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## Instability of a two-dimensional colloidal crystal at a water–air interface

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**Abstract.** The experimental observation of the sudden collapse of a two-dimensional colloidal crystal at a water–air interface is reported and explained here for the first time. A thin film of an aqueous suspension of polystyrene particles of 0.53  $\mu\text{m}$  diameter is confined between a smooth glass plate and an air bubble. A single layer of a 2D colloidal crystal is observed in this thin film using an optical reflection microscope equipped with a video camera and an image processor. On gradual draining of water from this thin film, particles forming a 2D colloidal crystal suddenly emerge to the water–air interface. At the interface they flocculate to form a compact 2D sheet of particles in which the particles touch each other, forming hexagonal and square 2D structures. This phenomenon is explained on the basis of the interfacial surface energies and the interparticle interaction potential at the water–air interface.

### 1. Introduction

Aqueous suspensions of polystyrene colloidal particles are known to exhibit crystal-like ordering (Clark *et al* 1979, Lindsay and Chaikin 1982, Pieranski 1983, Hirtzel and Rajagopalan 1985, Ise 1986, Robbins *et al* 1988, Russel *et al* 1988, Kesavamoorthy *et al* 1988, Rundquist *et al* 1991). Ordering of colloidal particles near the container wall is influenced by the induced image charges in the container dielectric (Kesavamoorthy *et al* 1989a, b, 1991, 1992, Sogami and Yoshiyama 1990, Tandon *et al* 1993). The induced image charge interactions enhance the order in a plane nearest to the wall such that a 2D crystalline-like order is observed in the plane near to the wall, while at far distances the suspension exhibits liquid-like order (Kesavamoorthy *et al* 1992, Tandon *et al* 1993). A 2D colloidal crystal has been observed in a suspension confined between two glass plates (Pansu *et al* 1983, Murray *et al* 1990), which is stabilized by the induced image charges in the glass plates. A single layer of the 2D colloidal crystal confined between two glass plates forming a wedge is found to melt when the wedge thickness increases beyond a critical value (Murray *et al* 1990). Richetti *et al* (1984) have observed the growth of a fractal aggregation of colloidal particles from a 2D colloidal crystalline suspension confined between two glass plates on the application of an AC electric potential.

Very little work has been reported on the structural ordering of particles trapped at the water–air interface. Pieranski (1980) has observed for the first time a 2D colloidal crystal at the water–air interface using an optical microscope. He has reported that the surface energy for the particle is a minimum when a polystyrene particle floats in the suspension immersing about two thirds of its diameter into the suspension. He also has pointed out

that under such circumstances the particles interact via a dipole-dipole repulsion potential owing to the formation of the electric dipole at each such floating particle. In addition, these particles are subjected to the van der Waals attraction. Pieranski (1980) observed a stable 2D crystal on the water-air interface and on adding a monolayer of impurities on the interface he noticed a few cluster formations (dimers, trimers, etc) on the interface. Hurd (1985) reported that the polystyrene particles at the water-air interface repel each other by dipole-dipole interaction for large interparticle separations, whereas for small separations they repel each other through a screened Coulomb interaction. Armstrong *et al* (1989) spread polystyrene colloidal particles of submicron size on the water-air interface to form a 2D colloidal particle layer and studied the 2D crystal melting by varying the concentration of the particles at the interface. However, further work is needed to understand the stability of the colloidal crystal at the interface.

In this work, we investigated a single layer of polystyrene particles  $0.53 \mu\text{m}$  in diameter confined between a glass plate and the water-air interface using an optical reflection microscope equipped with a video camera and an image processor. The particles were arranged hexagonally with about  $1.3 \mu\text{m}$  interparticle separation. The distance between the glass surface and this particle layer was about  $1\text{--}2 \mu\text{m}$ . We observed specific cases where the water was gradually drained from the thin film, thus reducing the thickness of the suspension film. In due course, suddenly, the hexagonally ordered particles about 200 in number moved collectively to form a compact 2D sheet of particles where they touched each other, forming hexagonal and square structures. We observed this kind of collapse of the colloidal crystals in many regions in the thin film of the suspension. Also, it occurred in succession at neighbouring regions of about 200 particles. We explain these observations on the basis of the instability of the 2D colloidal crystal at the water-air interface even though it was stable within the suspension film. We show that at the water-air interface the van der Waals attraction dominates and brings the interface particles together. We also show by the same calculation that the particles observed by Pieranski (1980) at the water-air interface are indeed stable, forming a 2D crystal and a 2D liquid as reported by him.

