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## The two-dimensional crystalline-like ordering at the surface of a bulk colloidal suspension

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**Abstract.** Ordering in dilute charged colloidal suspensions is investigated using an optical reflection microscope, a video camera and an image processor. The surface of the bulk suspension contained in a glass container is imaged and analysed. The fraction of six coordinated particles and the distribution of nearest-neighbour distances are computed from the micrograph and are used to characterize the degree of ordering in different layers. The degree of ordering is found to reduce from the surface layer towards the inner layers. The pair-correlation functions and angular correlation functions are computed from the micrographs. Algebraic decay of the pair correlation function and the distance independent angular correlation function indicates two-dimensional crystalline-like ordering of the particles at the surface of the bulk colloidal suspension. A possible cause for such an ordering is discussed.

### 1. Introduction

Ordering phenomena in dilute charged colloidal suspensions have been investigated intensively. Since the interparticle separation in these suspensions is of the order of the wavelength of visible light, light scattering has been used extensively to study the ordering of the colloidal particles in these suspensions. Static light scattering measurements (Schaefer 1977, Hartl *et al* 1983, Brown *et al* 1975, Kesavamoorthy and Arora 1985, Tata *et al* 1987, Kesavamoorthy *et al* 1988, Kesavamoorthy *et al* 1989a) on dilute charged colloidal suspensions have helped in understanding the structure and elastic properties of colloidal liquids, their mixtures and glasses and the phase transitions from liquid to crystalline or to glassy order. Bragg diffraction of laser light has been used to study the structure and elastic properties of colloidal crystals (Williams and Crandall 1974, Udo and de Souza 1980). Also, the dynamic light scattering technique has been used to study phonon dispersion, sound velocities, structure factor and diffusion characteristics in colloidal systems (Brown *et al* 1975, Schaefer 1977, Gruner and Lehmann 1982, Tsang and Tang 1982).

Optical microscopy is also widely used to see directly the arrangement of particles in monodisperse as well as binary suspensions in a variety of sample cell shapes (Pieranski 1980, Ise 1986, Pansu *et al* 1983, Kesavamoorthy *et al* 1989b, Yoshimura and Hachisu

1985). In addition to a number of investigations in three-dimensional colloidal suspensions, the optical microscopy technique has also been effectively used in two-dimensional colloidal suspensions. Pieranski (1980) formed a two-dimensional colloidal crystal at the air-water interface and studied it using an optical microscope. Pansu *et al* (1983) have studied thin layers of colloidal crystals confined between two glass plates using a microscope. When the two plates form a wedge a continuous passage from two-dimensional to three-dimensional ordering was realized. Microscopy has also been used to study the two-dimensional aggregation and crystallization of a colloidal suspension confined between two glass plates (Richetti *et al* 1984). The micrograph of a layer of colloidal particles in a bulk suspension has been analysed using a two-dimensional Fourier transformation to study the ordering phenomena (Ito *et al* 1988). Murray and Van Winkle (1987) have studied the melting transition in a two-dimensional colloidal suspension of charged polystyrene spheres confined between two flat glass plates which form a wedge. Recently Armstrong *et al* (1989) also studied the melting of two-dimensional colloidal monolayers on the surface of water using an optical microscope and computing the pair correlation function,  $g(r)$ , and the angular correlation function  $g_6(r)$  from the micrograph. They observed that the two-dimensional colloidal crystal of  $1.01 \mu\text{m}$  diameter particles melted by a weak first-order transition while that of  $2.88 \mu\text{m}$  diameter particles showed evidence of an intermediate hexatic phase before going to isotropic liquid.

