in Ref. 7, the data can be represented very well at $q < 2 * q_{\text{max}}$, where q_{max} is the q -value where the minimum of $D(q)$ appears. Most parameters entering the MPB-RMSA calculation are known experimentally such as the temperature, $T = 293$ K, the dielectric constant of water, $\epsilon = 80.23$, the salinity and the concentration of the colloidal particles, while the charge, $Z_A = 300$ and $Z_B = 100$, and the effective diameters, $d_A = 161$ nm and $d_B = 81$ nm, were determined as was discussed in Ref. 7. Only D_0 was a fit parameter, with $D_{0,A} = 2.5 \cdot 10^{-12}$ m²s⁻¹ for sample A which is somewhat lower, 20%, than what is calculated from Eq. (1), showing a very good agreement between the theoretically predicted $D_{t,A}^0$ and the experimentally determined $D_{0,A}$. Even though the hydrodynamics in concentrated, but still isotropic, platelet systems is different from a concentrated spherical system the good agreement with

FIG. 5. $D(q)$ as a function of q for (a) sample A and (b) sample B. Black circles are the experimental values, red solid lines represent a fit with the self part corrected $\delta\gamma$ approximation using MPB-RMSA as input.

experiment and the lack of available other approaches supports the validity to use the same approach as in Ref. 7 for this investigated system. For sample B, the determined $D_{0,B} = 2.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ is only 55% of what is theoretically expected. In light of previous experiments⁷ this is not surprising since the slowing down of the dynamics of platelet systems close to the L-LC transition is much stronger than it is predicted for spherical particles. I.e., because the theoretical fit approximates the platelets as spheres, the same slowing down as for spheres of the theoretically calculated dynamics with concentration is expected for the theoretical $D(q)$. It has been verified that the dynamics of platelets slows down more with concentration⁷ and it is, therefore, expected to find a smaller D_0 using this approach. We can see that this simple approach to approximate the platelets as spherical particles seems to hold for platelets at concentrations much lower than the L-LC transition while closer to the transition it can only qualitatively describe the data. We are not arguing that the hydrodynamics is the same for spheres and platelets, but since the platelet systems are isotropic the orientational averaged pair correlation function, an input function for the calculation of $D(q)$, will have similar shape and form as for a spherical systems. At the present moment this is the best simple approach to analyze this complex data. In addition, in sample A,

where we were able to measure at large q 's, no large q peak effects the $D(q)$. Unfortunately, due to experimental restrictions it was not possible to measure the dynamics for sample B at large enough q where this peak is found. As is evident for both systems in comparison to the theoretical predictions, $D(q)$ increases with increasing q at $q > 2 \cdot q_{\text{max}}$. This systematic increase in both systems indicates that this effect has a physical origin and is not an experimental artifact. Since $S(q)$ is, in principle, equal to one at larger q the effect has to be related to the dynamic form factor for platelets, $g_{1,\text{plat}}(q, t)$, similar to what was discussed for dilute systems in Ref. 8 and which can be expressed as

$$g_{1,\text{plat}}(q, t) = \exp(-D(q)q^2 t) \sum_{n=0}^{\infty} S_{2n}(q, d, l) \times \exp(-D_r 2n(2n+1)t). \quad (5)$$

Here, D_r is the rotational diffusion coefficient and S_{2n} reflects the contribution from the rotational modes, and d and l are the diameter and the thickness of the platelets, respectively. When applying this equation to higher concentrations, where the platelets start to interact, the pre-factors, S_{2n} , will change but not the multiple of the rotational modes, $2n(2n+1)$. Note that D_r , the rate of the rotation, is now affected by interactions which are not taken into account in Eq. (5). However, the intensity due to the particle orientation, which no longer can be simply averaged, determines the pre-factors, S_{2n} , and will be affected by the concentration. To calculate the S_{2n} s at higher concentration is challenging and has not been performed at present time. Even if the individual $S_{2n}(q, d, l)$ are changing their amplitude and shape at higher concentration the sum at each q value has to remain the same at all concentrations in an isotropic system since $\Sigma(S_{2n})$ is nothing more than the normalized form factor of the platelets. When using our experimental parameters in the expression for the dynamic form factor of Eq. (5) to simulate correlation functions, by calculating S_{2n} for dilute systems, only an averaged contribution of the rotational relaxation would be visible in our systems, as depicted by the solid line in Fig. 6. This line was simulated by generating correlation function using Eq. (5) with dilute input parameters for $D(q)$, D_r , and S_{2n} and fitted with Eq. (4). The result was then normalized with the slowing down found experimentally for sample A. This shows that using the prediction for a non-interacting dynamic form factor cannot describe our data.