## 2. Experimental details

The monodisperse aqueous suspension of polystyrene spheres of  $0.53 \mu\text{m}$  diameter with 2.5 vol.% (from Polysciences Inc. USA) was sonicated for a few minutes in order to redisperse the loosely bound aggregates (Kesavamoorthy *et al* 1989a, b, 1992). This suspension was passed through a column of mixed-bed ion-exchange resins (cation, Ambercep 252; anion, Ambercep 900) repeatedly until it reached a conductivity of about  $0.5 \mu\text{mho cm}^{-1}$ . The suspension was placed in an observation cell to one third of its volume and the rest of the cell was filled with mixed-bed ion-exchange resin. The cell was a cylindrical quartz tube of 1 cm diameter and 1 cm height with the top and bottom surfaces diamond ( $1 \mu\text{m}$  grit) polished and closed with cover-glass plates  $133 \mu\text{m}$  thick on either side. The cylindrical tube and the cover-glass plates were cleaned with chromic acid and distilled water. Epoxy resin (Araldite) was used at the outer side of the observation cell to seal it.

A few observation cells were prepared by the above-described procedure with the particle concentration  $n_p$  ranging from  $10^{10}$  to  $10^{11} \text{ cm}^{-3}$ . The charge  $Ze$  on the particle was determined using a zeta potential measurement (Rank Brothers, UK, mark II, microelectrophoresis apparatus) to be  $1800e$  where  $e$  is the electronic charge. The mixed-bed ion-exchange resins remove ionic impurities from the suspension, while the wall might

leach ionic impurities into the suspension. Since the cell was closed, the ionic impurity concentration  $n_i$  was reduced continuously owing to the action of the resin and reached a steady value. It was estimated that the equilibrium value of  $n_i$  was reached in about 10 d (Kesavamoorthy and Arora 1985, Okubo 1987). The minimum value of  $n_i$  in equilibrium with the resin has been measured by Fujita and Ametani (1977) to be about  $4 \times 10^{15}$  ions  $\text{cm}^{-3}$ . Many of our earlier experimental results on colloidal suspensions have been successfully interpreted using an impurity concentration ranging from  $2 \times 10^{15}$  to  $10 \times 10^{15}$  ions  $\text{cm}^{-3}$  (Kesavamoorthy *et al* 1988, 1989a, Tata *et al* 1986, 1987). Hence, it is reasonable to assume that the minimum value of  $n_i$  in our observation cells is  $2 \times 10^{15}$  ions  $\text{cm}^{-3}$ .

These observation cells were prepared 4 years ago; a few investigations were carried out on them (Kesavamoorthy *et al* 1989a, 1991) and they were then preserved. In the present experiments the colloidal suspensions in these cells showed crystalline-like order as before. All the observations reported earlier were observed in the present work also, but an air bubble had formed inside the cell because of the slow evaporation of the solvent (water) and the escape of vapour through possible micropores in the epoxy seals. The air bubble floated in the suspension, touching the top cover-glass plate. The resins settled at the bottom because they are heavier than the suspension. The size of the air bubble varied from cell to cell in the range 2–5 mm diameter. A film of suspension was confined between the lower surface of the top cover-glass plate and the water-air interface of the air bubble. This film was not continuous. The suspension did not wet the glass surface all over. There were many islands of the suspensions wetting the glass surface. The suspension film contained in a single layer of colloidal particles. At some places, only the water film (without any particles) was observed. Also, at other places neither the suspension film nor the water film was observed.