Usually, a two-dimensional crystal is formed by spraying electrons on the surface of liquid helium (Grimes and Adams 1979), adsorption of Xe, Kr, etc on a substrate-like graphite (Abraham 1984), spraying organic surfactants on the surface of water (Kjaer *et al* 1987), etc. The  $g(r)$  and  $g_6(r)$  of these two-dimensional distributions of atoms or molecules show characteristically different behaviour when compared with those of three-dimensional distributions. In a two-dimensional crystal the heights of the peaks in  $g(r)$  show algebraic decay with  $r$  suggesting transitional quasi-long range order, while  $g_6(r)$  remains constant representing long-range orientational order (Kosterlitz and Thouless 1973, Nelson and Halperin 1979). On the other hand, in three-dimensional crystals, the  $g(r)$  shows sharp peaks of varying height for different  $r$  values, which is the characteristic of a long range translational order. The colloidal particles trapped at the air-water interface showed a two-dimensional crystalline order (Armstrong *et al* 1989). Few experiments have been carried out to investigate the melting phenomena in a two-dimensional colloidal suspension formed in a thin wedged glass cell or on the air-water interface (Clark *et al* 1983, Armstrong *et al* 1989). Murray *et al* (1990) have investigated the particle positions and trajectories of a layer of highly charged  $0.3 \mu\text{m}$  diameter polystyrene spheres in a water suspension using a digital imaging method. The layer was rigidly confined in two dimensions between two smooth glass plates. They varied the in-plane particle density and observed a two-stage melting transition.

Unlike metallic crystals, colloidal crystals require a container. Quartz or glass containers have been used to confine colloidal crystals. The quartz or glass container wall surfaces can also acquire a negative charge due to the dissociation of the OH group on the surface, making the particle-wall interaction predominantly repulsive in nature (Murray *et al* 1990). The effect of the container wall on the colloidal crystal has not been analysed thoroughly. Kesavamoorthy *et al* (1989b) have suggested that an electrostatic interaction among the charges in the suspension and their image charges induced in the container wall appear to be important in the phenomena of ordering. They came to this conclusion by noting the special features of the surface layer of the bulk suspension in comparison to other layers. They noticed that the degree of ordering in the surface layer

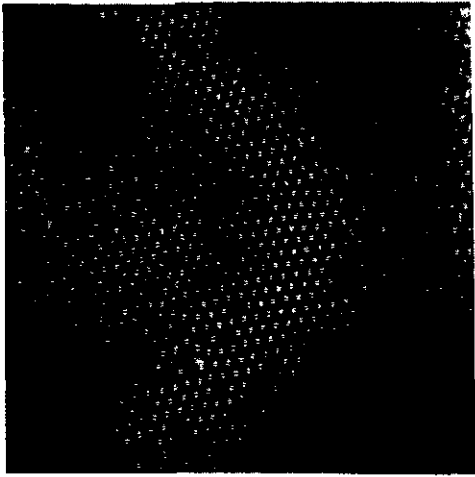
is larger than the other layers and the surface layer happens to be the high density plane of the corresponding crystal structure. They have conjectured that the image charge interaction potential must have a series of minima, with the value of the minima decreasing with the distance from the container wall. But the surface layer has not been investigated as to whether it has two-dimensional characteristics. In the absence of any calculation on the image charge potential, it is difficult to predict the behaviour of the surface layer of the bulk suspension.

In this work, we report the optical microscopic observation of the ordering of polystyrene particles of diameter  $0.53\ \mu\text{m}$  in an aqueous suspension. We have taken micrographs of the first layer (surface layer), second layer and fourth layer and computed  $g(r)$ ,  $g_6(r)$  and the fraction of the six coordinated particles from these micrographs with the aim of investigating the characteristic of ordering in the surface layer.

