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SHORT COMMUNICATION

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Scattering experiments on the structure of concentrated dispersions

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Abstract In this work the Couette cell is compared with a more recently constructed disk shear cell. There are distinct advantages of the disk over the Couette cell, in particular, when it comes to the determination of the intensity along certain Bragg rods.

Key words Concentrated colloidal dispersions · Shear-induced layers · Sample rotation · Intensity distribution along Bragg rods

Introduction

The structure of a charge-stabilized colloidal dispersion can be manipulated by the application of shear. Three typical examples are shown in Fig. 1. Figure 1a is a light scattering (LS) result in which the hexagonal structure can be seen easily. It was obtained in our laboratory by allowing the dispersion to flow between two parallel cuvette walls. Figure 1b is a small-angle neutron scattering (SANS) result obtained at the ILL in Grenoble with the D11 spectrometer and Fig. 1c shows the hexagonally arranged Bragg reflections as obtained with the charge-coupled-device detector of the ESRF line ID2 (small-angle X-ray scattering, SAXS), also in Grenoble. Details of the type of shear cell used in the neutron and the synchrotron scattering experiment are presented later. In all three cases shown we were working with layered samples and the colloid particles were ordered by shear.

The interest in colloidal systems first concentrated on the structure of dilute dispersions, LS being the method of choice. Meanwhile interest has shifted to the technologically more relevant, concentrated dispersions. A similar shift has taken place for the experimental methods. LS, the method of choice at the beginning, became useless with higher and higher sample concentration. The importance of LS decreased and the new methods are now SANS and SAXS. Today SAXS radiation is usually generated by a synchrotron. Both methods require considerable resources and for that reason are performed only at special research centers.

This work is concerned with an analysis of the structure of concentrated colloidal dispersions. As suggested by a large number of experiments (see also Fig. 1) we assume that after the application of shear the particles are arranged in layers. In a layer, spherical colloidal particles are usually found in hexagonal order. For Bragg scattering, the Ewald construction which requires the reciprocal lattice is of importance. The reciprocal lattice is obtained from the particle positions in the well-known manner [1, 2]. For a hexagonal layer, the reciprocal lattice is also a hexagonal layer, rotated in plane, however, by 90°. This is shown in Fig. 2, where we also introduced the Miller indices h, k. Further, the direction of flow (for ordering the sample) is indicated. In Fig. 3, radiation with wave vector $|\mathbf{k}_i| = 2\pi/\lambda_i$ is diffracted from a structure existing in the scattering volume with origin 0 in the center of the sphere. The origin of the reciprocal space, 0*, is drawn at the end of a second vector $\mathbf{k}_i$ in Fig. 3. The Ewald sphere with radius $2\pi/\lambda_i$ also passes through 0*. (If the wave length, λ_i, of the radiation to be scattered is much smaller than a typical value of the length, a, of the structure, the Ewald sphere looks more like a plane.) A reciprocal lattice point rotated onto the surface of the Ewald sphere indicates that the Bragg condition is fulfilled for this point. This defines a scattering vector $\mathbf{k}_\mathrm{f}$ such that $\mathbf{k}_\mathrm{f} = \mathbf{Q}_{h,k} + \mathbf{k}_i$, where $\mathbf{Q}_{h,k}$ is a reciprocal lattice vector with Miller indices h, k. So far we have neglected the third dimension (Miller index l). For two-dimensional objects (layers) the l coordinate is perpendicular to the

