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ORIGINAL CONTRIBUTION

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Scattering experiments on the structure of colloidal dispersions: hexagonal layers or cubic crystals?

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Abstract A description is given of how colloidal hexagonal layers and cubic crystals can be interrelated. The experimental preparation of 2D layers by shear, their recrystallization to form 3D crystals, and the scattering of light, neutrons and X-rays by these structures are considered. The scattering intensity is best described by Bragg rods. It turns out that the transition from 2D layers to 3D crystals leads to an intensity redistribution along certain Bragg rods which allows the crystallization kinetics to be investigated.

Key words Colloidal crystals · Hexagonal layers · Sheat · Scattering

Introduction

For a number of years, a puzzling situation concerning the scattering of light [1, 2], neutrons [3–5], and synchrotron X-rays [6] from ordered colloidal dispersions exists in the relevant literature: a sixfold symmetry of the scattering pattern is identified with a cubic [face-centered cubic (fcc) with twinning] crystals structure. In this paper we point out that things can be more complicated than this. In particular, hexagonal layers provide an interesting alternative interpretation of the experimentally observed pattern. A check of the temporal and special distribution of the scattering intensity seems to be necessary for a sure identification of the structure; this check is not usually carried out.

Since sixfold symmetry plays an important role in our discussion, we recall that perhaps one of the oldest and most popular tilings of a plane is hexagonal. As an example there is the honeycomb, which, in view of the small amount of material required to build it, is extremely stable. It is now used as a construction element for wings of airplanes or gliders and for very light surfboards. As a second example we consider a fish from the Australian Barrier Reef (Fig. 1). The sixfold regular tiling of the skin is quite common among animals. Biologists may explain why this pattern makes the fish fitter than others.

In the past artists and architects frequency used sixfold tiling when creating mosaics and ornaments. Escher [7] was fascinated by tiling a plane all his life. He performed several group-theoretical investigations on 2D groups and presented lectures on that topic. One example of an ancient hexagonal tiling of a plane [7] is shown in Fig. 2.

Crystallographers know that the hexagonal planar structure is closely related to the cubic one. These two structures and their interconversion play an important role in modern chemistry, physics, and material science. However, the identification of the structures hexagonal planar, simple cubic (sc), body-centered cubic (bcc), or fcc is, in many cases, unsatisfactory in the literature. We present here some simple ideas of how these structures can be distinguished and how a comparison could or should be performed.

The present article is organized as follows. The next section familiarizes the reader with hexagonal planes. In the following section a description of the

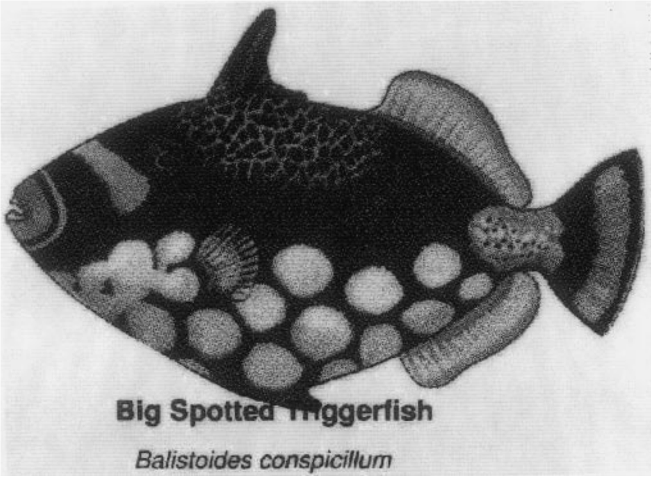

Fig. 1 Big spotted triggerfish from the Australian Barrier Reef. The spots on the lower side form the hexagonal pattern

