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LETTER TO THE EDITOR

Formation of dried colloidal monolayers and multilayers under the influence of electric fields

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Abstract

In this letter I investigate the crystallization of colloidal monolayers and multilayers under convective self-assembly using inclined deposition and under the influence of electric fields. Applying a periodic external field during the crystallization process parallel to the substrate and perpendicular to the growth direction of the layer, the particles order along the field lines and attach as strings to the crystalline interface. The crystalline interface itself melts and freezes periodically due to the applied shear; grain boundaries can be annealed and the formation of large monocrystalline arrays on a very short timescale can be observed. Application of electric fields may thus yield a significantly improved quality of the resulting synthetic opals.

(Some figures in this article are in colour only in the electronic version)

Crystalline arrays of colloidal particles (colloidal crystals, synthetic opals, photonic crystals) show interesting optical properties with potential application as new types of optical grating, optical filter, antireflective coating and selective solar absorber, and in data storage and data processing [1]. In particular, such colloidal crystals serve as a starting material for producing 3D photonic band gap materials [2]. Structures based on a fcc crystal have an approximately spherical Brillouin zone and wide band gaps. Crystalline defects break the symmetry of the crystal and create defect states which can destroy the photonic band gap [3, 4]. Therefore it is necessary to prepare dried colloidal crystals with fcc structure, large monocrystalline areas, and a minimal number of stacking faults, packing faults, dislocations and bad spots. Consequently there is great interest in having methods available for preparing high quality dried colloidal crystals in a fast and reproducible way.

Colloidal suspensions of spherical particles are valuable model systems in which to study the physics of many body systems in general. The formation of colloidal crystals in suspension and the phase behaviour of such systems has been studied for many years [5, 6]. In sterically

stabilized systems, crystals form at a volume fraction larger than 49.4% for entropic reasons. In hard sphere suspensions, homogeneous nucleation leads to a polycrystalline material with a rhcp structure. In charge stabilized systems the fluid–crystal phase transition is observed at much lower volume fraction (about 0.1%) if the amount of screening electrolyte is kept low. Here crystals with a twinned bcc structure or with a rhcp structure are observable—as a function of the volume fraction and the salt concentration. To obtain colloidal crystals for technical devices a number of special preparation methods were used. Gravity sedimentation of colloidal particles is a very simple and popular method [7]. The disadvantage of this method in general is the resulting polycrystalline sample of small domain size and a crystallization time of the order of weeks or months. To fabricate colloidal crystals more efficiently, more sophisticated procedures have been developed such as colloidal epitaxy [8], spin coating [9], electrodeposition [10], flow through very thin cells (physical confinement) [11], polymerization of the solvent in the crystalline state [12] and controlled drying (capillary forces, convective self-assembly) [13–15]. All these methods yield large arrays and some of them are rather quick. However, stacking faults, point defects, dislocations, polycrystallinity and cracks are still abundant. Also the reproducibility of the results remains a challenge.

On the other hand, it is known that shearing fields can induce an ordered structure in colloidal suspensions, depending on the shear rate, volume fraction and salt concentration. It is possible to prepare large oriented crystals in colloidal suspensions using shear during the crystallization process in combination with a restricted geometry [16–18]. In the present letter I shall use shear forces to improve the quality of colloidal monolayers grown by inclined deposition. I investigated the formation of the colloidal arrays by light microscopy and using light scattering.

We prepared the colloidal arrays with the inclined deposition method following Dimitrov and Nagayama [14]. Here a drop of suspension is placed onto an inclined substrate. A straight contact line is formed at the upper end of the wetted area and during the evaporation process unidirectional growth of the colloidal array appears. On the substrate a wetting film is formed with a suspension–air interface inclined to the suspension–substrate interface. This causes a film thickness decreasing from the bulk suspension to the suspension–substrate–air interface. If the film thickness is in the range of the particle diameter, the particles are pulled to the suspension–substrate–air interface by capillary forces and in addition by a water flux caused by evaporation, so the crystalline array nucleates. The water evaporation from the freshly formed particle array causes a water flow from the bulk suspension into the array. This water flow further transports particles to the crystalline interface, the particles attach to the crystal and the array grows. This type of crystallization has been termed convective self-assembly and is further closely related to the well known coffee ring problem, where, however, most often disordered deposits were formed [19].