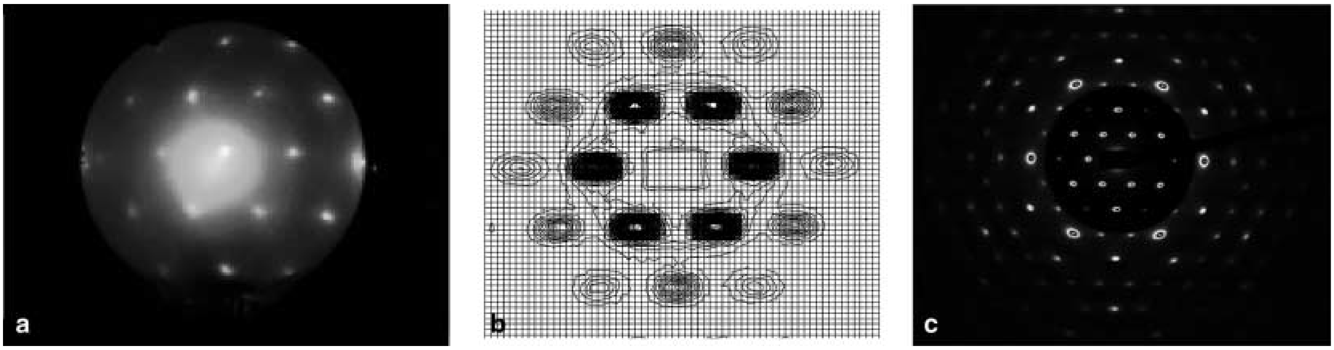

Fig. 1 **a** Light, **b** neutron, and **c** synchrotron X-ray Bragg diffraction from colloidal samples ordered in layers

surface and one obtains the well-known Bragg rods in reciprocal space. Diffraction spots, i.e. intersections of the Bragg rods with the Ewald sphere, always occur for layers. Further, for layered hexagonal systems, two orthogonal rotational axes can be defined (Figs. 2, 4), which we call α- and β-axes. They will be used to intersect the Bragg rods at different heights by the Ewald sphere (plane) in order to determine the intensity along a Bragg rod.

The behavior of the Bragg diffraction spots with sample rotation is different for layers and for crystals. For layers, the Bragg spots are continuously present and move during sample rotation, whereas for crystals they just blink as the Bragg condition is fulfilled and then disappear.

The next two sections are organized as follows. Since the Couette cell is available at most neutron scattering and synchrotron X-ray research centers it will be treated first. It will become apparent that this cell is not the best solution for scattering experiments. Physicists, crystallographers, and chemists used different constructions as soon as they wanted to investigate single crystals. Although it is possible to obtain large hexagonal layers with the Couette cell, it is rather difficult to rotate the sample about independent orthogonal axes, which seems to be necessary for a complete characterization of the structure. Following the section on the Couette cell, the description of a disk shear cell is given. This cell has been used by us recently both for neutron and for synchrotron X-ray scattering (Fig. 1b, c). It offers some advantages. The article closes with the conclusions which can be drawn from such a comparison of the cells.

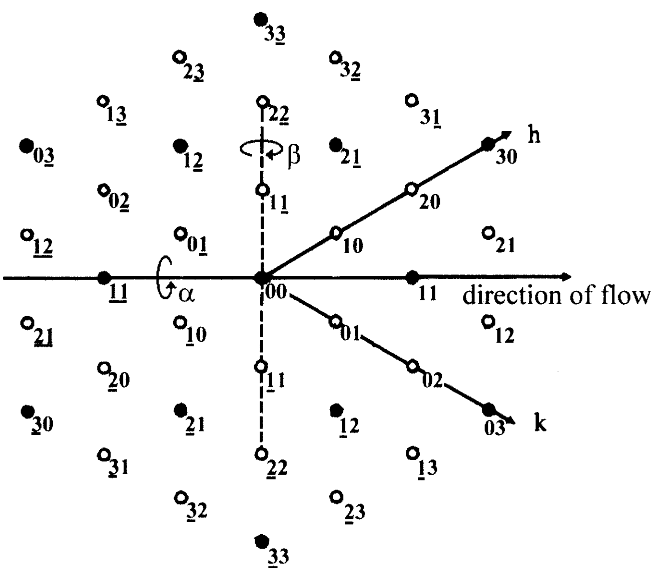

Fig. 2 A hexagonal layer in reciprocal space with Miller indices *h*, *k*

The Couette shear cell

In order to get familiar with the Couette cell we consider Fig. 5. Shear is usually generated by the outer rotating cup. For neutron scattering the cup and the central static cylinder are made from quartz glass (free of boron) to prevent the neutrons from interacting with the cell. The

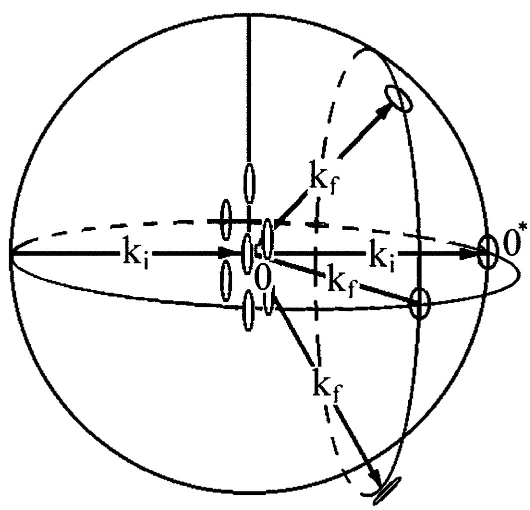

Fig. 3 Scattering experiment: real space (with origin 0), reciprocal space (origin 0*), and Bragg reflections are shown simultaneously