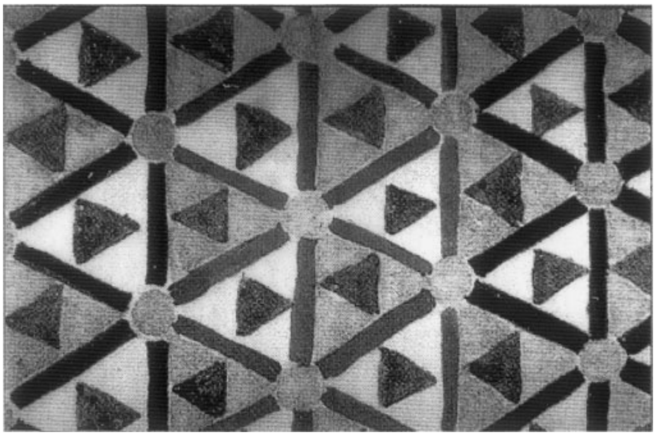

Fig. 2 Ancient hexagonal division of the plane collected by MC Escher. Taken from Ref. [7]

3D cubic structure and its relationship to 2D layers is presented.

Scattering experiments which allow the two structures to be distinguished are then considered. The paper closes with a summary.

Hexagonal layers

The question which matters first is how can one relate 2D hexagonal layers to a 3D cubic structure. A simple interrelation can be made for a cube standing on one of its corners. As indicated in Fig. 3a, the top corner (the one oriented towards the reader) defines the three axes x, y, and z. Similarly, the bottom corner defines three axes, x', y', and z', which are rotated by 60° relative to the x-, y-, and z-axes about the diagonal of the cube. Projection of all six axes along the diagonal onto the bottom plane

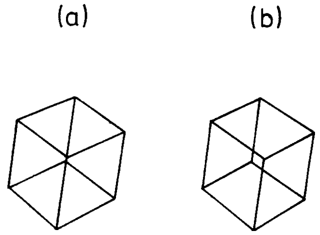

Fig. 3a, b Stereo picture of a cube, **a** perspective view (right eye), **b** view along the diagonal (left eye), showing the two sets of coordinate axes: x, y, z (*top edge*) and x', y', z' (*bottom edge*). After projection of the two sets of axes along the diagonal onto the ground plane one obtains the sixfold tiling of the plane

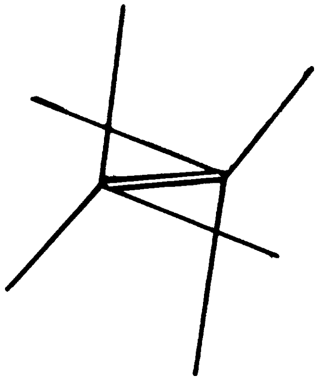

Fig. 4 Detail of the projection shown in Fig. 3. The two sets of axes, x, y, z (*top edge*) and x', y', z' (*bottom edge*) before the projection onto the ground plane

results in Fig. 3a. Through this projection we obtained a 2D (layer) picture of the 3D cube. In passing we mention that Fig. 3a and b form the two parts of a stereo picture. The axes of the two coordinate systems defined by the top corner (x-, y-, and z-axes) and the bottom corner (x'-, y'-, and z'-axes) are shown in Fig. 4.

Experimentally, colloid particles arranged in layers can be obtained most easily by the application of shear. If one is interested in scattering experiments these can be carried out in a Couette cell [8] or in a cell with a shear wheel [9]. The neutron Bragg diffraction pattern of hexagonal layers as obtained with the D11 small-angle neutron-scattering spectrometer at Grenoble, France [9], is shown in Fig. 5. One essential component of the experiment was our shear cell. At a shear rate of about 1000 Hz the sample was first aligned and ordered for a few minutes. After stopping the shear wheel the neutron scattering as reproduced in Fig. 5 was recorded. Although this is essentially identical with the result obtained by Ashdown et al. [4] with a Couette cell, we interpret it as scattering from hexagonal layers [10].