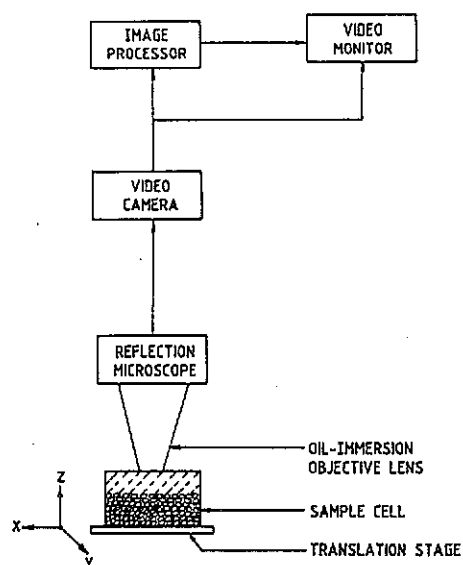


Figure 1. Schematic diagram of the experimental setup.

All these observations were carried out using an optical reflection microscope (Zeiss, Germany) (figure 1). This microscope was equipped with a video camera (Andrex, Denmark). The poor contrast of the image was enhanced using an image processor (Andrex, Denmark). The use of the image processor circumvented the need to use high-speed film

for taking micrographs of the particles which vibrated around their equilibrium positions in the crystalline phase and performed Brownian motion in the disordered phases. The image processor had a provision for obtaining 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. We used an  $100\times$  oil immersion objective. The finite field depth of the microscope did not permit us to determine exactly the distance of the particles from the glass surface. We could estimate its position to within  $\pm 0.5 \mu\text{m}$  accuracy.

The distinction between the particles in the suspension film and those at the water–air interface was clear because of the enhanced optical contrast of the particles at the interface. This contrast occurs as a result of the larger difference between the refractive indices of the particle and air compared with that between the particle and water (Pieranski 1980).

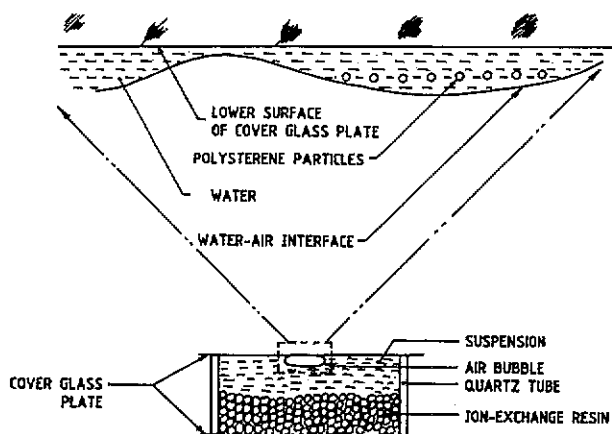
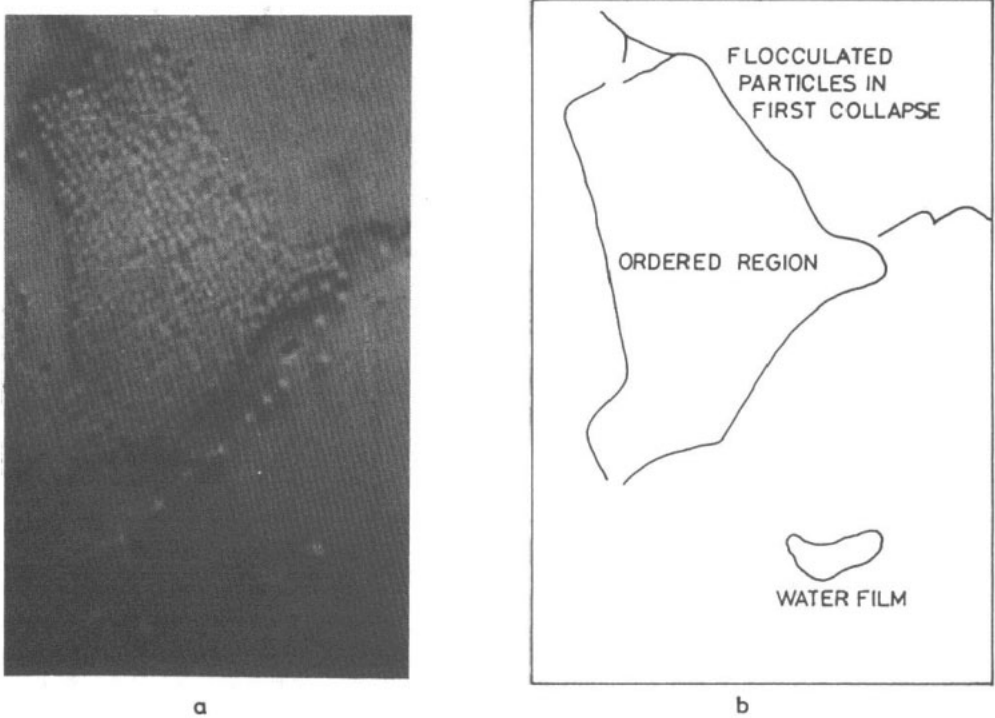