In my experiment a border made of Teflon is pressed on the substrate to get a well defined drop form in a restricted geometry (see figure 1). The Teflon border has a rectangular shape (20 mm $\times$ 23 mm), a thickness of 3 mm and an inner angle of 30°. Due to the contact angle of 120° of water and Teflon, a flat water surface parallel to the substrate can be prepared. To apply an electric field parallel to the substrate and parallel to the contact line, platinum electrodes with a thickness of 1.5 μm were used which are positioned on the substrate at a distance of 19.9 mm. I used charge stabilized suspensions of polystyrene spheres with particle diameters of 1.8, 1.4 and 1.0 μm (IDC Batch Nr/CV: 1098/3.6%; 970/3.5%; 754.1/2.4%). For dilution of the stock solution to a definite volume fraction, deionized water for a MilliQ water system was used. The glass substrates are first cleaned with hot sulfuric acid for 12 h; then they are rinsed with ultrapure water and dried under a stream of nitrogen. The platinum electrodes are fixed on the substrate and the Teflon border is pressed on it. A drop of 200 μl suspension is placed

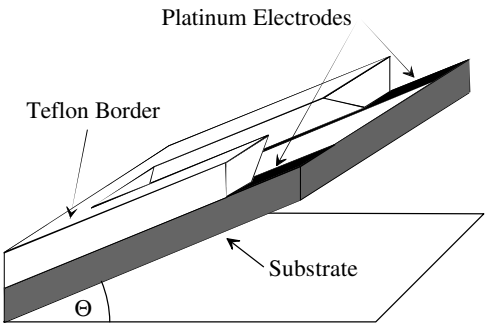

Figure 1. The experimental arrangement used for preparing the crystalline colloidal layer (schematic).

on the substrate and the set-up is inclined at a desired angle Θ. During the layer formation a low frequency ac voltage of 1–10 Hz is applied over an amplitude range of 0.5–5 V peak to peak. All experiments were done at a temperature of 22 °C and under a humidity of 60%. The wettability of the substrates is kept constant by the cleaning procedure. The particle size and charge and the volume fraction were varied. The inclination angle of the substrate was 7°. The particle array formation was observed using a Leica IRB inverse microscope.

In figures 2 and 3 the formation processes with and without electric field are shown under identical boundary conditions. The particles have a diameter of 1.4 μm and the sizes of the pictures are 553×419 μm^2. In both experiments the growth velocity is about 0.4 cm h^{-1}. Figure 2 shows the formation of a colloidal monolayer without applying an electric field. The time interval between this two pictures is 2.5 min. On the left-hand side of the picture the fluid bulk suspension is shown; the separated particles can be observed. The right-hand side shows the polycrystalline densely packed monolayer formed. Due to the low magnification (resolution), single particles cannot be seen, but dislocations, bad spots and grain boundaries can be easily identified. The grain boundaries in the resulting material are aligned approximately perpendicular to the fluid–crystalline interface. In the grains there are bad spots and dislocations observable. The main causes for the building of grain boundaries, dislocation and bad spots are inhomogeneities in the wetting conditions (curved wetting line), polydispersity, aggregates, dust and the adsorption of particles on the substrate in the bulk suspension.

Applying an electric ac field during crystallization, the particles order along field lines and build chains, so the particles can be ordered easily into the crystalline interface (figure 3). The time interval between these two pictures is 3 min. Depending on the electrophoretic mobility and the applied field strength and frequency, the particles move with an amplitude of 1–3 times their diameter in the bulk suspension. The electric field causes a shear gradient in the forming layer. In the dried area of the layer (the darker right-hand region in the pictures) the particles are fixed on the substrate and the particle mobility is zero. At the fluid–crystalline interface the particles have approximately the same mobility as in the bulk suspension. Going from the dried layer to the interface the particle mobility is increasing. Applying a homogeneous electric field causes a shear gradient in the layer which is increasing towards the interface. Using an ac field a time periodic shear gradient perpendicular to the growth direction of the crystal can be realized. As the crystallizing layer is sheared periodically and the fluid–crystalline interface melts and freezes periodically during the crystallization process. Due to this effect grain boundaries and defects can be annealed. The resulting grains contain areas of high quality crystalline material with potential for optical applications. Figure 4(A) shows a microscope picture of

