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Influence of Gravity on Structure of Colloidal Crystal Using Simulated Microgravity

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Liquid mixtures of water and deuterium oxide as the liquid phase, were used to match the density of charged colloidal particles. Kossel diffraction method was used to detect the crystal structures. The experiments under the density-matched ($g=0$) and unmatched ($g=1$) conditions are compared to examine the influence of gravity on the crystal structures formed by self-assembly of 110 nm (in diameter) polystyrene microspheres. The result shows that the gravity tends to make the lattice constants of colloidal crystals smaller at lower positions, which indicates that the effect of gravity should be taken into account in the study of the colloidal crystals.

Key words: Colloidal crystal, Microgravity, Density-match, Lattice constant

I. INTRODUCTION

The colloidal crystals have lately gained great interest because they can serve as a model system to study the behavior of atoms on a much larger scale [1-15]. This is because the units in colloidal crystals are several orders of magnitude larger than those of atomic or molecular crystals. Therefore, studying colloidal crystallization as a model system makes it possible to observe and analyze the process of crystal growth by much simpler optical methods. Scientists expect to better understand how colloid structures grow and behave, aiming at learning how to control their growth to produce high-quality crystals and to create new materials. Therefore the study of colloids is casting new light on fundamental problems of condensed matter physics, from the kinetics of crystallization to the nature of glassy states [16-23]. However, the elastic moduli of colloidal crystals are extremely low and thus even rather weak external fields can distort the structure of colloidal crystals. In this aspect, the influence of gravity on the crystallization of colloidal particles have attracted great attention [24-38].

In order to study the influence of gravity on the crystallization, it is necessary to perform relevant experiments under microgravity conditions and to compare the results of microgravity experiments with those from terrestrial experiments. A spacecraft in orbit can provide a long-term and relatively stable microgravity en-

vironment. Therefore, an ideal option for exploring the nature of interesting colloid behavior would be to perform the experiments of colloidal crystallization under zero gravity conditions in space. However, this approach is very costly. On the other hand, parabolic flight and sounding rocket flight provide an economical solution to short-term low gravity environments but the stability of so-obtained low-gravity level is rather limited. The parabolic flight was used by Okubo *et al.* to study the crystal growth kinetics of charged colloidal particles [32,33]. However, the colloidal crystal structure under microgravity conditions could not be studied on parabolic flight due to the limited microgravity duration.

As an alternative approach, the method of density-matching between the solid and liquid phases is often adopted to effectively eliminate the effect of sedimentation of suspensions in studies on behavior of a colloidal system. This requires adjusting the solvent density to make the buoyancy cancel out the gravitational force on particles. In this case, an equivalent microgravity condition can be achieved for a long duration. By this means, we can study the influence of gravity on the colloidal crystal for long-duration crystallization with reasonable accuracy and economical cost. In this work, we present this the experimental observations on the influence of sedimentation on the structure and the lattice constants of charged colloidal crystals by using the density matching method.

II. EXPERIMENTS

In this study, liquid mixtures of water (H_2O) and deuterium oxide (D_2O) as the liquid phase, were used

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to match the density of charged colloidal particles. The densities of H₂O, polystyrene (PS) particles, and D₂O were approximately 1.00, 1.05, and 1.10 g/cm³ respectively, at room temperature (25 °C). The density of a 50% H₂O plus 50% D₂O mixture as the liquid phase was just matched to the density of PS particles. Monodispersed sulfonated PS spheres of diameter of 110 nm were used in the experiment. Thus, when the PS particles are dispersed in 50% H₂O plus 50% D₂O mixture, the gravitational force is balanced by buoyancy. Therefore we used the density-matching method to simulate the microgravity condition ($g=0$) to some extent.

The experiments are compared with unmatched experiments, in which the PS particles are dispersed in H₂O, to examine the influence of gravity on crystallization of suspensions of 110 nm (in diameter) polystyrene particles.

To increase the electric repulsion between particles, ions other than H⁺ and OH⁻ in the solution should be removed. The PS suspensions were ultra-filtrated with pure water repeatedly and treated by anion-and-cation exchange resins (G501-X8(D)). The final volume fraction of the PS particles in solution is 0.006 for both density matched and unmatched experiments. Each experimental PS suspension sample was introduced into a rectangular quartz cell (1 mm×10 mm×45 mm) together with a certain amount of exchange resins in the bottom of the cell. The typical colloidal crystals formed this way are shown in Fig.1.