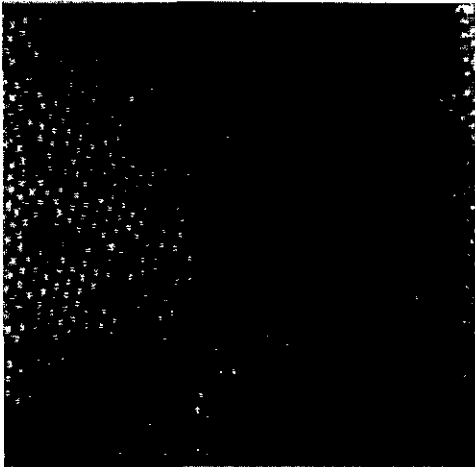
## 2. Experimental details

The monodisperse aqueous suspension of polystyrene spheres of  $0.53\ \mu\text{m}$  diameter and 2.5 vol. % (from Polysciences Inc, USA) was subjected to ultrasonic vibration for a few minutes in order to disperse the loosely bound aggregates. This suspension was passed through a column of mixed-bed ion-exchange resins (cation: Ambercep 252; anion: Ambercep 900) repeatedly. After it reached a conductivity of about  $0.5\ \mu\text{mho cm}^{-1}$ , it was sealed in the observation cell. The cell was a cylindrical quartz tube of 1 cm diameter and 1 cm height with the top and bottom surfaces nicely polished and closed with  $133\ \mu\text{m}$  thick glass plates. Epoxy resin (Araldite) was used at the outer side of the tube to close the cell. The mixed-bed ion-exchange resin was taken into the cell to fill nearly three-quarters of its volume and the suspension filled the rest without any air bubbles. Owing to the higher density of the resins, they settled down in the cell. The cell was shaken from time to time. It is known that the deionization equilibrium in such a sample is achieved in about 7 days (Kesavamoorthy and Arora 1985, Okubo 1987) and hence the observations were made only after about 10 days. 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 with an oil-immersion objective ( $\times 100$ ). The cell was kept under the microscope for about 3 h without disturbance and the observations were made later. This was to ensure that the sample had come to gravitational equilibrium (Kesavamoorthy and Arora 1985, Kesavamoorthy 1990). The intensity of the incident light was kept at the minimum necessary level in order to avoid local heating.

We could observe up to the sixth layer of particles starting from the one just below the glass plate. The surface layer (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 adding to the background. A video camera (Andrex, Denmark) was attached to the microscope. The poor contrast of the image was enhanced using an image processor (Andrex, Denmark). The use of the image processor circumvented the necessity of using high-speed film for taking micrographs. It had the 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.



(a)



(b)

Figure 1. Micrographs showing 2D crystalline-like ordered colloidal suspension of  $0.53 \mu\text{m}$  diameter particles; (a) the first layer; (b) the fourth layer (see text for further details).

### 3. Computation

We describe briefly in this section the method followed to compute the translational correlation function, orientational correlation function and the fraction of  $n$ -coordinated particles (where  $n$  is 1, 2, 3, . . . , 10) from the micrograph. The micrograph of the surface layer is shown in figure 1. The micrograph is nearly square in shape and contains typically 2000 particles. A simple program in advanced FORTRAN language is written to compute  $g(r)$  and  $g_6(r)$  and is executed on a personal computer (PC AT). The important logistics are explained here. The coordinates  $(x, y)$  of the centre of the particles from the micrograph are transferred to the PC AT using a digitizer. The error in identifying the centre of a particle is about  $0.01 \mu\text{m}$ . The coordination number could be defined by constructing a minimum area polygon made by the intersection of the perpendicular bisectors of the bonds joining a particle to a set of its nearest neighbours

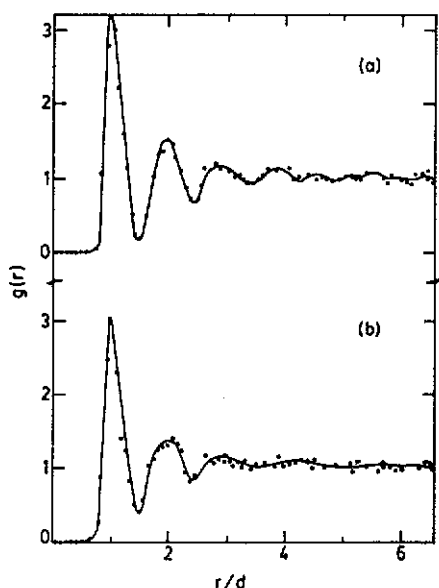


Figure 2.  $g(r)$  versus  $r$  (expressed in units of  $d$ ) for (a) first layer; (b) fourth layer.