Figure 2. Schematic diagram of the observation cell having an air bubble highlighting the colloidal particles in the water film.

### 3. Results

Figure 2 shows the observation cell having an air bubble and the layer of the colloidal particles in the suspension film confined between the glass surface and the water–air interface. The interparticle separation in the layer is  $1.3 \mu\text{m}$ . This 2D hexagonal layer is stabilized at a distance of about  $1\text{--}2 \mu\text{m}$  from the glass surface. The polystyrene particle suspended in water acquires negative charge owing to the dissociation of the acidic end groups of the particle. The particle charge is screened by the counter ions and the impurity ions. These charges induce their image charges in the glass dielectric as well as in the air bubble. The glass surface also acquires a negative charge when it comes into contact with water because of hydrolysis of silanol groups. In addition, there will be a screening ion cloud near the glass surface. This cloud, too, induces image charges in the glass. The net interaction of the particle on these charges and their image charges decides the stability of the particle in the suspension film. A theoretical stability investigation is not within the scope of this paper and will be published later elsewhere. Tandon *et al* (1993) have theoretically investigated the stability of layers of particles near the glass plate and concluded that the glass plate provides a deeper potential well for a plane near to it than for a plane far away from it.

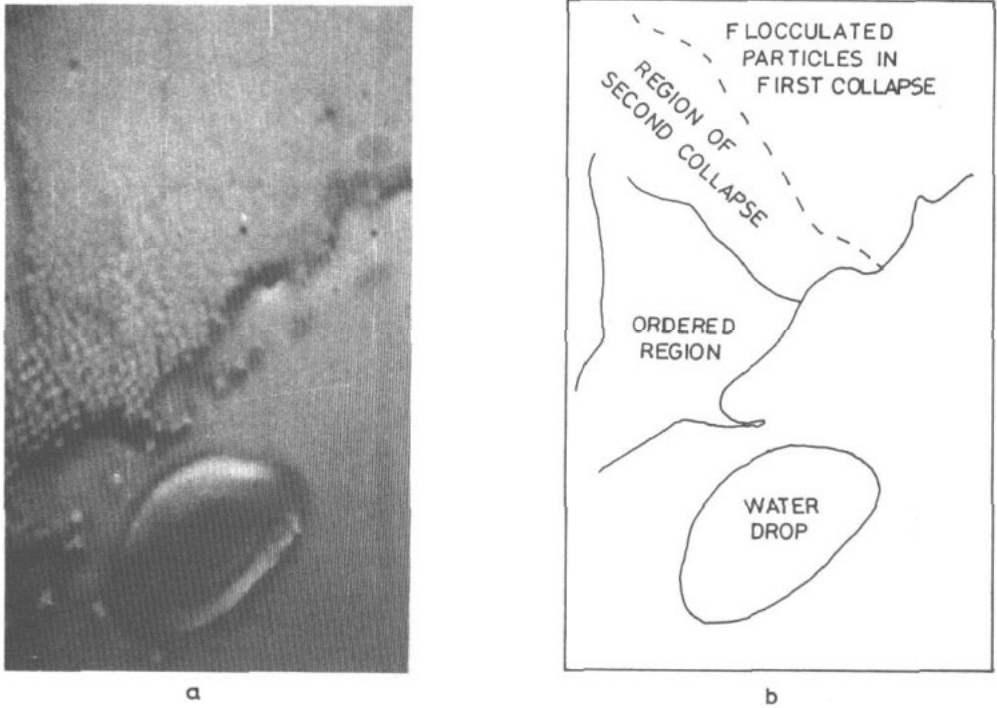
Using the minimum illumination intensity in the microscope, this single layer of particles in the suspension was observed to be stable during the total observation time (5 h). The relatively poor contrast of the particles indicates that they are within the suspension. We increased the illumination in order to heat the film. The water in this film slowly drained to the surrounding, causing a decrease in the film thickness.



