Microscopic observations of ordering in dilute charged colloids

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Abstract. Ordering in dilute charged colloids is investigated using an optical reflection microscope, a video camera and an image processor. About six layers of colloidal crystal have been observed from the wall of the container. Grain boundaries, dislocations, voids and vacancies are observed along the depth of the colloidal crystal. The stable crystal structure and orientation of the crystal are identified and understood. The effect of the container wall on the ordering is analysed. The individual and collective motions of particles in the crystal are reported. The effect of aggregates on the crystalline order and the vibration of aggregates in the crystal are studied. The controversy over the inter-particle potential is addressed and the potential appears to have an attractive term like that in a Sogami potential.

1. Introduction

Ordering phenomena in dilute charged colloidal suspensions have been investigated intensively (Ise and Okubo 1980, Pieranski 1983, Hirtzel and Rajagopalan 1985, Kesavamoorthy *et al* 1989, Ise 1986, Ito *et al* 1988). Ise (1986) and Ito *et al* (1988) have carried out a detailed microscopic study on aqueous suspensions of polystyrene particles of diameter ranging from 0.25 μm to 0.5 μm with particle concentration of a few volume per cent. They have shown the coexistence of crystalline-like ordered phase and disordered phase, the dynamic character of the boundary between them and the thermal motion of particles at various temperatures in these phases. Their micrograph clearly shows the presence of ordered dense phase floating in a sea of disordered rare phase. They have concluded that this phase separation is due to the presence of an attractive term in the inter-particle potential like that in a Sogami potential (Sogami 1983). In favour of this conclusion Ito *et al* (1989) have demonstrated the phenomenon of Ostwald ripening in the growth of colloidal crystals using an optical microscope. Okubo (1987a, b) has observed only the ordered phase in colloidal suspensions of particles of diameter ranging from 0.37 μm to 1.02 μm by ultramicroscopy and concluded that the attractive term in the inter-particle potential is not needed and that the Yukawa potential (Verwey and Overbeek 1948) is good enough. Arora *et al* (1988) have studied the re-entrant phase transition in dilute charged colloids at various impurity concentrations and particle concentrations and concluded that a Sogami potential is needed to explain the features of the phase separation. They have shown that the homogeneous disordered colloidal suspension phase-separates into ordered (crystalline or liquid-like) dense phase and disordered rare phase and then transforms into a homogeneous ordered single phase as

the impurity concentration is reduced continuously. In the homogeneous ordered single phase, an unambiguous choice between Sogami potential and Yukawa potential could not be made (Tata *et al* 1989). The controversy on the potential still remains (Overbeek 1987).

An important aspect about which very little is known is the effect of the container wall on the phenomena of ordering. Pansu *et al* (1983) have studied thin layers of colloidal crystals of 1.1 μm particle diameter confined between two glass plates. When the two plates form a wedge a continuous passage from two to three dimensions was realised. There was no particle in the wedge up to a thickness of 1.43 μm. They have claimed that, though a particle of 1.1 μm diameter can be found in this region of the wedge, repulsion due to the plates forming the wedge caused the particle to move away. Pieranski *et al* (1979) have observed a system of concentric dislocation loops in colloidal crystal confined between a glass plate and a glass sphere. Clark *et al* (1979) have developed colloidal single crystals in thin rectangular cells. They used 0.109 μm and 0.234 μm diameter particles with 0.1 volume per cent in aqueous suspensions. They identified the structure to be BCC with (1 1 0) plane parallel to the container wall. The crystal shear-melted on rocking the suspension. If the rocking was stopped suddenly, polycrystalline order was formed. If it was stopped slowly, randomly packed two-dimensional HCP layers oriented parallel to the container wall were formed. This structure was unstable and in several hours a single crystal of BCC structure with [1 1 0] plane parallel to the wall was formed. On the other hand, the micrographs reported by Ise (1986) and Okubo (1987a) on a few volume per cent polystyrene suspensions of 0.5 μm particle diameter have all shown the hexagonal arrangement in all layers parallel to the container wall. The effect of the container wall on ordering has not been analysed thoroughly.

Another interesting aspect of the colloidal crystal is its defects. The lattice distortion around a point defect, a line defect, etc, are very well known in atomic systems (Hirth and Lothe 1968). But very little has been reported in colloidal crystals. It is known that the particles aggregate if the impurity concentration is high enough (Castillo *et al* 1984). These aggregates are the defects in the colloidal crystal. Their behaviour in the crystal is not yet known.