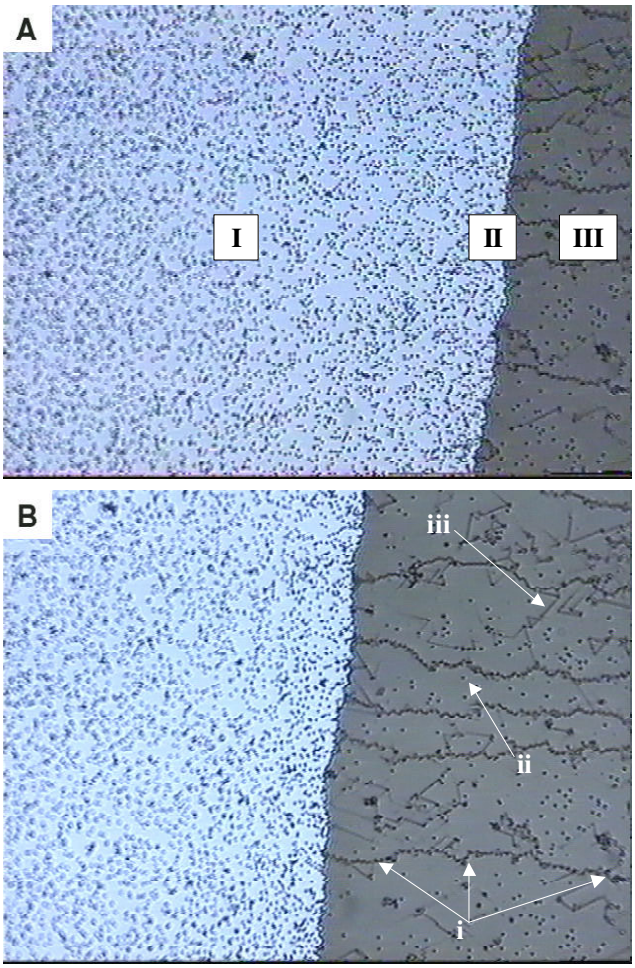

Figure 2. A series of two images (553 × 419 μm^2) of monolayer formation without applying an electric field. The time interval between this two pictures is 3 min. The particle diameter is 1.4 μm. The fluid bulk suspension is shown on the left-hand side (I). II indicates the fluid–crystalline interface and III the crystalline monolayer. In the crystalline layer, grain boundaries (i), bad spots (ii) and dislocations (iii) can be easily identified.

137.5 × 10^2 μm^2. There are no faults in the crystalline structure observable. Figure 4(B) shows a static light scattering pattern of the same area. The sample is illuminated with white light perpendicular to the (111) plane. The scattering pattern reflects the high quality of the prepared monolayer.

In the following I will compare the properties of the prepared layers without and with an applied electric field. Without an electric field, formation of large colloidal monolayers and multilayers up to several mm^2 with a constant number of layers can be observed. Altogether, 29 experiments were evaluated. The resulting material is polycrystalline with an averaged grain size of 0.05 mm^2, containing 1.73 × 10^4 particles in a monolayer and with a maximum grain size up to 0.33 mm^2 (1.19 × 10^5 particles). In the non-shearing case the number of grain boundaries stays nearly constant during the layer formation process. The content of bad spots

