Light Diffraction from Shear Ordered Colloidal Dispersions

Christian Dux and Heiner Versmold
Institut für Physikalische Chemie, RWTH, D-52062 Aachen, F.R. Germany
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Light diffraction from shear ordered colloidal dispersions is discussed in terms of the scattering power distribution $I(l)$ along Bragg rods of hexagonal layers. For a charge stabilized dispersion the angle dependence of the light scattering intensity is used to determine $I(l)$, from which conclusions on the mutual registration of the layers, the stacking order, and the kinetics of crystallization can be drawn. For the system under study a structural transition from random close-packed hexagonal layers to faulted twinned fcc is identified. [S0031-9007(97)02367-3]

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The equilibrium phase behavior of charge stabilized colloidal dispersions has been investigated as a function of particle concentration and ionic strength [1–4]. At low particle concentration and low ionic strength the equilibrium structure is liquidlike or bcc. A region of fcc follows at higher particle concentration and ionic strength. At very high particle concentration, finally, glasslike behavior has been observed [2], the ultimate equilibrium structure of which is not yet known. After the application of shear, such dispersions often show a high degree of order which, according to small angle neutron scattering (SANS) experiments [5–7], is not in agreement with the above mentioned equilibrium structures [8,9]. It has therefore been proposed to consider hexagonal layers as the basic structure element for concentrated shear ordered colloidal dispersions [8–12]. The three-dimensional structure obtainable from such layers depend on (a) the packing of the layers and (b) the stacking sequence of the layers [13].

By measuring the SANS Bragg spot intensity at various sample orientations we were recently able to determine the scattering intensity $I_{hk}(l)$ along Bragg rods with Miller indices (h, k) [9,12]. In the present letter we show that the method of determining the intensity distribution $I_{hk}(l)$ along Bragg rods of shear ordered dispersions can be extended to light scattering (LS). First, we present explicit experimental determinations of $I_{hk}(l)$ by light scattering and show further how the structure of dispersions and the kinetics of recrystallization after the application of shear can be investigated by this method. We also mention that light scattering "powder" diffraction from hard sphere colloidal systems has been interpreted in terms of close-packed random stacking layers [14,15].

Our experiments were performed with polystyrene latex dispersions, charge stabilized by sulfat surface groups. The particle diameter was $\sigma = 240$ nm with a polydispersity of about 6% as determined by transmission electron microscopy. Ordering of the dispersions was achieved by first completely deionizing the sample with ion exchange resins and then applying shear. For this the dispersion was filled in a rectangular quartz cell of dimensions 0.5 mm thickness $\times$ 10 mm width $\times$ 40 mm length, equipped with an inlet and an outlet through which flowing was achieved by means of a peristaltic pump. The cell was mounted on a rotation stage which allowed its reorientation about the vertical axis by an angle α. It was placed in the center of a spherical screen, filled with water as index match fluid. A photodiode mounted on a separate rotation stage served to determine the scattering intensity as the sample was rotated at various angles α. Figure 1 shows a typical Bragg spot pattern from a shear ordered layered dispersion on the spherical screen.

A brief summary of the Bragg spot description used to analyze the LS data is presented next. The reciprocal space of a hexagonal layer with interparticle distance a is a system of hexagonally arranged Bragg rods [13] with a rod spacing in reciprocal space of $a^* = 4\pi/(a\sqrt{3})$. Figure 2(a) shows a view from the top of such a system of Bragg rods with Miller indices (h, k). For a series of laterally uncorrelated layers the intensity would be uniformly distributed along the rods. On the other hand,

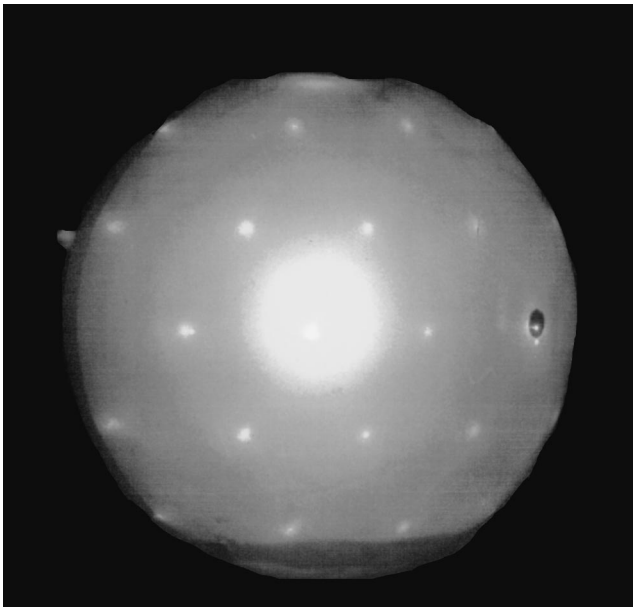

FIG. 1. Light scattering pattern from Bragg rods on a spherical screen as described in the text.