(McTague *et al* 1980). However, it could also be obtained by defining the range of nearest-neighbour separation. The first neighbours are defined as the particles situated at  $r \leq 1.37d$  where  $r$  is the centre to centre interparticle distance and  $d$  is the average interparticle distance. This is justified since the first peak in the computed  $g(r)$  ends at  $r \approx 1.37d$  as seen in figure 2. An inner square is defined in the micrograph by leaving  $1.37d$  from the boundary of the micrograph. This is done to account for first neighbours for all particles in the inner square. For a particle  $i$  in the inner square, the bond orientational angle  $\theta_{ij}$  (which is the angle between the line joining the  $i$ th and the  $j$ th particles and some fixed axis) is calculated for all its first neighbours  $j$ . The maximum value of  $j$  for a particular  $i$  denotes the coordination number  $n_i$ , of the  $i$ th particle. The fraction of  $n$  coordinated particles  $f_n$  (the ratio between the number of particles with coordination  $n$  and the number of particles in the inner square,  $M$ , where  $n = 1, 2, 3, \dots, 10$ ) in the micrograph can also be computed using the expression

$$f_n = (1/M) \sum_{i=1}^M \delta(n - n_i).$$

In order to compute  $g(r)$  and  $g_6(r)$ , another inner square is defined by leaving distance  $R$  from the boundary of the micrograph, where  $R$  is the range of  $r$  up to which  $g(r)$  and  $g_6(r)$  are required to be computed. This range of  $r$  is divided into many windows depending on the resolution ( $\Delta r$ ) required. For each particle  $i$  in this inner square, the interparticle distance  $r_{ij}$  is calculated where  $j$  is the particle anywhere in the micrograph and the occupation number of the corresponding window for the value of  $r_{ij}$  is incremented by one. This distribution  $N(r)$ , is averaged over  $i$ .  $g(r)$  is computed as  $N(r)/2\pi r \Delta r \rho$  where  $\rho$  is the average number of particles per  $\text{cm}^2$ .  $g_6(r)$  is computed from the expression  $g_6(r) = \langle \Psi_6(r) \Psi_6(0) \rangle / g(r)$  where  $\langle \dots \rangle$  denotes the average over  $i$ . Here

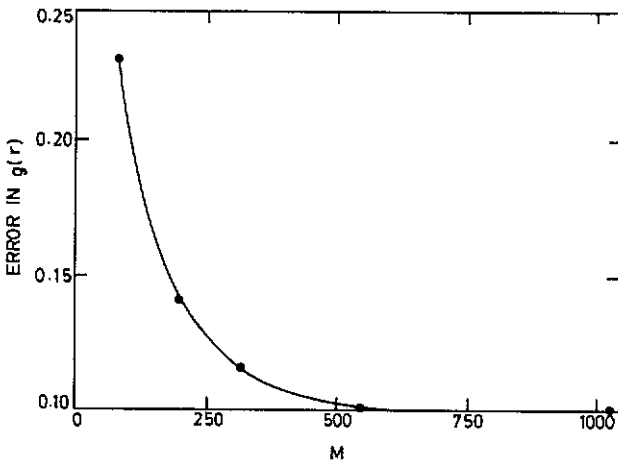


Figure 3. Error in  $g(r)$  versus number of particles ( $M$ ) over which the average has been taken to obtain  $g(r)$ .

$\Psi_6(r)$  is given as

$$\Psi_6(r) = \frac{1}{M} \sum_{i=1}^M \delta(\bar{r} - \bar{r}_i) \left[ \frac{1}{n_i} \sum_{j=1}^{n_i} \exp(i6\theta_{ij}) \right]$$

where  $\underline{i} = \sqrt{-1}$ , and the procedure of defining an inner square and taking the  $i$ th particle in it, avoids the boundary effects.