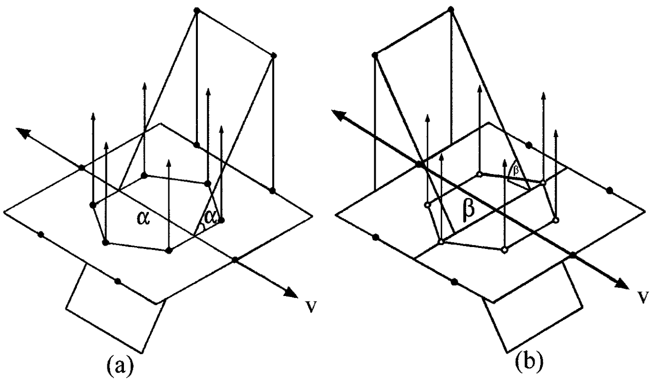

Fig. 4 Two possible orthogonal directions of intersecting the Bragg rods by the Ewald plane (sphere). The direction of shear flow is indicated by an *arrow*. The orthogonal axes for rotations of type α and type β are indicated. The β-type rotation of the Ewald plane does not change the height of the intersection for the rods (1,−1) and (−1,1). The β geometry is thus not suited to determining the intensity along the rods (1,−1) and (−1,1)

colloidal sample is kept between the cylinder and the cup. As the outer cup starts rotating, a linear shear gradient is set up in the gap filled with the sample. To the best of our knowledge the first neutron scattering experiment on colloids performed with a Couette cell was described by Ackerson et al. [3]. Usually, a translation of the beam is performed with such a cell, which is equivalent to a rotation. The standard shear cell at most research centers worldwide is at present such a Couette cell, the principle of which is shown in Fig. 5. Since its first use with colloids [3], it has been applied again and again [4, 12]. Despite its general distribution this cell has caused some confusion. In our group we have used a rotating disk shear cell, which seems to be advantageous for scattering experiments. It will be described later.

Shear is very important to manipulate colloidal dispersions. A competent description has been given by Ashdown et al. and Versmold and Lindner [4]. Usually the application of shear leads to layered systems first. In a second step, the layers may recrystallize to form three-dimensional crystallites. If one continues shearing, the system remains in the layered random stacking state.

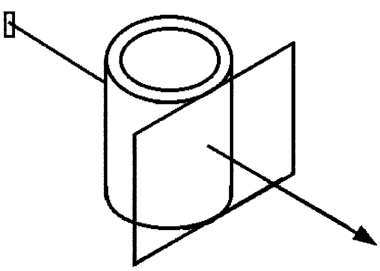

Fig. 5 The Couette shear cell

The recrystallization has been observed by LS recently [5].

A secure way to analyze the structure of a dispersion under shear is by measuring its Bragg intensity along a $(h-k)=3n \pm 1$ rod. Here h and k are Miller indices and n is a natural number. The l coordinate on the Bragg rod is given by the intersection of the rod in question with the Ewald plane (sphere). Different structures lead to different intensity distributions along the rods [1, 6], which allows one to characterize the structure. Thus, in order to determine the structure of a dispersion in an unambiguous way, the intensity at the points of intersection of a Bragg rod by the Ewald plane should be determined.

We now consider a Couette cell. In order to rotate the layers the cell is displaced (translationally) from its normal position, shown in Fig. 5, to a new position at constant height but parallel to the incident beam (see Fig. 1 of Ref. [3]). This is equivalent to a rotation of the layers about the symmetry axis of the cell (vertical axis). With different displacements of the incoming beam, different apparent rotations of the cell can be performed. We call these rotations β rotations. For a β rotation (Couette cell), the two Bragg rods (−1,1) and (1,−1) as well as all rods (n,−n) are positioned on the rotation axis. This means that these rods at normal incidence (0° scattering angle) and all other settings are intersected at $l=0$. For the first ring only, the four reflections, (0,1), (0,−1), (1,0), and (−1,0), not on the rotation axis give meaningful (identical) information at larger scattering angles. These four reflections have frequently been observed at larger scattering angles or sufficiently high shear rates [7]. Often shear experiments are carried out in the extreme positions, radial and tangential, of the Couette cell. With only two values the whole l distribution can hardly be obtained [5, 12].