**Figure 3.** (a) Micrograph of the thin layer of suspension after the first collapse. (b) Schematic representation of various regions in (a).

About 10 min after increasing the illumination, we observed a sudden collapse of the 2D colloidal crystal. About 200 particles took part in this sudden collapse. Figure 3(a) shows the suspension after collapse. This figure shows a hexagonally ordered 2D layer of particles with  $1.3 \mu\text{m}$  separation. However, many defects exist. These defects might be due to the high impurity concentration and very low shear strength of the 2D colloidal crystals. Since the photograph in figure 3(a) is not very clear, its main features are illustrated in figure 3(b). In figure 3(b), there is a water film below the ordered region. On the right of the ordered region, there are some particles trapped in small water droplets of about  $1 \mu\text{m}$  size. Above the ordered region there lies a region where the particles are flocculated together into a 2D sheet during this first collapse.

When observed through the eyepiece of the microscope (magnification,  $1250\times$ ) the contrast of the 2D sheet of particles is better than the contrast of particles inside the suspension, indicating that the 2D sheet of particles is floating in the water-air interface (Pieranski 1980). However, the 2D sheet of particles is not distinctly observed in figure 3(a) owing to the resolution limitation at video camera (magnification,  $500\times$ ). On continuing the increased illumination, a second collapse was observed within about 10 min.



**Figure 4.** (a) Micrograph of the thin layer of suspension after the second collapse. (b) Schematic representation of various regions in (a).

Figure 4(a) shows the suspension after this second collapse. The area of the ordered region had been reduced. The particles in the ordered region continued to be at  $1.3 \mu\text{m}$  separation. The particles in the collapsed region were touching one another, forming a 2D sheet of particles. This 2D sheet was observed to be continuous with the 2D sheet formed during the first collapse. The size of the water droplet lying below the ordered region had increased as observed in figure 4(a). This is due to the drainage of water from the ordered region. Figure 4(b) illustrates all these regions.

During the observation of the two-step collapse, the particles continued to be in good focus, implying that the distance of the particles from the glass surface did not change by more than  $\pm 0.5 \mu\text{m}$  (accuracy).

#### 4. Discussion

In this section, we discuss the stability of the 2D colloidal crystal confined inside the thin suspension film by considering the DVLO potential (Verwey and Overbeek 1948). Also, we discuss the instability of this crystal when it emerges out to the water–air interface by taking into account the screened Coulomb repulsion (Hurd 1985) and the van der Waals attraction.

The particles are arranged in a 2D crystal in the suspension. Their screening ions induce image charges in the glass dielectric as well as in the air dielectric and electrostatically interact with them (Tandon *et al* 1993). The effect of these interactions is to stabilize the 2D colloidal crystal layer (Kesavamoorthy *et al* 1989a, 1991, 1992, Tandon *et al* 1993). In

addition, the glass surface acquires a negative charge because of hydrolysis of the silanol group when it comes into contact with water and this charge repels the particles. However, the induced image charges by the screening ion cloud around the glass surface attract the particles. Such repulsion and attraction are absent at the water-air interface.