Figure 3 shows the error in  $g(r)$  versus the number of particles ( $M$ ) over which the average has been taken to obtain  $g(r)$ . We have computed  $g(r)$  using the above program for the published micrograph (figure 3 of Ise *et al* 1989). This micrograph has been used since it represents a weakly interacting system of colloidal particles and also since it contains a large number of particles (about 3000). The error in the computed  $g(r)$  is determined for various values of  $M$  at a large distance where  $g(r) \approx 1$ . Here  $M$  is the total number of particles in the inner square. For the same micrograph the inner square is defined with various lengths in order to have different values of  $M$ . From figure 3, it is observed that the error is high for small values of  $M$  but it decreases sharply as  $M$  increases and attains a saturation at about  $M = 500$ . This figure gives an idea about the value of  $M$  which is to be employed in the computation of  $g(r)$  and  $g_6(r)$  from our micrographs. The micrographs presented in this paper contain about 2000 particles and a value of  $M$  for the reported  $g(r)$  and  $g_6(r)$  is greater than 500. We have computed the error in  $g(r)$  for various values of  $M$  for our micrographs and found that it typically follows figure 3.

#### 4. Results and discussion

Figure 1 shows the micrographs of the surface layer and the fourth layer of an aqueous suspension of  $0.53 \mu\text{m}$  diameter polystyrene particles with a bulk particle concentration being  $n_p = 9.8 \times 10^{10} \text{ cm}^{-3}$ . The sample cell was prepared as described in section 2. As soon as the sample was prepared, it was noticed, using the experimental set-up, that the particles perform random Brownian motion, which is the characteristic of a gas-like order. At the same time it was also observed that the concentration of particles for some

distance from the container wall was not uniform but showed undulation. After a few days, the movement of particles was restricted (Pusey 1979) and the undulation in particle concentration was well developed. This was because the impurity ion concentration was reduced by the action of the mixed bed ion-exchange resin as time proceeded. After a week or so, the impurity ion concentration in the cell ceased to reduce further due to the equilibrium between the removal of impurities by ion-exchange resin and the addition of impurities from the wall, etc. The micrographs shown in figure 1 were taken after this equilibrium was reached. In figure 1(a), a few dislocations, grain boundaries, vacancies, voids, substitutional defects like a few-particle clusters are seen.

The surface layer is seen to be arranged hexagonally. In the fourth layer the particles are also arranged hexagonally as seen in figure 1(b), but the number of voids, vacancies, grain boundaries, etc are large compared with those in figure 1(a). By overlapping the image of one layer on the other layer (using the image processor) and measuring the interparticle distances in the layer and perpendicular to the layer, it is clear that these layers are stacked like (111) planes of the face centred cubic (FCC) structure (Kesavamoorthy *et al* 1989b). However, we have not observed iridescence in the suspension and hence the bulk of the suspension is not crystalline. We believe that the bulk of the sample is liquid-like ordered due to the presence of the mixed bed ion-exchange resin. Recently, Kesavamoorthy *et al* (1991) have also observed that the hexagonally ordered two-dimensional layers near to the wall stacked themselves into a FCC-like structure while deep inside the bulk suspension shows a liquid-like order. They arrived at this conclusion by performing two-dimensional and three-dimensional Bragg diffractions and static light scattering measurements on the suspension.