In this work, we report direct microscopic observation of ordering in an aqueous suspension of polystyrene particles of diameter 0.53 μm with volume per cent ranging from 0.05 to 2. We observed about six layers of ordered structure below the container wall. We present micrographs showing the structure and orientation of the crystals, grain boundaries, dislocations, voids and point defects. The interesting features of the behaviour of aggregates of a few particles are also given. Importantly, the effect of the glass plate on the phenomena of ordering is investigated. The collective and individual motions of the particles in the suspension are reported. Finally, an attempt to address the controversy over the inter-particle potential is made on the basis of our observations.

2. Experimental details

The monodisperse aqueous suspension of polystyrene spheres of 0.53 μm diameter with 2.5 volume per cent (from Polysciences Inc., USA) was kept in the ultrasonic vibrator for a few minutes in order to disperse the loosely bound aggregates. This suspension was then passed through a column of mixed-bed ion-exchange resins (cation, Ambercep 252; anion, Ambercep 900) repeatedly. After it reached a conductivity of about 0.5 μS
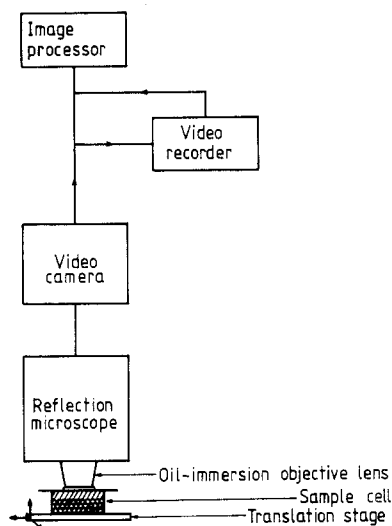
Figure 1. Schematic diagram of the experimental set-up.

cm^{-1}, it was sealed in the observation cell with various volume per cent ranging from 0.05 to 2 by dilution. The cell is a cylindrical quartz tube of 1 cm diameter and 1 cm height. The top and bottom annular (1 mm thick) surfaces are ground and polished to a fine finish using 2.5 μm grade diamond paste. After cleaning with chromic acid and deionised water, this tube is closed on one side with a similarly cleaned glass plate of 133 μm thickness by applying epoxy resin (Araldite) outside the tube. The mixed-bed ion-exchange resin is taken in the tube to nearly three-quarters of its volume. The colloidal suspension filled up the rest of the volume. Another cleaned glass plate is carefully placed on the tube so that no air bubble is trapped inside. This top plate is also fixed using Araldite by applying it only to the outside. By a separate test we found that the Araldite leaches out ions in water. But, since the tube is polished flat and the Araldite is applied only outside, the contamination is not found to be significant. The ordered structure in this cell continues to exist even after a few months.

Owing to the higher density of the resins, they settled down in the cell. The region of observation was close to the top glass plate and was away from the resin and other walls of the cell by at least 2 mm. We used an optical microscope (Zeiss, FRG) in reflection mode as shown in figure 1 with oil-immersion objective (100×). The cell was kept under the microscope for at least half an hour and then the recording was started. The intensity of the incident light was kept at the minimum necessary level in order to avoid local heating. All observations and measurements were carried out after the suspension reached deionisation equilibrium and gravitational equilibrium. Kesavamoorthy and Arora (1985) reported that an aqueous suspension of polystyrene particles of diameter 0.091 μm confined in a cylindrical glass cell of 2 cm height having mixed-bed ion-exchange resins reached deionisation equilibrium within 10 days. This meant that the impurity concentration in the suspension decreased due to the action of the resins and within 10 days attained an equilibrium value depending upon the properties of the resins and the addition of the impurity from the walls of the container. During this period, the inter-particle spacing at any height was reported to change (Kesavamoorthy and Arora 1985). Okubo (1987b) also observed this effect and reported

that the equilibrium was reached in about 5 to 7 days for particles of 0.369 μm diameter. In view of these results, we started our microscopic observation after 10 days from the preparation of the sample cell. We shook the cell and placed it under the microscope. The density of the polystyrene particles we used was 1.05 g cm^{-3}. Kesavamoorthy and Arora (1985) reported that the effect of gravity on the suspension was considerable due to the difference in densities of water and particle. They observed that the particle concentration at the bottom of the cell increased while that at the top decreased and attained gravitational equilibrium in about 3 h for the deionised aqueous suspension of 0.091 μm diameter particles. They observed the change in the inter-particle spacing at a fixed height as a function of time and concluded that within 3 h the change had ceased. In a similar manner, we observed the change in the average inter-particle spacing of our deionised sample (diameter 0.53 μm, density 1.05 g cm^{-3}) from the time we placed it under the microscope. We found that the change had ceased within half an hour for all the samples and hence we started our observation after half an hour from placing the at least 10 days old sample cells under the microscope.