Hence, during the drainage of water from the thin film, it is possible that repulsion due to the glass surface charge keeps the particles away from the glass surface, causing the moving water-air interface to touch the particle surface. This is the reason why the particles continued to be in focus before, during and after collapse.

#### 4.1. Stability of the 2D crystal confined inside the film

Let us consider a layer of colloidal particles arranged periodically (hexagonal 2D) inside the thin film of the suspension which is confined between the container glass surface and the water-air interface. These negatively charged particles are screened by the counter ions and the impurity ions. The total interaction  $U_T$  between two neighbouring particles in this 2D crystal is given by (Verwey and Overbeek 1948)

$$U_T = U_A + U_R \quad (1)$$

where  $U_R$  is the repulsive part and  $U_A$  is the attractive part.  $U_R$  is given by (Hirtzel and Rajagopalan 1985)

$$U_R = (Z^2 e^2 / \epsilon) [\exp(ka) / (1 + ka)]^2 [\exp(-kr) / r] \quad (2)$$

where  $k$  is the inverse Debye screening length given by

$$k^2 = (4\pi e^2 / \epsilon k_B T) (n_p Z + n_i) \quad (3)$$

in which  $Ze$  is the renormalized charge on the particle,  $n_p$  is the particle concentration,  $n_i$  is the impurity concentration,  $\epsilon$  is the dielectric constant of water,  $k_B T$  is the thermal energy,  $r$  is the centre-to-centre interparticle distance and  $a$  is the particle radius. The measured charge on the particle is  $1800e$ . Equation (2) is the solution of the linearized Poisson-Boltzmann equation. This solution does not hold good for particles having a charge greater than  $500e$ . However, Alexander *et al* (1984) have reported that the equation (2) could be used for highly charged particles if the measured charge is renormalized. They have presented a graph representing the measured charge and the renormalized charge. Monovoukas and Gast (1989) successfully used this graph to explain the colloid phase diagram. We obtain the renormalized charge on our particles to be  $1000e$  from the graph reported by Alexander *et al* (1984). The London-van der Waals attractive potential  $U_A$  is given by

$$U_A = -\frac{1}{6} A \{ 2a^2 / (r^2 - 4a^2) + 2a^2 / r^2 + \ln[(r^2 - 4a^2) / r^2] \} \quad (4)$$

where  $A$  is the Hamacker constant. We consider that  $A = 4 \times 10^{-12}$  erg (Verwey and Overbeek 1948, Hirtzel and Rajagopalan 1985),  $n_i = 2 \times 10^{15}$  ions  $\text{cm}^{-3}$  and  $n_p = 6.4 \times 10^{11}$  particles  $\text{cm}^{-3}$  and calculate  $U_T$ . Curve 1 in figure 5 shows  $U_T$  as a function of  $r$ . This value of  $n_p$  corresponds to the observed interparticle separation of  $1.3 \mu\text{m}$  in a hexagonal layer. The potential barrier observed in curve 1 in figure 5 will stabilize the 2D layer against collapse.



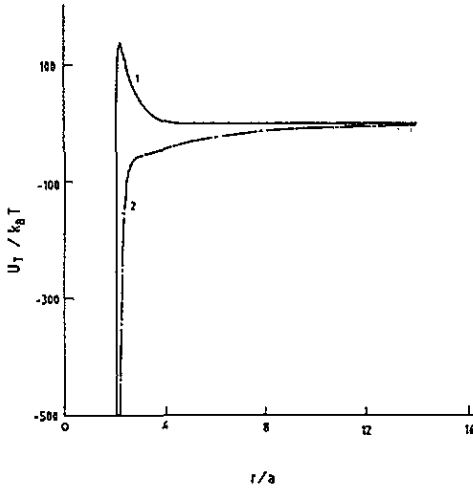


Figure 5. The interparticle potential energy as a function of interparticle distance for  $2a = 0.53 \mu\text{m}$ ,  $n_p = 6.4 \times 10^{11} \text{ cm}^{-3}$  and  $n_i = 2 \times 10^{15} \text{ cm}^{-3}$ : curve 1, particle inside the suspension,  $A = 4 \times 10^{-12} \text{ erg}$ ,  $Z = 1000$ ; curve 2, particle at the water–air interface,  $A_I = 5.14 \times 10^{-11} \text{ erg}$ ,  $Z_I = 870$ .