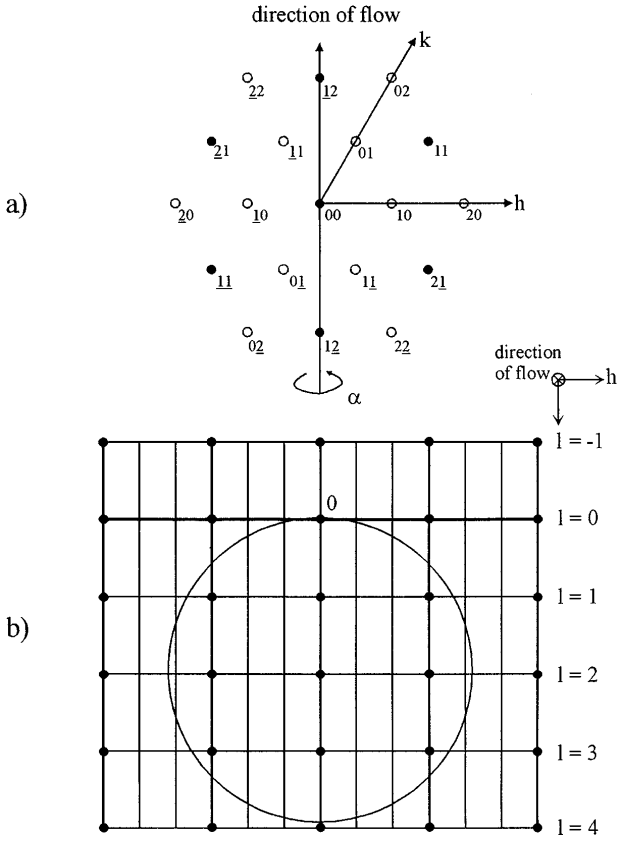

FIG. 2. (a) View from the top of hexagonally arranged Bragg rods with indices (h, k). (b) Rod system of (a) rotated by 90° about the $(\underline{1}, 0)$-$(0, 0)$-$(1, 0)$ axis. $(h - k) = 3n$ rods drawn as solid lines with intensity nodes (filled circles) for a close-packed system. $I(l)$ along $(h - k) = 3n \pm 1$ rods is drawn as light lines. The Ewald sphere for the orientation $\alpha = 0°$ is included as a solid circle.

for close-packed layers, a modulation of the intensity $I_{hk}(l)$ along the rods occurs. With a spacing between two closed-packed layers $c = a\sqrt{2}/\sqrt{3}$, one obtains $c^* = 2\pi/c$ as the unit along the rods.

In general, for close-packed hexagonal layers, there are two types of Bragg rods [13]. For rods with $(h - k) = 3n$, where n is an integer, reciprocal lattice points occur on the rods at integral values of l. In Fig. 2(a) the central (0,0) rod and the rods drawn as filled circles are of this type. On the other hand, for rods with $(h - k) = 3n \pm 1$, shown in Fig. 2(a) as open circles, the intensity distribution depends on the stacking order. A summary of the earlier x-ray literature on the intensity distribution $I_{hk}(l)$ is given in Ref. [13]. Recently, Loose and Ackerson [10] derived essentially identical results in a very compact and useful form. They introduced a stacking probability A of having two consecutive A → B translations (or A → C translations) for ABCABC... (or ACBACB...) layering. For $(h - k) = 3n \pm 1$ they obtain the following distribution:

$$I_{01}(l) = \frac{3A(1 - A)}{4(1 - 2A)(1 - \cos^2 2\pi l) + 5A^2 + 4A^2 \cos 2\pi l}. \quad (1)$$

With $A = 0.5$ in Eq. (1), the distribution of close-packed random stacking layers is obtained. For $A = 1$, the distribution for twinned fcc (ABCABC..., ACBACB...) and, for $A = 0$, the one of hcp (ABABAB..., ACACAC..., BCBCBC...) results. Distributions for intermediate stacking sequences can be modeled readily with intermediate values of A.