We could observe six layers of particles starting from the one just below the glass plate. The first layer (nearest to the glass plate) was clear, with good contrast between the particles and the background. The subsequent layers were less and less clear, with decreasing contrast due to the scattered light from other layers to the background. We calibrated the vertical movement of the cell so that quantitative measurement along the depth can be made. A video camera (Andrex, Denmark) is attached to the microscope. The poor contrast of the image is enhanced using an image processor (Andrex, Denmark). The use of the image processor circumvents the necessity of using high-speed film for taking micrographs. It has a provision to obtain an image in one frame time (40 ms). The micrographs presented in this paper are those of the images stored in the memory of the image processor and displayed on the monitor. The motion of the particles was studied by integrating the image over a number of frames. Relative motions were studied by freezing one frame and superimposing its negative image on the real-time image. The particles of the frozen frame appear darker, making them easier to tag.

3. Results and discussion

3.1. Structure of colloidal crystal

Figure 2 shows micrographs of the first two layers of the colloidal crystal having 0.73 volume per cent with various integration times. A few aggregates and vacancies are seen in this figure. The particles are arranged hexagonally. By storing one frame of the first layer in the image processor and overlapping the second layer on its negative image, we determined the distance between the particle of the second layer and that of the projection of the first layer to be $\sim 0.6d$, where d is the inter-particle separation. We found that this is the distance between the particles of any two consecutive projected layers. Moreover, we observed that the projected image of the first layer coincides exactly onto the fourth layer. The perpendicular distance between any two adjacent layers was $\sim 0.8d$. All these results confirm that the structure is FCC with (1 1 1) plane oriented parallel to the glass plate. Since the vertical movement of the microscope has been calibrated, the inter-particle separation (d) could be determined. The distribution of d is obtained from 200 pairs and is shown in figure 3. The distribution along the $[1\bar{1}0]$ direction in the first layer is shown in figure 3(a) and those along $[\bar{1}01]$ and $[01\bar{1}]$ are the same and shown in
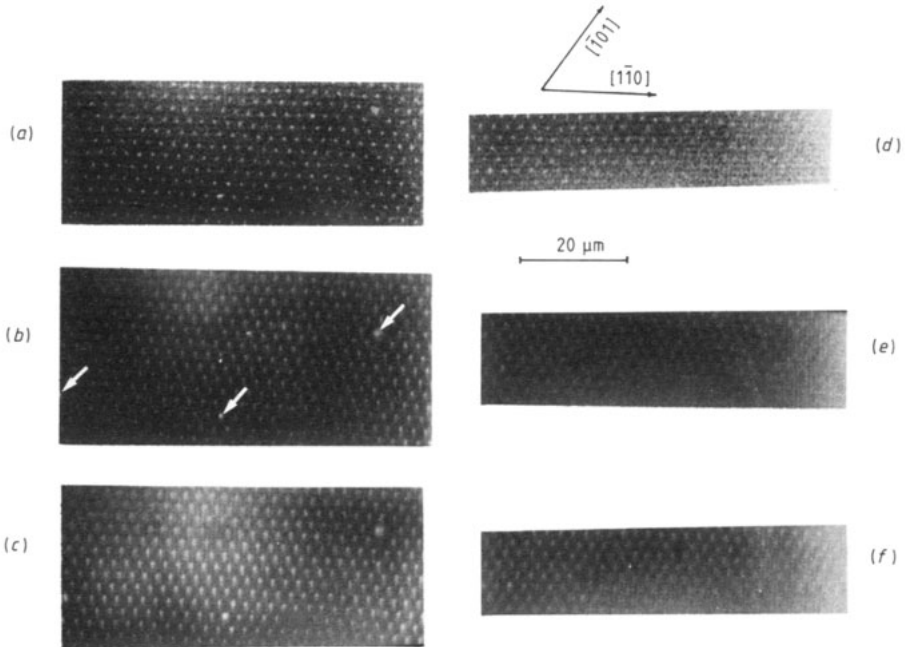
Figure 2. Micrographs showing crystalline-like ordered colloidal suspension of 0.53 μm diameter particles. Particle concentration is 0.73 volume per cent. The first layer of the colloidal crystal is integrated for 40 ms (a), 320 ms (b) and 10.24 s (c). The second layer is integrated for 40 ms (d), 320 ms (e) and 10.24 s (f). Marked spots are the aggregates that look brighter than other spots and have distortion around them. Note the hexagonal order. The spot size increases with the integration time. A few vacancies are also seen.
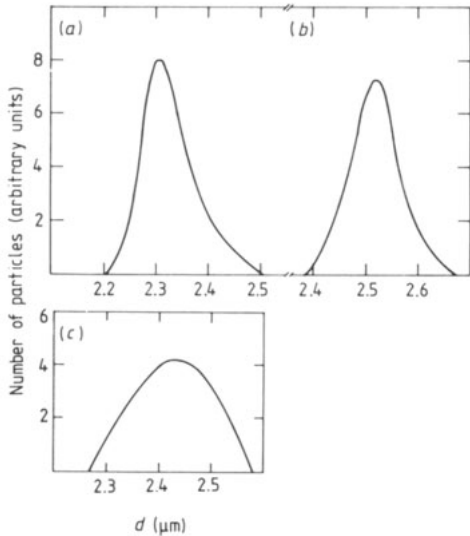

