

Colloidal Crystallization in Microgravity

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Abstract

Kinetic study on the colloidal crystallization of single component and mixture of different sizes or densities of spheres was made in the exhaustively deionized suspensions and in microgravity, and compared with the results in normal gravity. Colloidal crystallization rates were retarded in microgravity for single component of spheres, whereas rates of alloy crystallization were enhanced substantially in microgravity. The rotational diffusion coefficients of colloids and the formation reaction rates of colloidal silica spheres were also studied in microgravity

Introduction

Colloidal crystals, crystal like distribution of colloidal particles in suspension, are packed densely and separated to each other with the grain boundaries like other crystals such as metals, ice and proteins¹). However, colloidal crystals are so soft (10^{-3} to 10^3 Pa) and compressed easily even by the gravitational force. When the lattice structure of the single crystals is assumed to be simple-cubic and their nearest-neighbored intersphere distance is 500 nm, for example, number of spheres composing a single crystal, $0.1\text{mm} \times 0.1\text{mm} \times 0.1\text{mm}$ in volume is estimated to be 8×10^6 . Thus, it will be easily understood that each single crystal is composed of a huge number of colloidal particles and sediment on the whole quite quickly compared with the respective spheres. From the microscopic and spectroscopic measurements in sedimentation equilibrium in normal gravity, rigidities of colloidal crystals have been determined. No compression takes place in microgravity and the strictly homogeneous crystal structure should be formed. However, the wall effect, i.e., most dense crystal lattice planes orient always parallel to the cell wall is still important. The diffuse equilibrium measurements were made to evaluate the rigidity of colloidal crystals. The centrifugal compression of colloidal crystals was studied in detail by our group. In order to compensate the sedimentation effect in normal gravity some researchers have studied the colloidal dispersions where the densities of the particles and solvent are matched using

sucrose-water mixtures instead of water as solvent, or *d.c.* electric field is applied perpendicularly for anionic charged colloidal particles, for example. However, these ideas are not so excellent to mimic the microgravity environment, since the *convection* of suspensions is still not eliminated and the extra interactions of the particle with solvent are added further. We should note that influence of the convection is quite significant in normal gravity and give substantial effect on suspension properties. Critical sphere concentration of crystallization and melting temperature for colloidal crystals, for example, are influenced substantially by the convection of colloidal suspensions. Thus, studies on the colloidal suspensions in microgravity are very important for determination of precise parameters in physico-chemistry including colloidal crystallization kinetics discussed in this report and also for syntheses of highly monodispersed colloidal spheres.

Experimental

Reflection spectroscopy is very convenient to study the kinetics of the colloidal crystallization. The size of the colloidal single crystals formed from the homogeneous nucleation, L is estimated using Scherrer's equation from the half-width of the reflection spectra,

$$L \propto n(\Delta q)^{-1} \quad (1)$$

Where n is the number of the order in the Bragg equation. q is the scattering vector, and Δq denotes $q_l - q_s$, with q_l and q_s referring the largest and smallest wavelengths corresponding to the half-width of the reflection peak.

On the other hand, the peak intensity, I of the reflection spectra is approximated by Eq 2.

$$I \propto N_{\text{cryst}} L^3 \propto L^3 \quad (2)$$

Here N_{cryst} is the number of single crystals in the reflection volume, which is directly proportional to the number concentration of crystals in the final stage of crystallization process, being equal to the total number of nuclei, which are formed in the whole course of crystallization. Most kinetic measurements on the colloidal crystallization have observed an induction period, after which

the crystal growth started especially in the diluted suspensions. This observation suggests that the kinetics of colloidal crystallization theory including nucleation and crystal growth processes. The number of nuclei that germinate per unit time, the nucleation rate, v_n is given by

$$N_c = \sqrt{2L^3/l^3} \quad (3)$$

where L and l are the mean size of single crystals formed and the closest intersphere distance, respectively. Thus, the nucleation rate is given by Eq 4, since the total number of colloidal spheres (N_T) is given by $\phi/[(4/3)\pi(d_0/2)^3]$.

$$v_n = N_T(N_c t_i) = \phi^3/[(4/3)\pi(d_0/2)^3 \sqrt{2L^3 t_i}] \quad (4)$$

According to Wilson and Frenkel, the crystal growth rate of a crystal, v is given by

$$v = v_\infty [1 - \exp(-\Delta\mu/k_B T)] \quad (5)$$

Here, v_∞ is the maximum growth rate and $\Delta\mu$ is the chemical potential difference between the crystal and liquid phases and is given by

$$\Delta\mu = \Delta\mu_{\text{cryst}} - \Delta\mu_{\text{liq}} \quad (6)$$

$\Delta\mu > 0$ means that crystallization will proceed. We should note that Eq 7 holds.

$$\Delta\mu/k_B T = \ln(\phi/\phi_c) - \sigma \quad (7)$$

where σ is the relative supersaturation given by $(\phi - \phi_c)/\phi_c$, ϕ_c denotes the critical sphere concentration of melting. From Eqs 6 and 7, Eq 8 is derived.

$$v = v_\infty [1 - \exp(-\sigma)] \quad (8)$$

Eq 8 is further simplified as

$$v = v_\infty - v_\infty \phi_c / \phi \quad (9)$$

Results and Discussion

In 1996 Okubo et al. started to do microgravity experiments, produced by parabolic flights of an aircraft, on colloidal crystallization kinetics of colloidal silica spheres in highly deionized and diluted aqueous suspensions²⁾. Sphere concentrations ranged from 0.0016 to 0.0045 in volume fraction.

The induction period of the crystallization was observed for the low sphere concentrations. Slightly longer induction periods were obtained in microgravity. The nucleation rates, v_n were evaluated to be 9.2×10^1 , 4.2×10^3 and 2.6×10^7 spheres mm^{-3} for 0G at $\phi = 0.00185$, 0.0022 and 0.00275, respectively. The v_n values at 1G were 2.8×10^2 , 5.4×10^3 and 2.1×10^8 spheres $\text{mm}^{-3} \text{s}^{-1}$ at the same sphere concentrations, respectively. Nucleation rates decreased in microgravity.

Crystal growth rates of the fcc (face-centered cubic) lattices decreased in microgravity (0 G) by about 25% compared with those in normal gravity (1 G). One of the main causes for the retardation in microgravity was suggested to be

elimination of the downward diffusion of spheres, which may enhance the inter-sphere collisions. No convection of the suspensions in microgravity was also or much more important than the elimination effect of the downward diffusion.

Recently colloidal crystallization rates were studied in the presence of sodium chloride³⁾. The rates decreased as the salt concentration increased both at 0 G and 1 G, and the rates in microgravity were smaller than those in normal gravity by 16 % (maximum) especially in the presence of a small amount of the salt lower than 2×10^{-6} mol/L.

Crystal growth rates of the colloidal alloys of binary mixtures of monodispersed polystyrene and/or silica spheres have been studied in microgravity using aircraft⁴⁾. The rates increased substantially up to ca. 1.7 folds in microgravity compared with those in normal gravity. We should note that the segregation effect is familiar for binary mixtures of colloid and powder science, i. e., large spheres are segregated upward and small ones downward in normal gravity. In microgravity such segregation should disappear and the homogeneous mixing should take place by the packing model described above. In other words, the alloy structure is determined by the condition whether the maximum packing density is achieved or not for a given ratio of the sphere sizes including surrounding electrical double layers.

Several other kinds of experiments on colloidal systems such as the rotational diffusion coefficients⁵⁻⁷⁾ and the reaction rates of formation of colloidal silica spheres⁷⁾ were also made in microgravity.

References

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