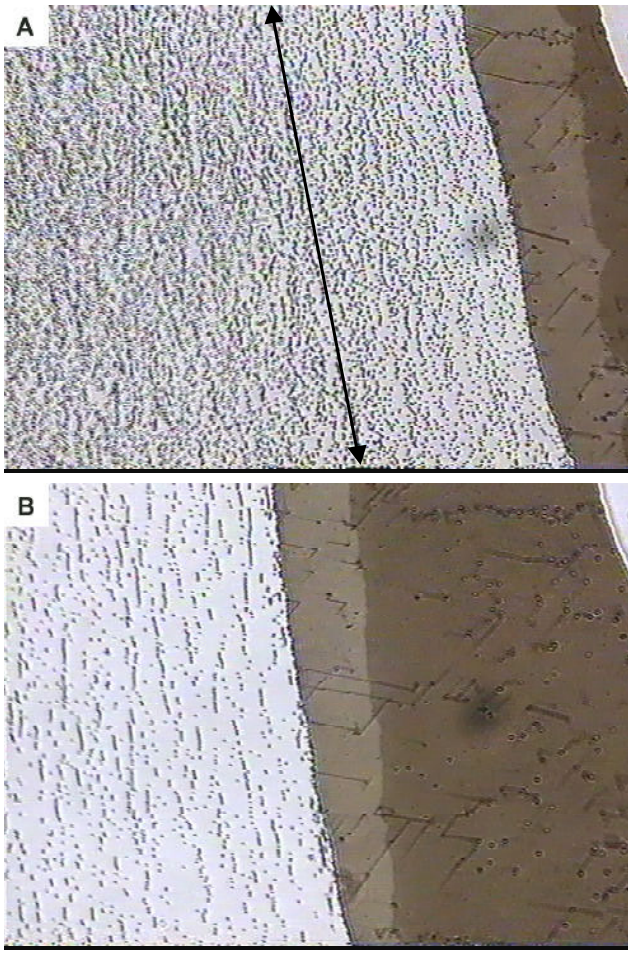

Figure 3. A series of two images (553 × 419 μm^2, 1.4 μm particles, time interval of 2.5 min) of monolayer formation applying an electric field parallel to the substrate and parallel to the crystalline interface. The direction of the ac field is shown by the arrow. The particles order along the field lines and attach as strings to the crystalline interface. The electric field causes a time periodic shear gradient in the growing layer. Due to the applied shear, grain boundaries can be annealed.

(No of bad spots/No of particles in the grain) is 0.31% and the content of dislocations (No of particles in the dislocation/No of particles in the grain) is about 3.512%. The biggest perfect crystalline areas contain about 2.1×10^3 particles in a monolayer.

Using a periodic shearing field perpendicular to the growth direction, better results can be achieved. With this method the area of monocrystalline regions can be increased up to an averaged size of 0.18 μm^2 containing 1.068×10^5 particles (26 experiments with a shearing field were evaluated). The maximum grain size is about 1 mm^2 (5.895×10^5 particles) which is built on a timescale of only three hours! In the grains the contents of bad spots and dislocations are 0.097 and 2.32%. The largest perfect layer contains 8.3×10^3 particles. Compared with the non-shearing method (see table 1) the averaged grain size can increase by a factor of 6, the maximum grain size by a factor of 5; the content of bad spots can be reduced by a factor of 3 and that of dislocations by a factor of 1.5. The number of particles in the perfect layer increases by a factor of 4.