Figure 3. The distortion of the inter-particle separation d along the $[1\bar{1}0]$ direction (a) and along the $[\bar{1}01]$ direction (b) in the first layer and in any direction in the second layer (c). Figures 2(a) and (d) were used to obtain this distribution. The distribution is isotropic and has more spread in the second layer. The distribution in the first layer is anisotropic.

figure 3(b). The distribution along $[1\bar{1}0]$ peaks at 2.31 μm while that along $[\bar{1}01]$ or $[01\bar{1}]$ peaks at 2.51 μm. Both these distributions have a width of about 0.1 μm. Figures 3(a) and (b) show that the hexagonal ordering in the first layer is distorted. The weighted
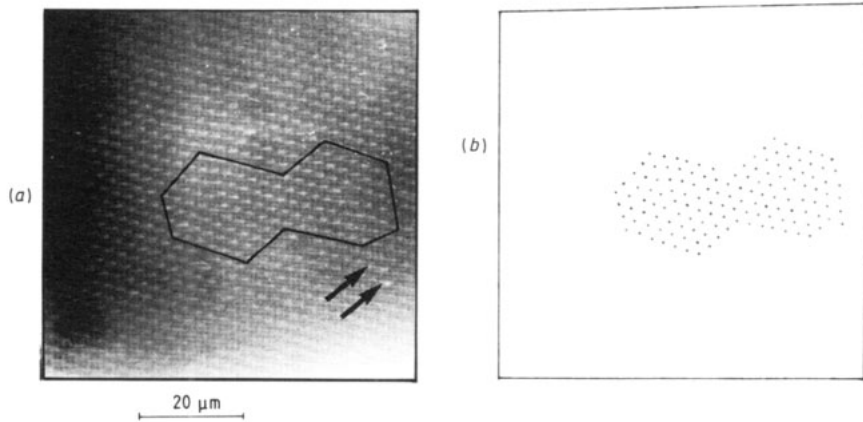
Figure 4. Micrograph of colloidal crystal of $0.53\,\mu m$ diameter particles integrated over 160 ms. Particle concentration is 0.73 volume per cent (a). Dislocation is seen in the encircled area. The lattice distortion around the dislocation is nicely seen. Marked spots are the aggregates. The centres of the spots in the encircled areas are shown in (b).

average of d in the first layer is $(2 \times 2.51 + 2.31)/3 = 2.44\,\mu m$. It is worth mentioning here that this micrograph has been taken after keeping the cell under the microscope for half an hour. The micrograph that has been taken after 1 day has shown the same distribution of d in all these three directions with a peak at $2.44\,\mu m$. This result shows that in half an hour the first layer is not fully annealed out. Similar features have been observed by Clark *et al* (1979). Figure 3(c) shows the distribution of d in the second layer. It is observed that this distribution is the same in all these three directions. It peaks at $2.43\,\mu m$, which is the same as that for the first layer. Its width, $0.21\,\mu m$, is larger than that of the first layer, indicating that the degree of ordering is less in the second layer.

The average sizes of the particle images in the first and second layers were determined from figures 2(a) and (d) by averaging over 200 spots. The spot size in the first layer comes out to be $0.86 \pm 0.05\,\mu m$ and that in the second layer is $0.95 \pm 0.06\,\mu m$. Since the diameter of the particle ($0.53\,\mu m$) is of the order of the wavelength of the light used, the image formed by the scattered light from even the static particle will have a distribution of intensity. It is very difficult to obtain the particle diameter from this image. But the observation that the spot size is larger in the second layer compared to that in the first layer indicates that the particle in the first layer has performed diffusion in 40 ms (time for one frame) to cover $0.86\,\mu m$ diameter spot and that the diffusion in the second layer is faster. This also indicates that the degree of ordering in the second layer is less than that in the first layer. On comparing figures 2(a), (b) and (c) or 2(d), (e) and (f), it is clear that the spot size increases with integration time. Figure 4 shows the micrograph of the first layer of the colloidal crystal having 0.73 volume per cent. Here, two dislocations and the lattice distortion around them are nicely seen. A few aggregates, looking brighter than the other spots, are also seen.