It has long been known [11] that Bragg scattering of colloidal crystals can be observed by light scattering. One interesting light-scattering observation has been

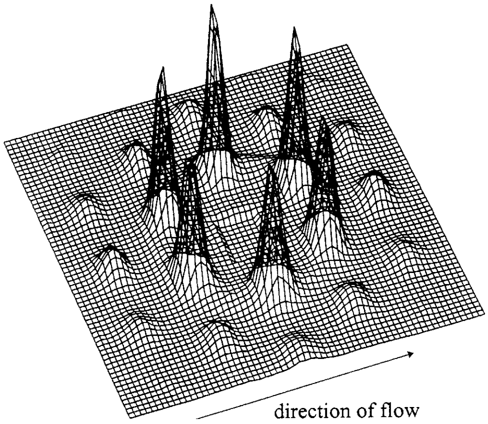

Fig. 5 Neutron Bragg scattering at normal incidence ($\alpha = 0°$) from a layered colloidal sample (D11 Grenoble, France; particle diameter $\sigma = 92$ nm; volume fraction $\phi = 0.36$)

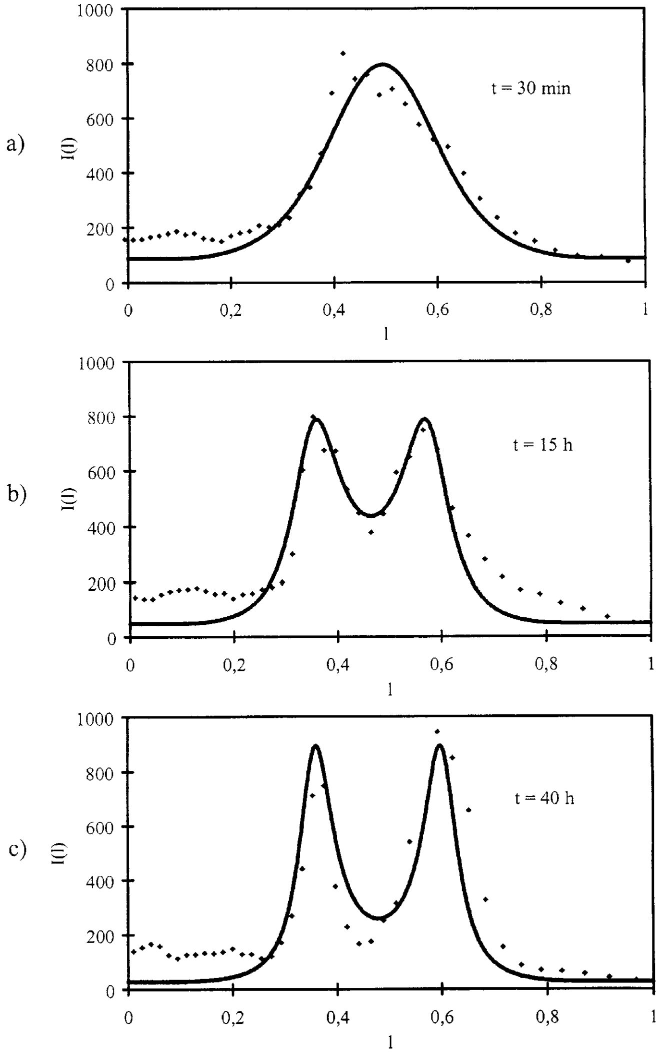

Fig. 6 Light-scattering intensity along a Bragg rod for three different waiting times [12]: **a** 30 min; **b** 15 h; **c** 40 h

obtained for a system similar to the one shown in Fig. 5. We show some results taken from the literature [12] in Fig. 6. The intensity distribution along the *l* direction of the Bragg rods for a layered system is shown. Figure 6 shows that different intensity distributions were determined for different waiting times. The third intensity distribution (Fig. 6c) was obtained after about 40 h. Obviously, a very slow recrystallization occurs such that, directly after stopping the shear, the intensity along the rods indicates random stacking which becomes more and more fcc-like with time [13–15].