The disk shear cell

Our disk shear cell is shown schematically in Fig. 6. It consists of a shear disk powered by a little electronically stabilized motor. By selecting the rotational speed the desired shear rate can be chosen. For neutron scattering the shear disk and the front and the rear windows are made from quartz glass free of boron. In a second cell, for synchrotron X-ray scattering, almost perfect transmission is obtained with polycarbonate windows and disks. The shear disk rotates in an aluminum case coated with Teflon on the inner side which is in contact with the dispersion. In Fig. 6 two axes, called the α-axis and the β-axis, are visible. Reorientation of the cell about these axes is possible and necessary for a determination of the intensity along all the Bragg rods. It should be noted that for α rotations also the intensity along the rods (−1,1) and (1,−1) is accessible which, as mentioned

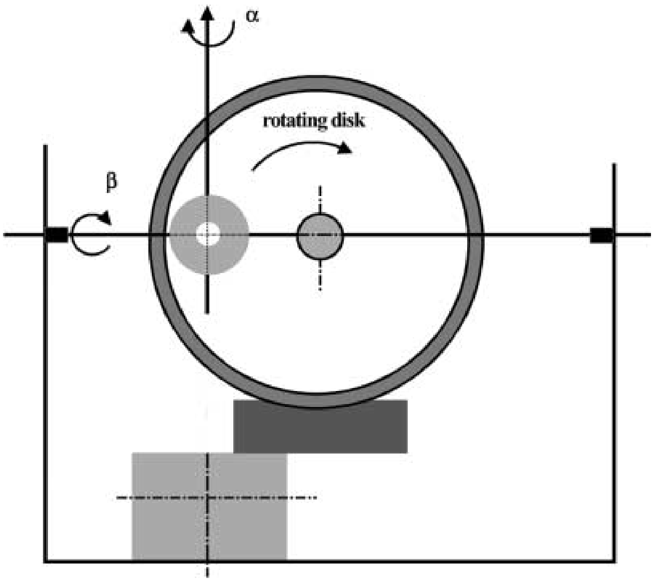

Fig. 6 A disk shear cell: The two types of axes for α and β rotations are indicated

previously, cannot be determined with β rotations. It seems important to recall that the rotations usually performed with the Couette cell correspond to β rotations.

Previously, we also mentioned an observed similarity of the scattering pattern concerning a variation of the shear rate, $\dot{\gamma}$, and of a corresponding sample rotation. It can be explained similarly. A shear rate $\dot{\gamma}$ obviously produces layers which are displaced with respect to each other. As shown in Fig. 7, the displacement defines a tilt angle with respect to the normal of the layers which can be used to generate the same configuration of layers by a rotation. In order to explain the scattering pattern one has to go to the reciprocal lattice. Here, the tilt defines an Ewald plane and a scattering angle according to the Ewald construction.

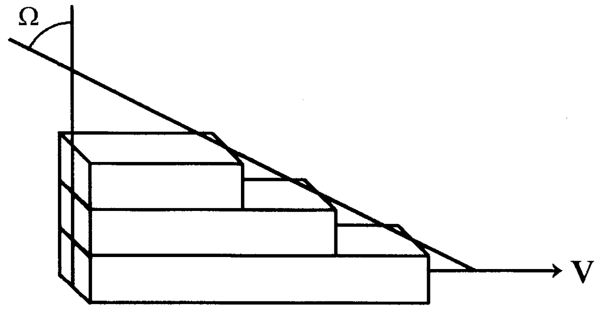

Fig. 7 Tilt angle, Ω, due to trailing of the layers

Conclusion

In this section a summary of our comparison of the Couette cell and our disk shear cell is presented. First, it should be mentioned that we were not the first to use a shear disk cell. A disk cell was described and used by Ackerson and Clark [9] long before us. Surprisingly, Ackerson et al. [3] returned to the Couette cell later for their neutron scattering experiments. One advantage of our disk cell is that the necessary sample rotations (α and β) can easily be carried out about the two perpendicular axes, whereas the translational displacement which is usually carried out with the Couette cell is merely equivalent to a β rotation. The advantage is that the Bragg rods (−1,1); ($-n$,n) and (1,−1); (n,$-n$) are intersected by an α rotation at variable height, whereas a β rotation always intersects these rods at $l = 0$. Angular α and β measurements at rest can be performed with the disk cell as well as α and β measurements under shear.

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