Lindsay and Chaikin (1982) have reported that the crystal structure of $0.109\,\mu m$ diameter polystyrene spheres in water as deduced from the Bragg diffraction is FCC for volume per cent greater than 3 and BCC for more dilute samples. The same conclusion is reached by Udo and de Souza (1980). But for higher-diameter particles ($\geqslant 0.5\,\mu m$) Okubo (1987a) observed FCC structure even at 0.262 volume per cent. Ito *et al* (1988) also observed FCC structure in a suspension of $0.25\,\mu m$ to $0.5\,\mu m$ diameter particles with
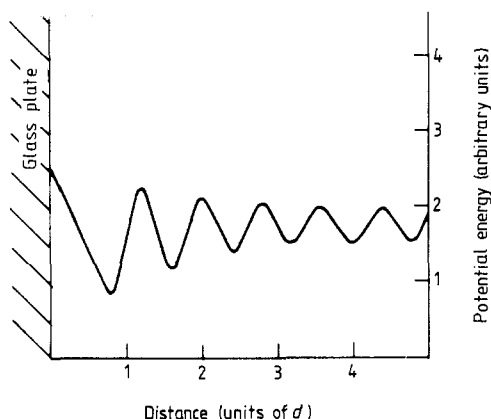
Figure 5. Qualitative representation of the effective potential energies near the glass plate. Note the modulation in the depth of the potential well along the distance, in units of d.

volume per cent of 0.5 (see also Ise *et al* 1989a). But BCC structure has not been reported yet for higher-diameter ($\geqslant 0.5$ μm) particles. Hence, the stability of the crystal structure appears to depend on both volume per cent and diameter, with FCC being favoured for large volume per cent or large diameter. We observed FCC structure in our sample of 0.53 μm diameter particles with volume per cent as low as 0.05%; of course, for low volume per cent the crystal was highly defective with a lot of grain boundaries, dislocations, voids and point defects.

3.2. Effect of the container wall

We observed that the first layer was at $\sim 0.8d$ from the inner surface of the glass plate. The inner surface of the glass plate was identified with the help of a few particles stuck to it. It is worth recalling that the observed distance between any two adjacent layers also was $\sim 0.8d$. The first layer followed the surface of the glass plate. To confirm this, we made the glass plate a little curved by applying pressure at the centre of the plate while fixing it using Araldite. In this cell, all layers were found to be curved in the same way as the plate. (The curvature was followed by observing the region of focus.) Hence it appears that there exists a deep potential minimum for the particles at a distance of $\sim 0.8d$ from the glass plate (see figure 5). From figure 2 it is obvious that the (1 1 1) plane of FCC is parallel to the glass plate. Clark *et al* (1979) have reported that the (1 1 0) plane of BCC in 0.109 μm diameter particle suspension with volume per cent 0.1 is oriented parallel to the container wall. The common feature in these planes ((1 1 1) of FCC and (1 1 0) of BCC) is that the planar density of particles is the maximum. This result implies that there exists a deep potential well near the glass plate (at a distance of $0.8d$) and the depth of this minimum decreases as one goes away from the plate as shown qualitatively in figure 5. The total potential energy is lowered by bringing the highest-density plane near to the plate (at a distance of $0.8d$) where the potential energy is the minimum.

There is more evidence for the existence of deep potential minima at about $0.8d$, $1.6d$, $2.4d$, etc., from the glass plate, with the depth being maximum at $0.8d$ and continuously decreasing away from the glass plate. We observed gas-like and liquid-like Brownian motion of the particles just after preparing the cell. We found that the density of particles was not uniform in the region of observation. We noticed a clustering effect of particles in layers at different distances from the glass plate. In other words, as we go away from the glass plate the particle density is modulated in layers with decreasing

extent of modulation. In addition to this observation, figure 2 shows that the spot size increases as one goes away from the glass plate, indicating that the extent of ordering in a layer decreases away from the glass plate. All these results point towards the fact that the potential well exists in layers parallel to the glass plate, with its depth decreasing away from the glass plate. This effect can be understood qualitatively in the following way. The polystyrene particles, the counter-ions and the impurity ions induce image charges of opposite sign and the same magnitude inside the glass plate with which they interact. The resultant interaction causes the modulation in the potential as shown qualitatively in figure 5. As one goes away from the glass plate, the modulation decreases due to larger and larger distances from the images. A detailed calculation of potential energy near the glass plate is to be carried out to explain the effect of the glass plate quantitatively.