In order to show how $I_{hk}(l)$ can be obtained from the LS scattering intensity we consider a different presentation of the reciprocal space which results from Fig. 2(a) by a 90° rotation about the $(\underline{1}, 0) - (0, 0) - (1, 0)$ axis. The resulting view along the Bragg rods is schematically shown in Fig. 2(b). Here, the $(h - k) = 3n$ rods are drawn as solid lines with intensity nodes (filled circles) according to perfectly close-packed hexagonal layers at $l = 0, \pm 1, \pm 2, \ldots$ [9,10,13]. By contrast, the $(h - k) = 3n \pm 1$ rods are indicated by the light lines in Fig. 2(b). No intensity distribution is indicated for these rods because, according to Eq. (1), this strongly depends on the stacking order. The Ewald sphere with radius $k_i = 2\pi n^*/\lambda_0$ is included in Fig. 2(b) for the sample orientation $\alpha = 0°$. The Ewald sphere is draw to scale for $\lambda_0 = 543.5$ nm and $a = 1005$ nm, the values applying to our experiment, i.e., $k_i/a^* = a\sqrt{3}/2\lambda = 2.14$ and $c^*/a^* = 3/2\sqrt{2} = 1.061$. Several of the rods with low Miller indices are intersected by the Ewald sphere. As the sample is rotated to different angles α, the Ewald sphere rotates about the origin of reciprocal space (indicated by 0) and, thereby, intersects the rods indexed by (h, k) at the following l values:

$$l_{1,2} = \frac{k_i \cos\alpha \pm \sqrt{(k_i \cdot \cos\alpha)^2 - [(h^2 + k^2 + hk)(a^*)^2 + 2a^*(h + k/2)k_i \sin\alpha]}}{c^*}. \quad (2)$$

A wave vector k_f, extending from the center of the Ewald sphere to any of the intersections with a rod (h, k), fulfills the Bragg conditions. Thus, on a spherical screen diffraction spots from rods (h, k) with intensities $I_{hk}(l)$ are observed in the directions k_f. Figure 1 shows a typical Bragg spot pattern from a shear ordered layered dispersion. By varying the orientation α of the sample and measuring the intensity $I(\alpha)$ of a rod (h, k), one obtains the corresponding $I_{hk}(l)$ by calculating l from h,k and α via Eq. (2). Corrections due to the particle form factor $P(Q)$ and the change of the size of the scattering volume with sample orientation can be taken care of.

In the following, we present results for the $(h - k) = 3n$ rod $(1, 1)$ and the $(h - k) = 3n \pm 1$ rod $(0, 1)$. First, in Fig. 3 the experimentally determined intensity distribution $I_{11}(l)$ along a $(1, 1)$ rod is shown for l values

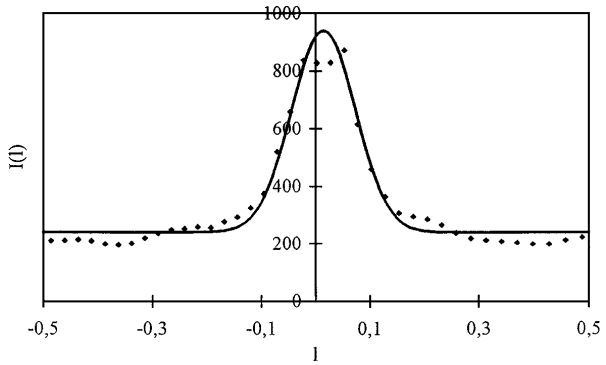

FIG. 3. Intensity distribution $I_{11}(l)$ along a $(1,1)$ rod 3 h after the shear was stopped. The solid curve is a fit by Gaussian plus a background.

between -0.5 and $+0.5$. The intensity maximum is located at $l = 0$ as expected. The distribution shown was determined 3 h after the shear was turned off. It differed little from profiles obtained at shorter times, with 0.5 h being the lower limit with the present setup. The solidly drawn line was obtained by fitting a Gaussian plus a background to the data. The intensity distribution shows that the hexagonal layers are locked essentially in close-packed positions.

Some interesting information concerning the stacking order was obtained from the intensity distribution $I_{10}(l)$ along the $(1,0)$ rod. This is shown in Figs. 4(a), 4(b), and 4(c) for times 0.5, 15, and 40 h after the shear had been turned off. The dots again represent experimental data. In Fig. 4(a), 0.5 h after terminating the shear, the intensity distribution is close to that of random close-packed hexagonal layers. At later times, Figs. 4(b) and 4(c), obviously the stacking order changes such that the profile $I_{10}(l)$ becomes double peaked and develops in the direction of faulted, twinned fcc. By fitting Eq. (1) to the $I_{10}(l)$ obtained at different times (shown as solid lines in Fig. 4), the stacking probability A was determined. The time dependence of A is shown in Fig. 5. A clear tendency from random stacking layers ($A = 0.5$) to fcc ($A = 1$) is apparent. Finally, as no theory seems to be available for the stacking redistribution kinetics, we fitted the data to a stretched exponential $A(t) = 1 - 0.5\exp(-t/\tau)^{\beta}$. A good fit was obtained with $\tau = 120$ h and $\beta = 0.33$, as shown in Fig. 5.