Cubic crystals

Fcc crystals consist of hexagonal layers showing the well known A, B, C stacking order. Synchrotron X-ray diffraction studies concerning the phase diagram of charge-stabilized dispersions have been carried out by Sirota et al. [16]; their results are redrawn in Fig. 7.[1] At sufficiently high colloid particle concentrations an amorphous state of the dispersions next to a fcc phase was observed with a structure factor $S(Q)$ indicating a vitreous or a liquidlike structure. More recently, it has been found that this poorly defined state can be transferred to a hexagonal-layered state by the application of shear [3, 4, 5, 11, 12, 16, 18]. At least in those cases in which experiments have been carried out for sufficiently long times the layers became interconnected to form cubic crystals [12].

We recall that in highly concentrated form such dispersions are viscous and that a given state of the dispersions changes only very slowly. Despite the fact that the powder scattering pattern indicates an amorphous state, the thermodynamic stable structure of these dispersions also appears to be fcc. Due to the strong kinetic hindrance a very long time is required until the

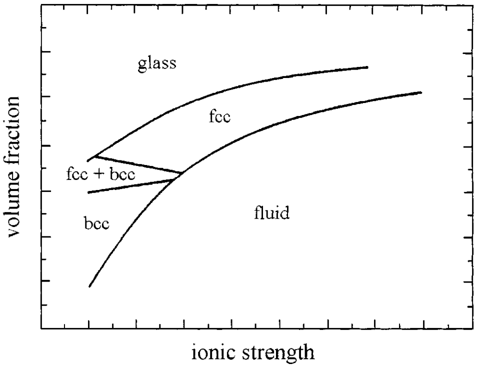

Fig. 7 Phase diagram for a charge-stabilized colloidal dispersion. Redrawn from Ref. [16]

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[1] See also Ref. [17]

system is recrystallized, and its complete kinetic identification requires the intensity determination along the Bragg rods. We and others have found that charge-stabilized dispersions crystallize more readily after being manipulated by shear. This is also demonstrated by the light-scattering data shown in Fig. 6 [12]. To the best of our knowledge no small-angle neutron scattering or synchrotron X-ray scattering experiments have so far confirmed these structural changes.

Kinetics of the phase transition

At sufficiently low particle densities the kinetics of a hexagonal layer-to-cubic crystal transition should be observable via the powder diffraction pattern. This is due to the fact that the (h, k, l) expressions are slightly different for the two structures. For hexagonal layers the expression according to which powder pattern reflections occur is $(h^2 + k^2 + hk)$. Values such as 0 for $(h,k) = (0,0)$ or 1 for $(h,k) = (1,0)$ or $(0,1)$ etc. have been observed. For layers for which $(h^2 + k^2 + hk)$ holds, it is impossible to obtain values of 2,.... In contrast, the corresponding factor for cubic crystals is $(h^2 + k^2 + l^2)$ with additional selection rules for the three cubic structures sc, bcc, and fcc. Thus, values such as 2,... are now allowed. In otherwise similar Bragg diffraction patterns certain reflections are missing for a layered system. The solid line in Fig. 8 gives the powder pattern from a bcc system and the broken curve gives the scattering from hexagonal layers. Both curves were obtained at different heights in a cuvette for the same system [20]. Thus, this is one possibility to distinguish between layers and crystals.

An even better identification of layered systems is possible by measuring the intensity along the $(h - k) = 3n \pm 1$ rods [13–15]. The stacking order is best characterized by plotting the scattering intensity as a function of l, the Miller index in the direction perpendicular to the surface of the layers. In Fig. 2 of Ref. [14] such a plot is shown as an example for hexagonal close-packed, random stacking, and fcc. The phase transition from random stacking layers to fcc is characterized by the occurrence of a minimum on the broad random stacking distribution. It is interesting to note that such a transition has been observed by light scattering, as shown in Fig. 6. Apparently, Ackerson et al. [3] were the first to measure the Bragg intensity along such rods by neutron scattering. Their Fig. 3 is in part redrawn as our Fig. 9. For the sample at rest, the data points represented by triangles apply. They obviously observed a tendency towards fcc which, however, was ignored by the authors at that time. Measuring the intensity along $(h - k) = 3n \pm 1$ rods is certainly the best method to determine the structure of a dispersion; it is, however, rather time-consuming. For this reason this technique may not become the method of choice in every case.