Sometimes, we observed flow of the crystal. The collective movement of all the particles in the first layer is shown in figure 4. In this figure, a few dislocations are also seen. This micrograph is obtained by integrating the image over four frames (i.e. 160 ms). The image of each particle in figure 4 is nearly the same and is quite different from that shown in figure 2. The spot size in figure 2 is 0.86 μm whereas the physical diameter is only 0.53 μm. The apparent increase in the size is attributed to the extent of movement of the particle in 40 ms (one frame time). Hence, the image of the particle in figure 4 is due to the movement of the particle in 160 ms. It is very clear that the image is not circular. It is observed that the particles collectively drifted along the long axis while they perform random motion around the equilibrium position. The collective drift velocity is deduced from figure 4 as 7.5 ± 0.08 μm s^{-1} by measuring the long axis of the image and subtracting the short axis. The extent of individual random motion is deduced by measuring the short axis (spread of the image perpendicular to the long axis). It comes out to be 1.33 ± 0.06 μm. We observed the same collective drift velocity in all other layers, also indicating the flow of the crystal as a whole. The interesting feature to be mentioned here is the fact that the movement of all the particles in any layer is always parallel to the glass plate. No particle was found to drift perpendicular to the layer. The observed drift of the crystal might be due to a possible convection current of the solvent in the sample cell. Since the region of observation is close to the glass plate ($\sim$5 μm) the flow of solvent will be restricted parallel to the glass plate. The particles might be moving along with the solvent.

More interestingly, we have observed the coexistence of (1 1 1) plane and (1 0 0) plane of FCC in a layer for the samples with volume per cent between 0.3 and 0.05, while for volume per cent above 0.3 only the (1 1 1) plane has been observed. Figure 6 shows the coexisting orientations. Within a few hours after shaking, we found that the first layer with (1 1 1) planes and (1 0 0) planes existing in different grains is at a distance of $\sim$0.8d and the similar second layer is at $\sim$1.6d and so on. But after a day or so the same sample showed a first layer with (1 1 1) and (1 0 0) planes at 0.8d but the second layer was broken into two, with one sublayer containing (1 1 1) planes at 0.8d from the first layer and the other containing (1 0 0) planes at 0.7d from the first layer. Other layers were also broken in a manner consistent with a perfect FCC structure with different grains having (1 1 1) or (1 0 0) orientation parallel to the glass plate. The reason for (1 0 0) planes of FCC being parallel to the glass plate in some grains at lower volume per cent is not yet clear but it may depend on the effect of induced images in the glass plate and on the low volume per cent.

Our report on the effect of the glass plate on the ordering would not be complete if we did not mention the behaviour in the case of an uncleaned glass plate. A few sample
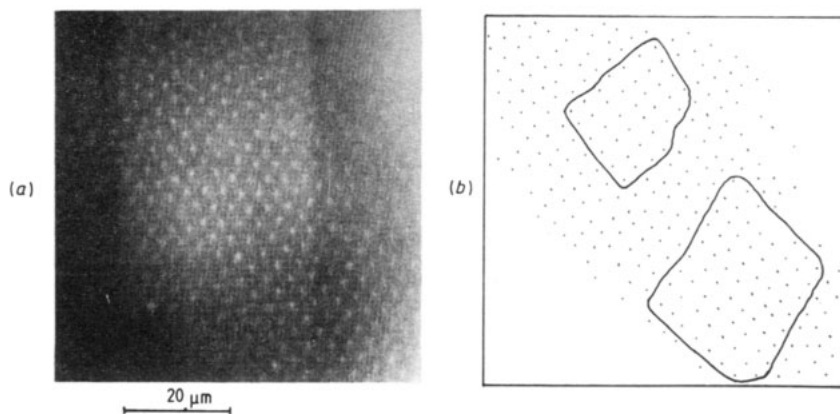
Figure 6. Micrograph showing the coexistence of (1 1 1) and (1 0 0) planes of FCC structure aligned parallel to the glass plate (*a*). Diameter of the particle is 0.53 μm. Particle concentration is 0.3 volume per cent. The centres of the spots of this micrograph are shown in (*b*). Grain boundaries are marked in (*b*).

cells were prepared after thoroughly cleaning the glass plates with chromic acid while a few others were prepared without cleaning. We observed that the polystyrene particles were stuck to the uncleaned glass plate. They were stuck at random with some distance from each other. They did not fill the surface of the glass plate. No two particles were sticking together. In this cell also, the first layer of crystalline order was seen at $0.8d$ from the surface of the glass plate. However, we did not find any polystyrene particle stuck to the cleaned glass plate. The reason may be the following. There may be a layer of oil or grease or some oxidisable impurity sticking to the glass plate. Just after preparing the cell, the gas-like Brownian particles reach the glass plate by thermal motion and there they are chemisorbed onto the impurity layer. However, these stuck particles have effective negative charges to repel any other particles coming very close to them. Since chromic acid oxidises the impurities and removes the greasy layer, the clean plate does not chemisorb the polyballs.