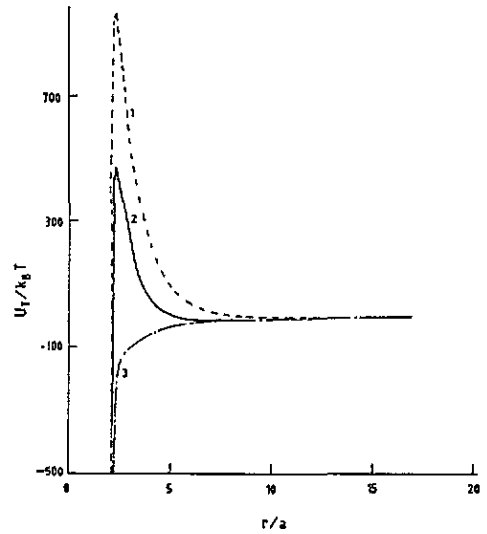


Figure 6. Interparticle potential energy as a function of interparticle distance for the particles at the water–air interface (Pieranski 1980) ( $A_I = 5.14 \times 10^{-11} \text{ erg}$ ;  $n_i = 2 \times 10^{15} \text{ cm}^{-3}$ ;  $Z_I = 870$ ;  $2a = 0.25 \mu\text{m}$ : curve 1,  $n_p = 4 \times 10^{11} \text{ cm}^{-3}$ , interfacial liquid with  $1.5 \mu\text{m}$  interparticle separation; curve 2,  $n_p = 4 \times 10^{12} \text{ cm}^{-3}$ , interfacial crystal with  $0.7 \mu\text{m}$  interparticle separation; curve 3,  $n_p = 4 \times 10^{13} \text{ cm}^{-3}$ , probable scenario when Pieranski (1980) interfacial crystal is compressed further.

4.2. Instability of the 2D crystal at the water–air interface

Pieranski (1980) considered the surface energy of a polystyrene particle at the water–air interface and shown that a water-immersed particle pops out partially into air when the water–air interface touches the particle. For completeness the surface energy calculation is given here.

There are three contributions to the surface energy:  $E = E_{P-A} + E_{P-W} + E_{W-A}$ .

(i) The energy of the polystyrene–air interface is

$$E_{P-A} = \sigma_{P-A} 2\pi a^2 (1 + \bar{Z}). \tag{5}$$

(ii) The energy of the polystyrene–water interface is

$$E_{P-W} = \sigma_{P-W} 2\pi a^2 (1 - \bar{Z}). \tag{6}$$

(iii) The negative energy of the missing water–air interface is

$$E_{W-A} = -\sigma_{W-A} \pi a^2 (1 - \bar{Z}^2). \tag{7}$$

The  $\sigma$ -values are the corresponding surface tensions and  $\bar{Z}$  is the vertical coordinate of the centre with respect to the water level in the units of radius. Considering  $\sigma_{P-A}$ ,  $\sigma_{P-W}$ , and  $\sigma_{W-A}$  to be respectively  $35.3 \text{ erg cm}^{-2}$ ,  $10.1 \text{ erg cm}^{-2}$  and  $72 \text{ erg cm}^{-2}$ , Pieranski (1980)

calculated the surface energy as a function of  $\bar{Z}$  and reported that the immersed particle will pop out to  $\bar{Z} = -0.35$  as soon as the water-air interface touches it.