We used the Kossel diffraction method to detect the crystal structures formed under the density-matched ($g=0$) and unmatched ($g=1$) conditions. The samples were examined by laser (He-Ne: $\lambda=532$ nm) in a dark box at 25 °C temperature. The direction of incident beam is vertical to the broad side of the cell. Diffraction phenomena were measured using an apparatus similar to that employed by Yoshiyama [4], which is shown schematically in Fig.2. A fine laser beam di-



FIG. 1 The colloidal crystals in sample cell.

rected through an incident aperture with a 1.0 mm² pinhole randomly interacts with a disordered region that exists between crystal grains in the suspension so that the region becomes a point light source of divergent beams. Parts of the divergent beams from the point light source within the crystal are reflected by lattice planes only at angles satisfying Bragg's law. The principle for the Kossel diffraction method is shown in Fig.3. The reflected beams from a set of planes with the index hkl will then generate the surface of a cone (Kossel cone) whose central axis is parallel to the reciprocal lattice vector G_{hkl} . The magnitude G_{hkl} of the reciprocal lattice vector and the semiapex angle α_{hkl} of the cone are related by:

$$G_{hkl} = \frac{2n}{\lambda} \cos \alpha_{hkl} \quad (1)$$

where λ/n is the wavelength of the beam within the crystal and n is the refractive index of the crystal.

Coordinates of three points on a Kossel line are sufficient to define the geometry of the Kossel cone within the colloidal crystal. Therefore, by measuring the coordinates of three points on a Kossel line, we are able to determine the semiapex angle α_{hkl} of the Kossel cone and the direction of its axis. Then the magnitude of the reciprocal lattice vector G_{hkl} is obtained from Eq.(1),

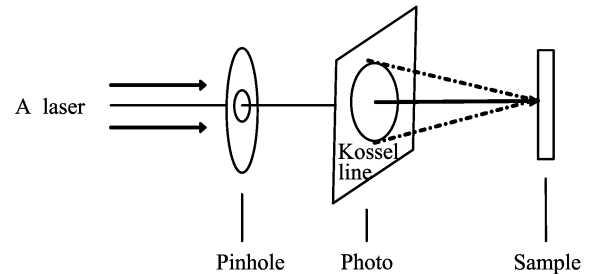


FIG. 2 The schematic image for the apparatus of measuring the Kossel lines.

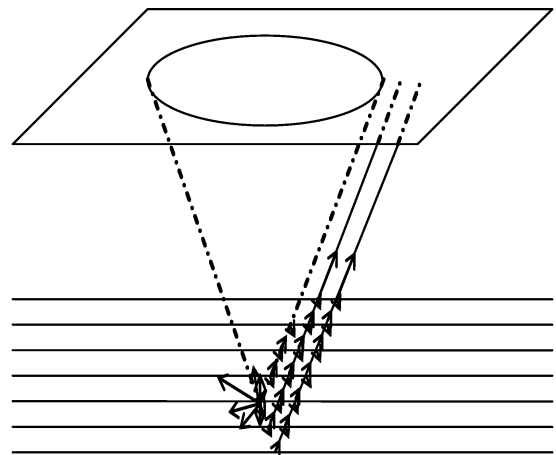


FIG. 3 The principle for the Kossel diffraction method.

since the wavelength λ of the beam in vacuum and the refractive index n of the crystal are known beforehand. For crystals with a cubic structure, the interplanar spacing d_{hkl} , which is the inverse of the magnitude G_{hkl} of the reciprocal lattice vector, is given by the lattice constant l_a as:

$$d_{hkl} = \frac{1}{G_{hkl}} = \frac{l_a}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

As the structure (bcc, fcc, etc.) and the index hkl of colloidal crystal can be determined from each Kossel patterns, using Eq.(1) and Eq.(2) we can evaluate the lattice constant of the colloidal crystal with reasonable accuracy. Therefore, the structures and lattice constants at different heights in sample cells for both density matched and unmatched samples can be determined from the corresponding Kossel patterns. By comparing these results, we can investigate the influence of gravity on the crystallization of charged colloidal particles.

III. RESULTS AND DISCUSSION

The Kossel patterns at some different heights of the sample cells were measured. A typical Kossel diffraction pattern obtained from a certain height of one of the specimen of colloidal crystals in this study is shown in Fig.4. The twofold symmetry of the pattern in Fig.4 shows that the colloidal crystal has a bcc structure. All the patterns are not shown here.

All the measured Kossel patterns for both density-matched or unmatched samples showed twofold symmetry, which indicates that gravity has no influence on the structural types of colloidal crystal. However, the shapes and positions of each Kossel line for different Kossel patterns are different. By analyzing each Kossel line at different height of the sample cells, we can determine the lattice constants of related colloidal crystals, as introduced in the previous section using Eq.(1) and Eq.(2). The results at different height for both the density-matched and unmatched samples are shown in Table I.

TABLE I Height dependence of the lattice constants for the density-matched and unmatched samples after they were introduced into the cells for five days. Crystal structure type are bcc.