Conclusion

Shear has two effects concerning the structure of charge-stabilized dispersions. First, it orients the colloid material such that the direction of closest packing equals the direction of the flow lines. Second, the material is ordered in layers parallel to the container walls. This was first shown by light scattering for highly dilute bcc dispersions by Clark et al. [19].

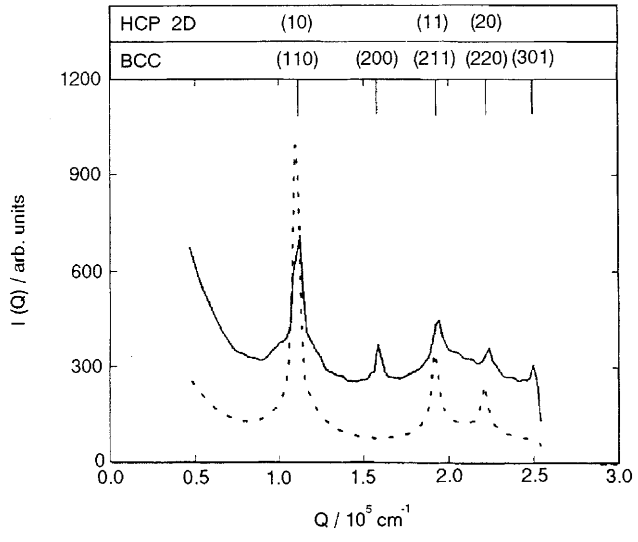

Fig. 8 Powder pattern of a 3D cubic and a 2D hexagonal layered system. Redrawn from Fig. 6 of Ref. [20]

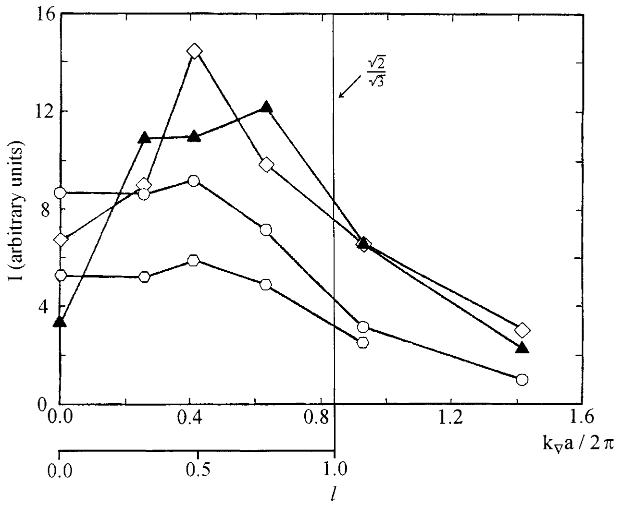

Fig. 9 Neutron-scattering intensity along a Bragg rod for several shear rates. The *triangles* represent the system at rest. Redrawn from Fig. 3 of Ref. [3]

Microscopic investigations as well as neutron-scattering experiments have confirmed this behavior. At higher concentrations, however, recrystallization and stacking of the hexagonal layers leads to fcc crystals. As previously pointed out, there exists a simple mechanism for hexagonal layers to form cubic crystals. Light-scattering experiments have demonstrated the usefulness of this approach at rather low particle concentrations. For larger volume fractions X-ray scattering or neutron scattering would be the proper experimental techniques. They have, however, not yet been applied to study the recrystallization kinetics of charge-stabilized dispersions.

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