When the particle is trapped at the interface, the portion of the surface of the particle which is immersed in water has a negative charge and is surrounded by the screening ion cloud, while the portion which is exposed to air does not have the charge and the screening ion cloud (Pieranski 1980). Hurd (1985) calculated the repulsive interaction between these particles at the water-air interface. For short interparticle separations (i.e. for  $kr < 10$ ), the repulsion potential can be given as (Hurd 1985)

$$U_H = [2\epsilon Z_1^2 e^2 / (\epsilon^2 - 1)] [\exp(ka)/(1 + ka)]^2 [\exp(-kr)/r] \quad (8)$$

where  $Z_1 e$  is the renormalized charge on the particle at the interface. The fraction of the particle surface immersed in water is 0.825 and hence the actual charge on the interface-particle would be  $1485e$ . The corresponding renormalized charge is  $Z_1 e = 870e$  (Alexander *et al* 1984). For our interface colloidal crystal in which the particles are separated by about  $1.3 \mu\text{m}$ , the value of  $kr$  is about 6.2.

The total interparticle interaction energy  $U_T$  of the particle trapped at the water-air interface is then calculated as

$$U_T = U_{A_1} + U_H \quad (9)$$

where  $U_H$  is given by equation (8) and  $U_{A_1}$  is obtained using equation (4) where  $A$  is replaced by  $A_1 = 0.85A + 0.15\epsilon A$ ; here 0.85 represents the fraction of the particle volume immersed in water. Curve 2 in figure 5 shows  $U_T$  as a function of  $r$ . It is clear from this curve that there is no potential barrier to stabilize the particles against collapsing into the van der Waals primary minimum. Hence, the 2D colloidal crystal trapped at the interface collapses.

Pieranski (1980) has observed a stable 2D colloidal liquid and crystal at the water-air interface. For these systems also,  $kr < 10$ . We calculate the total interaction potential energy of his particles trapped at the interface. This shows that his interface particles have indeed been stabilized against collapse.  $U_T$  is calculated using equation (9) with  $Z_1 = 870$ ,  $n_i = 2 \times 10^{15} \text{ cm}^{-3}$  and  $a = 0.1225 \mu\text{m}$  for different values of  $n_p$ .  $n_p$  is obtained from the reported micrographs (Pieranski 1980):  $n_p = 4 \times 10^{11} \text{ cm}^{-3}$  for the interfacial colloidal liquid and  $4 \times 10^{12} \text{ cm}^{-3}$  for the interfacial crystal. Curves 1 and 2 in figure 6 also show  $U_T$  as a function of  $r$  which illustrate that a potential barrier stabilizes Pieranski's 2D liquid as well as the crystal at the water-air interface. When the interface 2D crystal is compressed further (i.e.  $n_p = 4 \times 10^{13} \text{ cm}^{-3}$ ), our calculation predicts that the interface crystal becomes unstable and the particles flocculate together in the van der Waals primary potential minimum as illustrated by curve 3 in figure 6.

We can understand the stepwise collapse of the 2D colloidal crystal as follows. As shown in figure 2, the suspension film thickness is not uniform to start with. In the course of drying, the thickness of the film gradually decreases. In due course also the water-air interface touches a particle and the particle pops out partially to the interface. The neighbouring particles rearrange their positions suitable for the popped-out particle and, in doing so, they too touch the interface and pop out partially. This kind of avalanche popping out occurs until the rearranging neighbouring particles cannot touch the interface. This avalanche causes the first collapse. After further heating, the interface moves towards the particles and touches once again, which triggers another avalanche which leads to a second collapse.

## 5. Conclusion

We have reported for the first time the observation and explanation of the instability of a 2D colloidal crystal at the water–air interface. We have observed a thin film of an aqueous suspension of polystyrene colloidal particles  $0.53\ \mu\text{m}$  in diameter confined between a glass surface and an air bubble using an optical reflection microscope equipped with a video camera and an image processor. The crystal is shown to be stable when fully immersed in water. When the thickness of the suspension film is reduced, the water–air interface touches the particles, constituting a 2D crystal inside this film. The particles emerge partially to the water–air interface. These particles become unstable and flocculate at the water–air interface into a 2D sheet of particles where they touch one another, forming square and hexagonal structures.

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