3.3. Behaviour of aggregates

Polystyrene particles in aqueous suspension are stabilised electrostatically (Castillo *et al* 1984). There is a Coulomb barrier between these particles, which prevents them coming into contact with each other. This barrier reduces in height and width if the impurity concentration increases. A few particles cross over this barrier at appropriate impurity concentrations by thermal motion and form an aggregate of particles separated by ~ 10 Å surface to surface. In our samples, we have observed aggregates of two, three, four and more particles. The brightness of an aggregate is more than that of a single particle as shown in figure 7. This feature is observed in figures 2 and 4 also. The brightness increases with the size of the aggregate. This is so because single particles separated by ~ 2 μm scatter the incident light of ~ 0.5 μm wavelength incoherently while particles separated by ~ 10 Å surface to surface scatter it partially coherently. Since the coherently scattered intensity goes like n^2 while the incoherently scattered intensity goes like n (where n is the number of scatterers in the scattering volume) (Kerker 1969), the brightness increases with the size of the aggregate.

20 µm

Figure 7. Micrograph of the second layer of the colloidal crystal of 0.53 µm diameter particles. Integration time is 160 ms. Particle concentration is 0.73 volume per cent. A number of aggregates brighter than the single particle are found in substitutional positions.

We have observed that the coordination number in a layer around an aggregate is larger than 6. It varies from 6 to 9. In figure 2, the aggregates have the planar coordination numbers 6, 7 and 9 while in figure 7 all have coordination number 6. The aggregate is found often to be accompanied by a vacancy. At many places the aggregate sits in the in-between position of two neighbouring vacancies. Hence, the planar coordination number around such aggregates is higher than 6. Very often we find that a dislocation ends at an aggregate and a grain boundary passes through the aggregate. This is so because the change in the coordination number and distances induced by the aggregate may be favourable enough for a dislocation to end and a grain boundary to pass through. The interesting observation is that the nearest-neighbour distances around an aggregate having planar coordination number 6 are only slightly more than average. This increase in the distance increases with the size of the aggregate. It is noted that the surface-to-surface distances from the aggregate and its nearest neighbours are nearly the same and equal to that between single particles. This is understandable in the sense that the charge of a particle resides on its surface and the surface charge density in an aggregate is the same as that of a single particle. It is observed that, in a linear aggregate of three particles, the first coordination shell is elongated in the direction of the aggregate. This is the case for two-particle aggregates also.

Another interesting feature about the aggregates is their vibration. The aggregates vibrate more than does a single particle. These vibrations are directional. A single particle can vibrate equally in all directions. But, we found that an aggregate of two particles vibrates much more in the direction along the line joining their centres. Ocassionally the line of centres turns in the layer about a vertical axis. Three-particle aggregates are found in different shapes. The line of centres of a linear aggregate (∗∗∗) turns in the layer about a vertical axis very rarely. The end particles vibrate vigorously. The five o'clock aggregate (∗∗∗) changes its shape often to seven o'clock (∗∗∗) and so on back and forth. The triangular aggregate vibrates less compared with the other two shapes of three-particle aggregates. We could not observe transitions from one shape to another among linear, five o'clock and triangular three-particle aggregates during the period of observation (∼10 h). We found a square type as well as a pyramid type of four-particle aggregates. They vibrate much less compared with other aggregates.

All these observations are qualitative. More work is to be done to quantify the vibration of aggregates and the arrangement of particles in them. The vibration can be

studied in detail by following the centres of the particles of an aggregate in time using the method of Ise *et al* (1989a). To study the arrangement of particles in an aggregate, three-dimensional information is required.

3.4. On the inter-particle potential

There is controversy over the inter-particle potential in polystyrene suspensions. Ito *et al* (1988, 1989), Ise (1986) and Ise *et al* (1989a) claimed that an attractive part in the inter-particle potential is a must in order to explain their observation of two-state coexistence with different particle concentrations and Ostwald ripening phenomena during growth of the crystalline-like ordered phase. On the other hand, Okubo (1987a) claimed that an attractive part in the potential is not needed and only a repulsive Yukawa potential (Verwey and Overbeek 1948) is good enough. He came to this conclusion on seeing the hexagonal arrangement of particles everywhere parallel to the bottom of the cell. Arora *et al* (1988) observed that the gas-like disordered homogeneous suspension phase-separated into a particle-rich phase and a rare phase when the impurity concentration (C) was reduced. The particle-rich phase might be crystalline-like ordered or liquid-like ordered depending on the particle concentration and C, whereas the rare phase was gas-like disordered. When they reduced C further, they observed a re-entrant homogeneous suspension with liquid-like order. They used the Sogami potential (having an attractive term in the inter-particle potential) (Sogami 1983) to explain all these effects. The interesting feature of their work is that the potential minimum lies in the region of $r < \bar{r}$ (average inter-particle separation) in the phase-separated suspension. But, for a homogeneous liquid-like ordered suspension, it lies in $r > \bar{r}$ and hence the repulsive part plays a dominant role. The behaviour of the second minimum in the DLVO potential (Verwey and Overbeek 1948) could not explain the above observed phase-separation phenomena (Arora *et al* 1988). Tata *et al* (1989) attempted to find the appropriate potential (either the Sogami potential or the Yukawa potential) for a homogeneous liquid-like ordered colloidal suspension using a simulation technique and concluded that both potentials could explain the liquid-like order for different values of C within the experimental error. Overbeek (1987) showed that the attractive term in the Sogami potential disappeared if another formalism (in his view, the correct formalism) was used. But Ise *et al* (1989b) claimed that the argument of Overbeek (1987) violated the Gibbs–Duhem equation, one of the fundamental axioms of thermodynamics. The controversy still remains.