	Height from the cell bottom/mm	Lattice constant/nm
$g \approx 1$	12	539
	10	521
	9	519
$g \approx 0$	9	520
	8	522
	7	527

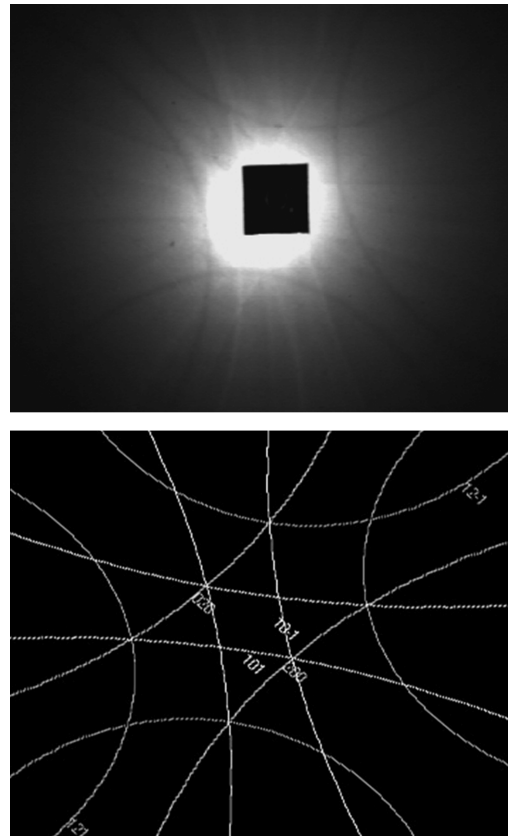


FIG. 4 Picture of Kossel lines obtained at height of 10 mm for the density-unmatched sample.

From Table I we can see the following characteristics: Gravity has no influence on crystal structural types, that is, all crystals have bcc structures for both $g \approx 1$ or $g \approx 0$, and no matter what the heights are in the sample cells. When $g \approx 1$ (for the density-unmatched samples), lattice constants increase with height of the crystal column. When $g \approx 0$ (for the density-matched samples), lattice constants decrease with height of the crystal column.

Actually, it should be expected that the lattice constant is independent of the height of the crystal column if there is no gravity. However, as mentioned in the experimental section, there is a certain amount of exchange resins in the bottom of the cell in order to reduce the ion concentration in samples. If the ion concentration is high, the colloidal particles will aggregate [39-42]. In order to form colloidal crystals in samples, the ion concentration has to be kept quite low. Therefore, the exchange resins are necessary for the crystallization of charged colloidal particles, so that the influence of exchange resins is inevitable. Considering that the influence of gravity can be neglected for density matched samples, the influence of exchange resins become the only reason for the difference of lattice constants at different heights of $g \approx 0$ samples. Actually, the formation of crystal is very sensitive to deionization-level of so-

lution which affects the repulsive interaction between particles. The repulsion between colloidal particles can be expressed as the Yukawa potential [4]:

$$U(r) = U_0 \frac{\exp(-\kappa r)}{r} \quad (3)$$

where r is the distance between particles, κ is the reciprocal of Debye length, and U_0 is a constant reflecting the intensity of the interaction. It is known that the value of κ is proportional to the square root of the ion concentration. For the locations closer to the exchange resins, the ion concentration would be smaller resulting in smaller κ . Therefore, Eq.(3) indicates that the closer the particles are to the exchange resins, the stronger become repulsive forces between particles. This will lead to larger lattice constants, as have been reported in Ref.[30].

For density-unmatched samples (namely in the $g \approx 1$ case), there are two factors to affect the height-dependence of the lattice constants: gravity and exchange resins. Although the density-matched experiment showed that exchange resins tend to make the lattice constants of colloidal crystals smaller at higher positions (where is far from the location of the exchange resins), the results of the density-unmatched experiments show the contrary. Therefore, this difference is caused by the effect of gravity. By comparing the results of density-matched and unmatched experiments, we can conclude that the gravity tends to decrease the lattice constants at lower positions.

The reason for the effect of gravity can be analyzed as follows. Due to the existence of gravity, self-weight subsidence of particles will compress the colloidal crystal. Because the weight force of particles above in the sample cell can be transferred on to the particles below through inter-particle repulsion, the colloidal crystals at lower positions of the sample cell would undergo larger pressure from above. This pressure will make the lattice constants smaller at lower height in the cell. As the elastic moduli of colloidal crystals are very low, the effect of self-weight subsidence of particles becomes noticeable.

Another effect of gravity is that it affects distribution of the number concentration of particles in the sample. With the increase of the height in the sample cell, the number concentration should decrease because of gravity, which also tends to increase the lattice constants.

IV. CONCLUSION

In summary, we used the method of density matching to study the influence of gravity on crystallization of charged colloidal particles. From the results of the colloidal crystal structural type and lattice constants at different heights of $g \approx 1$ and $g \approx 0$ samples, it is found that the gravity has no influence on the structural type of colloidal crystal. However, the result shows that

gravity tends to decrease the lattice constants at lower positions, and we have given a reasonable explanation of this effect.

For $g \approx 0$ condition, the exchange resins tend to make the lattice constants of colloidal crystals smaller at higher positions. For $g \approx 1$ condition, the combined effect of gravity and exchange resins make the lattice constants larger at higher positions. This result indicates that the effect of gravity is stronger than that of exchange resins. Therefore, the effect of gravity should be taken into account in the study of the colloidal crystals.

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