In conclusion, we have shown that for shear ordered colloidal dispersions the orientation dependence of the light scattering intensity distribution in combination with Eq. (2) allows the determination of the intensity distribution $I_{hk}(l)$ along Bragg rods (h,k). Immediately after the shear was turned off the structure of the system was found to be close to random close-packed hexagonal layers. With increasing time, reorganization from random stacking to fault twinned fcc, i.e., ABCABC... and ACBACB... stacking, was observed. Registration of the layers in close-packed position occurs on a much faster time scale than the stacking redistribution. The method presented appears to be unique for studying the structure of shear ordered dispersions, their crystallization kinetics, and the structure of dispersions under shear.

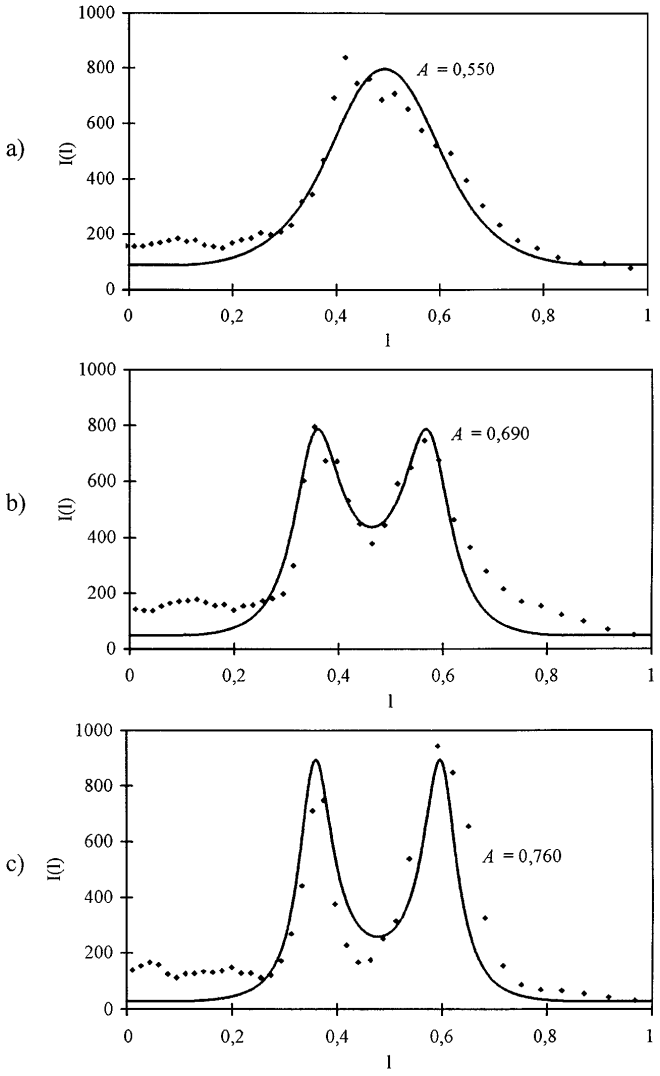

FIG. 4. Intensity distribution $I_{10}(l)$ along a $(1,0)$ rod (a) 0.5, (b) 15, and (c) 40 h after shear was stopped. Solid curves are fits of Eq. (1) with stacking probabilities A, as indicated.

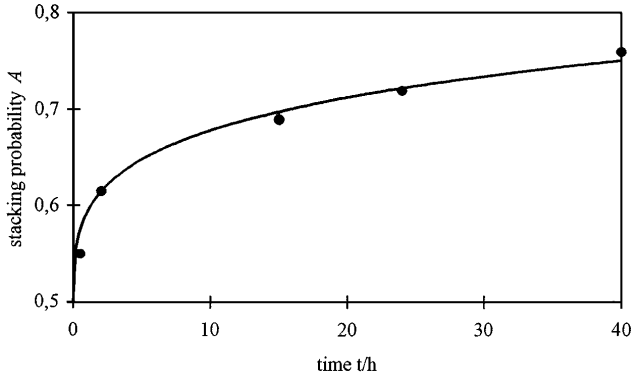

FIG. 5. Variation of stacking probability A with time t. Solid curve: $A(t) = 1 - 0.5\exp(-t/\tau)^{\beta}$ with $\tau = 120$ h and $\beta = 0.33$.

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