The particles in a layer of our sample are found to be confined to that particular layer. In other words, they moved within the layer but not to the adjacent layers. These observations indicate that the potential barrier perpendicular to a layer is relatively high as compared with that along the layer. This difference in the potential barriers is a maximum in the surface layer and decreases continuously as the distance from the surface increases. This feature has been attributed to the electrostatic interaction between the charges (polystyrene particles, counter ions and impurity ions) and their image charges induced in the container wall, and a qualitative representation of the effective potential has been given by Kesavamoorthy *et al* (1989b). According to this representation, the depth of the potential well is a maximum at the first layer and it decreases continuously as one moves on to the second layer, third layer and so on; and well away from the surface it will be same as that of the bulk without the effect of the image charges. Because of this effective potential near the surface, the surface layer and a few layers beneath it are found to behave as a layered structure. These layers, especially the surface layer, behave as a two-dimensional structure which is weakly coupled to the adjacent layers. The nature of the effective potential causes the first layer to be more ordered than the other layers. Figure 4 shows the distribution of interparticle separation in the first layer and the fourth layer. The centre-to-centre distances of nearly 200 pairs in each micrograph given in figure 1 are measured and shown in this figure. It is observed from this figure that the distribution in the first layer is sharp while that in the fourth layer is broad, indicating that the degree of ordering in the first layer is high compared to that in the fourth layer. The fraction of  $n$ -coordinated particles in these layers is shown in table 1. The fraction of six coordinated particles is high in the first layer as compared with that in the other layers indicating the degree of ordering. In addition, it was observed that on heating the suspension using the heat accompanied with the excessive light from the microscope the fourth layer disordered first, then the third layer and lastly the first



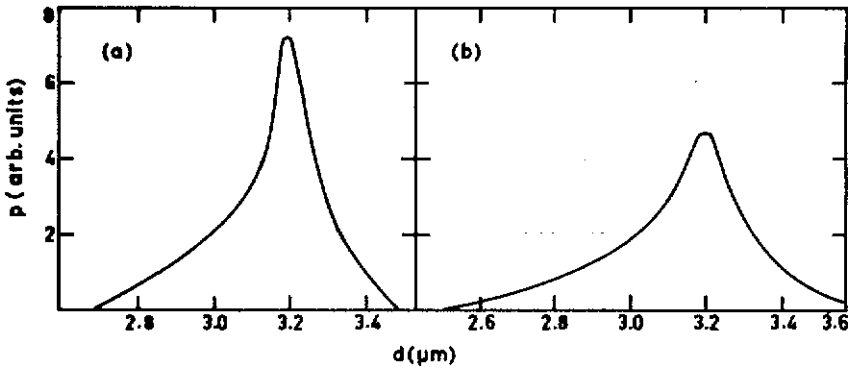


Figure 4. Distribution of interparticle separation  $d(\mu\text{m})$ ; (a) in the first layer; (b) fourth layer.  $P$  is the number of particles with distance  $d$ .

Table 1. Coordination number ( $n$ ) and its fraction  $f_n$ .

$n$	$f_n$	
	In first layer	In fourth layer
1	0	0.005
2	0.0008	0.043
3	0.005	0.092
4	0.053	0.22
5	0.126	0.32
6	0.756	0.31
7	0.016	0.01
8	0.027	0.00
9	0.014	0.00
10	0.0016	0.00

layer. The reverse sequence was followed in ordering while cooling the suspension by reducing the light from the microscope. This also indicates that the wall provides a stabilizing force for the layers near to the wall and this force decays with distance away from the wall.

Since a few layers near the surface of the colloidal suspension appear to behave as a layered structure, it will be imperative to analyse these layers for possible two-dimensional ordering characteristics. Kosterlitz and Thouless (1973) predicted that the translational correlation function,  $g(r)$ , decayed algebraically while the orientational correlation function,  $g_6(r)$ , remained constant in  $r$  for a two-dimensional crystal. Figure 2 shows the  $g(r)$  computed as described in section 3 for the first layer and the fourth layer. This  $g(r)$  is quite different from that of a three-dimensional crystal in the sense that the  $g(r)$  does not show a long range order with sharp peaks for all values of  $r$ , and also from that of an isotropic liquid in which only two or three peaks with decreasing height will be seen. The height ( $g_m$ ) and the position ( $r_m$ ) of the peaks in  $g(r)$  were considered for least-square fitting for an algebraic function,  $g_m(r_m) - 1 = Ar_m^{-B}$  and an exponential function  $g_m(r_m) - 1 = C \exp(-Dr_m)$  where  $A$ ,  $B$ ,  $C$ ,  $D$  are the parameters