In this paper, we are again addressing this controversy and show evidence supporting the Sogami potential. We did not observe a two-state coexisence but observed crystalline-like ordered phase everywhere in the layer. Figure 8 shows the presence of a void in the crystalline-like ordered suspension. In this figure, only the cross section of the void in the first layer is shown. We observed that the void extended well in the third dimension. It was a three-dimensional void and not a platelet. Above this void, the container wall was clean and did not have any abnormality. We found that the void was stable over the period of our observation (about 10 h). We observed that different voids had different shapes and noticed a few voids away from the first layer. Hence we feel that the effect of the container wall might not be the reason for the existence of the void. As mentioned earlier, owing to solvent current the void was slowly drifting, maintaining its shape intact. We observed voids even in a sample a few months old. Recalling the fact that all our observations were carried out after the suspension reached deionisation
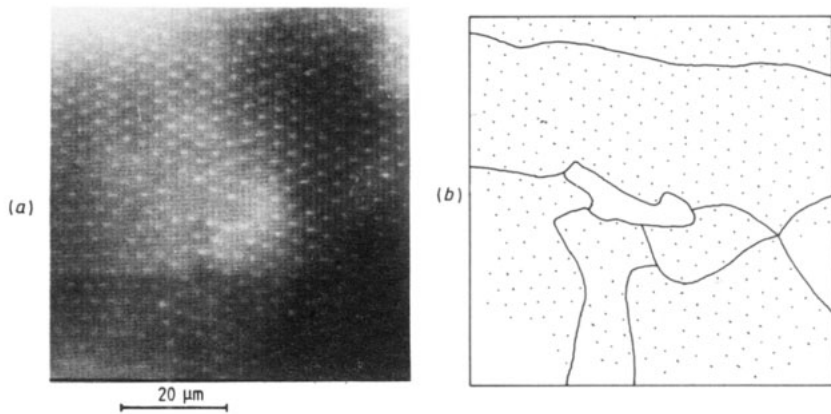
Figure 8. Micrograph of the first layer of the colloidal crystal of 0.53 μm diameter particles (*a*). Integration time is 160 ms. Particle concentration is 0.3 volume per cent. The centres of the spots of this micrograph are shown in (*b*). The boundary of the void and those of the grains are shown in (*b*).

equilibrium and gravitational equilibrium, we can ascertain that the void is a stable feature in the colloidal crystal.

If there exists only a repulsive part in the potential, the void cannot exist. Particles on the edges of voids will experience repulsion from all other sides except the void side. Hence these particles should move into the region of the void and the other particles will relax in such a way that the inter-particle spacing will be the same throughout. But, on the other hand, if there is an attractive part in the potential, then there exists a minimum in the pair potential. In the suspension that we observe, the impurity concentration may be low enough to cause crystallisation throughout the suspension. In this case, this potential minimum lies in $r > \bar{r}$. Hence, the repulsive part is the most dominant one in deciding the properties of the suspension. But when a void occurs, the particles along the edge of the void are free to relax towards the void. Since there exists a potential minimum at r_m ($> \bar{r}$), the edge particles are trapped in the well instead of going into the void. This situation gives a stable void, as we have observed. Also in this case, the inter-particle spacing along the edge of the void should be r_m (the position of the potential minimum) as against $\bar{r}$. Since $r_m - r$ is small and the inaccuracy in the measurement of r is large, we could not unambiguously demonstrate that r_m is greater than $\bar{r}$.

4. Conclusions

We have observed almost six layers of crystalline-like ordered colloidal particles, keeping track of their relative positions using an optical microscope, a video camera and an image processor. We have analysed the effect of the glass plate on the phenomena of ordering.We have reported the structure and orientation of the crystals, the individual motion and collective motion of particles, and the behaviour of aggregates in colloidal crystals. The stable configuration of particle aggregates and their light scattering efficiency have been demonstrated. Finally, the controversy over the inter-particle

potential in the colloidal suspension has been addressed, and the presence of stable voids appear to favour the Sogami potential.

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