Still the dynamic function can be represented by the theoretical $D(q)$ at low q values and has a systematic increase at large q 's. The sum in Eq. (5) can be approximated as an exponential, $\exp(-D_{r,\text{av}} t)$, where $D_{r,\text{av}}$ is a weighted average due to the S_{2n} . If at a specific q vector one S_{2n} is dominating, defined as S_{2a} , by being much larger than the sum of all other S_{2n} , $\Sigma(S_{2n}) - S_{2a} \ll S_{2a}$, the sum can be approximated as $\exp(-D_r 2a(2a+1)t)$. If one only looks at the relaxation rates of the rotational contribution one would expect a constant increase of the relaxation rate due to the addition of higher order n except at points where S_{2n} is dominating, where a plateau should be expected. To get a clearer picture of the extra contribution to the dynamic function ($D(q)$) the rotational part of Eq. (5) was extracted from our experimental

FIG. 6. The excess relaxation rate, Γ_{exc} , as a function of q^2 for sample A (black squares) and sample B (red circles). Arrows indicate the different multiples of the rotational mode $2n(2n+1)$. The line is Γ_{exc} from simulated $g_1(q, t)$ using Eq. (5) with dilute values for sample A where $g_1(q, t)$ then was treated exactly the same way as the experimental data but the result was reduced by 10% according to the experimental findings.

data using Eq. (5). As discussed above the determined relaxation rate is $\Gamma = D(q)q^2 + D_{r,\text{av}}$ and the excess relaxation rate, $\Gamma_{\text{exc}} = D_{r,\text{av}}$, was determined by subtracting the theoretical determined $D(q)$ from the self-part corrected $\delta\gamma$ approximation. The excess relaxation rate, Γ_{exc} , is plotted as a function of q^2 in Fig. 6.

It is now apparent that the excess relaxation rate is increasing stepwise with increasing q . Since in this representation the dynamic function ($D(q)$), which is related to the short time translation diffusion, has been subtracted from Γ and only the contribution from the sum in Eq. (5) should be left. Interestingly enough the plateau values (see arrows in Fig. 6) correspond to the rotational diffusion with pre-factors $2n(2n+1)$ as described in Eq. (5). This indicates that at these plateaus one pre-factor, S_{2n} , is dominating such that $\Sigma(S_{2n}) - S_{2a} \ll S_{2a}$, where $a = 1, 2, 3, \dots$ depending on the plateau, reducing Eq. (5) to $g_{1,\text{plat}}(q, t) = \exp(-D(q)q^2t) \cdot \exp(-D_r 2a(2a+1)t)$. The so determined rotational diffusion for sample A, $D_{r,A} = 258 \text{ s}^{-1}$, is what should be expected for this system when compared to the theoretical determined $D_{r,A}^0$, about 10% less than that estimated from Eq. (2). For sample B the same decrease in $D_{B,r} = 625 \text{ s}^{-1}$ (64% less than calculated from Eq. (2)) as for $D_{r,B}^0$ is found similar to what was reported in Ref. 7. It is clear that the increasing higher order terms of D_r are affecting the relaxation times of the experimental correlation functions but the pre-factors, S_{2n} , in Eq. (5) should not be calculated as in Ref. 8 for interacting systems. In summary, this finding shows that from XPCS measurements it is possible to determine the rotational diffusion of anisotropic particles.

CONCLUSIONS

Using XPCS we have measured the intensity auto-correlation functions of concentrated charged gibbsite platelets in water, 10^{-4} M NaCl , over a large range of wave

vectors at timescales in the micro- to millisecond regime. In doing so, we have shown that the relaxation spectra do not follow the same pattern as for spherical particles, but instead an extra contribution to the dynamics has been found. By analyzing the data qualitatively using available theories for non-interacting systems we found strong evidence that this deviation from the behavior of spherical systems arises from the influence of the rotational modes. By highlighting these modes as depicted in Fig. 6 we have shown that it is possible to measure the rotational modes of anisotropic systems using XPCS. This opens up the possibility to investigate not only the translational but also the rotational motion in anisotropic systems using XPCS. The use of the rotational-translational decoupling approximation and the self-part corrected $\delta\gamma$ approximation of Beenakker and Mazur for $D(q)$ have shown to be simple and useful tools for the analysis of these systems. Even though both methods are inaccurate at high concentrations, they give good indications and approximations of the systems physical characteristics. Until more elaborate and accurate methods are available, such tools are very helpful to understand and interpret experimental findings.

Furthermore, the appearance of a pre-translational peak in the static q -dependent intensity at large q values has been found. This peak has the characteristics of a structure peak for the face-to-face distance since no cluster formation, non-ergodicity, or birefringence was detected in the investigated samples. We, therefore, speculate that this peak originates from a strong local alignment between platelets before the actual phase transition takes place making the face to face separation a strong probable distance in the system.

The possibility to investigate the dynamics of anisotropic colloidal particles over a large q range with XPCS has become possible with the improved coherence properties of x-rays in facilities such as PETRA III. Further improvements of coherence, detector frame rates, and beam intensity could push the limits of the experiments to lower concentrations, larger wave vectors, shorter time-scales, and better statistics but the most needed development in order to understand these systems is today on the improvement and/or development of theory and simulation in order to explain the experimental findings.

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