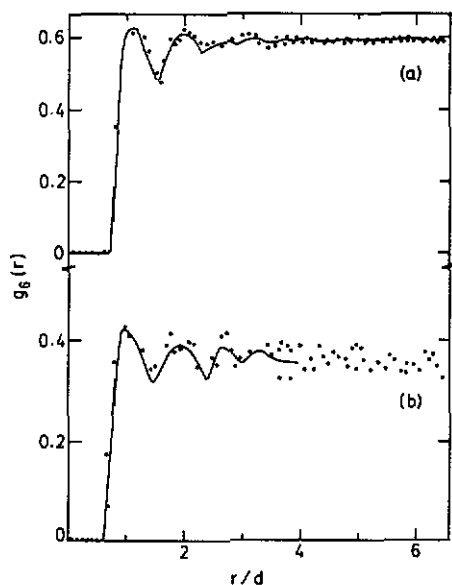


Figure 5.  $g_6(r)$  versus  $r$  (expressed in units of  $d$ ) for (a) first layer; (b) fourth layer.

and  $r_m$  is in the units of  $d$ . The values of the parameters for the first layer obtained from the fit are  $A = 2.1294$ ,  $B = 2.0786$ ,  $C = 9.14$  and  $D = 0.6977$ . The  $\chi^2$  value of the fit for the first layer is  $2.61 \times 10^{-3}$  for the algebraic function and  $1.11 \times 10^{-2}$  for the exponential function. Hence, it is clear that  $g(r)$  decays algebraically rather than exponentially indicating that the first layer has the characteristic of a two-dimensional crystal. For the fourth layer the parameters are  $A = 1.9744$ ,  $B = 2.6309$ ,  $C = 11.92$ ,  $D = 0.5593$ . The  $\chi^2$  value for the algebraic decay is  $2.54 \times 10^{-4}$  while that for the exponential is  $5.1 \times 10^{-3}$ . It is observed that the difference in  $\chi^2$  values in the fourth layer is not as large as that for the first layer indicating that the two-dimensional crystalline order is weak. One can notice from figure 2 that the  $g(r)$  of the first layer has oscillations up to  $r/d = 3.85$  and a smooth well-defined second peak, whereas the  $g(r)$  of the fourth layer has oscillations up to  $r/d = 2.77$  and has a broad second peak, in addition to this the first peak height in  $g(r)$  of the first layer is 3.14 and that of the fourth layer is 2.97 showing that the fourth layer is more disordered than the first.

Figure 5 shows the orientational correlation function for both these layers computed as described in section 3. It is noted from figure 5(a) that  $g_6(r)$  is a constant in  $r$  indicating the two-dimensional crystalline order of the first layer.  $g_6(r)$  for the fourth layer decreases slightly with  $r$  as seen from figure 5(b). The data is not sufficient to decide unambiguously whether the decrease in  $g_6(r)$  is algebraic or exponential. The decrease of  $g_6(r)$  could be produced by the disclinations in the fourth layer. This again indicates that the fourth layer is not as well ordered as the first layer. The results of  $g(r)$  and  $g_6(r)$  suggests that both the first layer and the fourth layer show two-dimensional crystalline order characteristics, and the order is weak in the fourth layer as compared with that in the first layer.

## 5. Conclusions

An optical reflection microscope, with a video camera and an image processor were used to investigate the ordering in dilute charged colloidal suspensions, and it was observed

that the surface layer has features of two-dimensional crystalline order. We have taken the micrographs of the first layer and the fourth layer and computed the translational correlation function, the orientational correlation function and the fraction of  $n$ -coordinated particles. The degree of crystalline order is reported to decrease with the distance from the surface. The surface layer is found to have the characteristics of a two-dimensional crystalline order because  $g(r)$  shows an algebraic decay while  $g_6(r)$  remains a constant. The effect of the image charge interaction in this layer is quite considerable and might be the cause for the two-dimensional crystalline order of the surface layer.

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