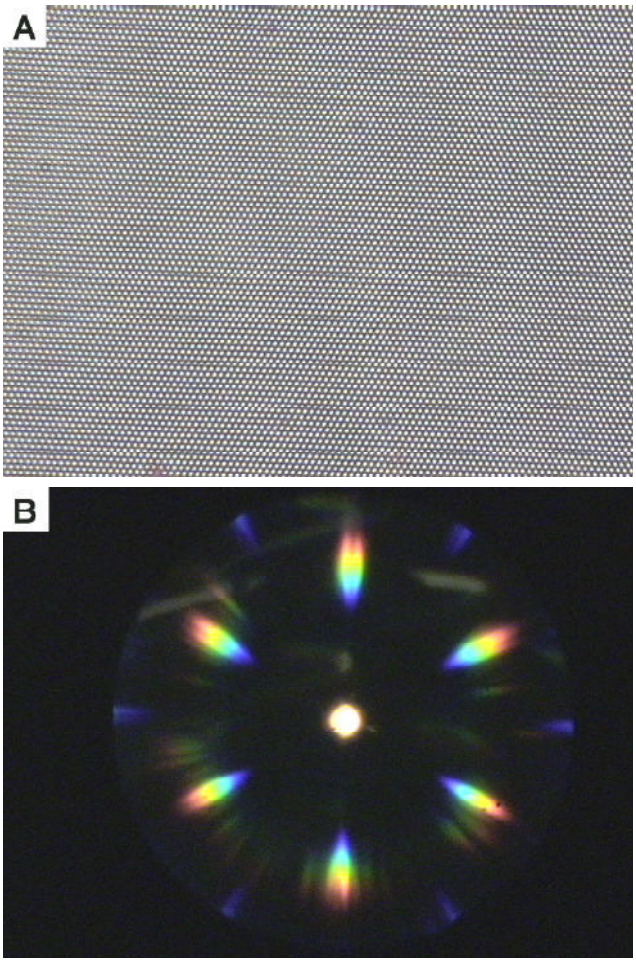

Figure 4. (A) An image (137.5×10^2 μm^2) of a high quality crystalline array. (B) The light scattering pattern of the array. The sample is illuminated with white light perpendicular to the (111) plane. The illuminated area is 137.5×10^2 μm^2.

Table 1. Comparison of the quality of the prepared crystals without and with a shearing field.

	Without field	With field
Averaged grain size	0.05 mm^2	0.18 μm^2
No of particles therein	1.73×10^4	1.068×10^5
Maximum grain size (mm^2)	0.33	1
No of particles therein	1.19×10^5	5.895×10^5
No of bad spots/No of particles in grain (%)	0.31	0.097
No of particles in dislocation/No of particles in grain (%)	3.512	2.32
No of particles in perfect layer	2.1×10^3	8.3×10^3

Both unidirectional flow and electric field have been used before to study the formation and quality of deposited crystals [10, 11, 13–15, 20, 21]. It is instructive to compare the present results to some of these findings. Kumacheva *et al* [20] combined flow with restriction of the

geometry of a 2D channel with a width of 2–15 particles. They observed a strong tendency of self-healing of defects and the repeated formation of meta-stable simple crystal structures instead of the formation of thermodynamically favourable superlattices of very large lattice constant. A similar effect is observed here. Referring to figure 2(B), just a minor fraction of bad spots leads to a long ranged disarrangement of the overall hcp lattice. Ristenpart *et al* [21] investigated the case of electric fields applied normal to the colloidal layer. They observed a pronounced dependence of the quality of the colloidal layer on the field frequency. In the experiments done here the ratio between field strength times particle mobility and field frequency determines the amplitude of the shear. Optimum annealing was obtained for particle elongations of 2–3 particle diameters. In addition the ratio between the velocity in the field direction and the velocity in the solvent flow direction, which is considerably faster than the interfacial growth velocity, seems to play a major role. For too large a ratio the interfacial region remains shear molten and solidifies upon solvent evaporation as a mainly disordered film. For very small ratios the situation approaches the field free case. The results shown here were obtained for ratios of the order of one.

In summary one can note that the formation of high quality crystalline layers with high growth velocity can be achieved by the use of a shearing field perpendicular to the growth direction. The proportions of grain boundaries and bad spots can be reduced noticeably; the proportion of dislocations can be slightly reduced. Grain boundaries are mainly caused by a curved interface at the beginning of the layer formation process. Resulting from the curvature of the interface, a global geometrical mismatch exists, which causes different orientations of the growing layer. A polycrystalline material is the result. Due to the periodic shear the number of grain boundaries formed can be reduced, whereby the stress in between the existing grains increases, so the number of grain boundaries can only be reduced to an equilibrium level. Dislocations are mainly induced by a local geometrical mismatch caused by polydispersity, dust or aggregates. Particles which are causing a geometrical mismatch represent a nucleus for the dislocation. The dislocations formed can be annealed during the growth of the layer, so their lengths can be reduced. Because the total number of nuclei remains constant, the total number of dislocations stays constant.

In this letter I have shown that applying a time periodic shearing field perpendicular to the growth direction improves the quality of the resulting synthetic opals. The best results in preparing dried colloidal crystals up to now were achieved using the vertical deposition method. In future we will combine the vertical deposition method with shearing fields, as suggested here, to prepare high quality dried colloidal crystals of controlled thickness on a short timescale.

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