Equilibrium Characteristic at Ordered−Disordered Phase Boundary in Centrifuged Nonequilibrium Colloidal−Crystal System

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Monodisperse colloidal particles form a three-dimensional periodic structure in a dispersion liquid under a sufficiently strong electrostatic interparticle interaction. This ordered state is called the colloidal crystal[1] and has received considerable attention with respect to its possible applications, particularly as photonic crystals[2] in the optical regime. Recently, the preparation of various functional particles has been reported,[3] and the development of the novel functionalities of their colloidal crystals is expected as the next stage. For the fabrication of charge-stabilized colloidal crystals, one of the most important characteristics is the critical particle concentration above which the ordered phase is stable. To date, the critical particle concentration has conventionally been determined using homogeneous colloidal suspensions with different particle concentrations.[4] This method requires a relatively large amount of specimen, which is a significant obstacle, since monodisperse colloidal particles are valuable, particularly in the early developmental stages. Here, we report that the critical particle concentration can be determined with an extremely small amount of specimen on the basis of the unique properties of the colloidal system, i.e., the large mass and slow diffusion of the particles and the Bragg reflection characteristic in the optical regime. A large concentration gradient including a crystalline−noncrystalline (ordered-disordered) phase boundary was temporarily generated by centrifuging the suspension. The distribution of particle concentration in the ordered phase was measured for the gradually homogenized suspension by spatially resolved spectroscopy, and the interfacial concentration was found to be almost always at an equilibrium value, although the entire system was neither at equilibrium nor stationary.

A suspension of uniform-sized polystyrene microspheres in water (Duke Scientific Corp.; particle volume fraction, 10%; diameter, 198 nm; standard deviation, 3%) of various salt (NaCl) concentrations was used as a test sample. A small amount of the suspension was hermetically sealed in a flat capillary cell (0.1 mm thick, 9 mm wide, and 50 mm long) and then centrifuged at 2000 rpm (ca. 700 G) for 5−20 h. After centrifugation, an iridescent crystalline region formed at the bottom of the cell, a turbid noncrystalline region in the middle, and a transparent region on the top (Figure 1A). After stopping the centrifugation, the biased distribution in the suspension was gradually homogenized by keeping the cell horizontal. Since the capillary gap is very small, the flow of the suspension is suppressed even when the cell is horizontal. We performed quantitative investigations into the change in the spatial distribution of the particle concentration for the transient specimen by imaging spectroscopy (ImSpector V10, Kawasaki Steel Techno-Research Corp.). Figure 1B shows the imaging spectrograph (RGB-composed image) for the centrifuged suspension (with a salt concentration of 1 mM) around the ordered−disordered phase boundary 1 day after the centrifugation, and the normal-reflectance
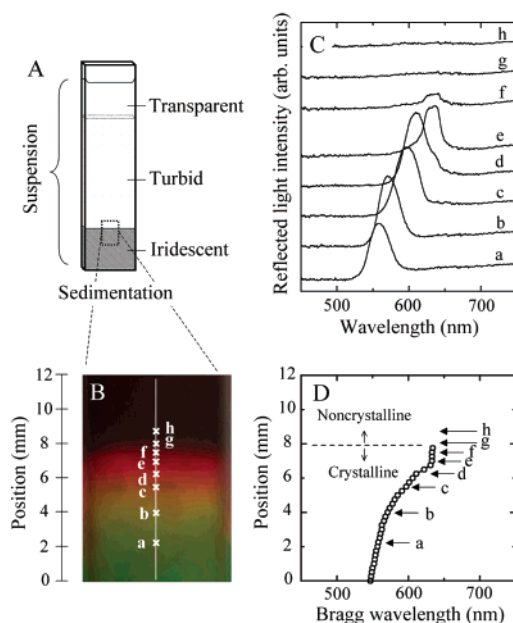

Figure 1. (A) Schematic representation of centrifuged suspension (with salt concentration of 1 mM) in flat capillary cell. (B) RGB-composed image for sample around ordered−disordered phase boundary. (C) Reflectance spectra at points a−h shown in part B. (D) Position-dependent Bragg wavelength along line normal to boundary shown in B.

spectra at various heights are shown in Figure 1C. Here, the in-plane spatial resolution was 100 μm. Note that this concentration distribution is not at a sedimentation equilibrium[5] but in a transient state toward homogeneous distribution. The rate of the change of the distribution is so slow that the imaging spectrograph, which is obtained in a few minutes at most, can be regarded as a snapshot. The peak in each spectrum is due to the Bragg reflection from the (111) lattice planes of the face-centered cubic structure[6] parallel to the cell surface, and therefore, the peak wavelength λ can be converted to the particle concentration ϕ.[7] (In this experiment, ϕ = 0.329 and $d\phi/d\lambda$ = −0.0020 nm^{-1} at λ = 600 nm.) The peak wavelength continuously shifted to longer wavelengths as the measurement position moved from the bottom of the cell toward the ordered−disordered phase boundary (points a−f), and no peaks appeared in the disordered region (points g and h). Figure 1D shows the position-dependent Bragg wavelength along the line normal to the boundary shown in Figure 1B. Approaching the boundary, the peak wavelength tends to become insensitive to the position, probably because the two phase coexistent state is formed locally around the boundary, which enables the clear determination of Bragg wavelength for the boundary.

From the spectrographs taken at different instances, we can obtain the time course of Bragg wavelength at the phase boundary. As

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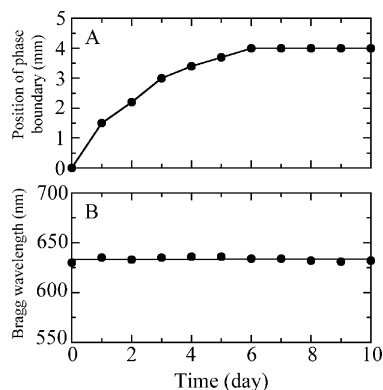[‡] Nagoya City University.

Figure 2. (A) Change in position of ordered−disordered phase boundary in centrifuged suspension (with salt concentration of 1 mM) after the centrifugation. (B) Change in Bragg wavelength at phase boundary.

Table 1. Comparison of Bragg Wavelength Obtained at Ordered−Disordered Phase Boundary in Centrifuged Suspension with That Determined by Conventional Method

salt concentration (mM)	$\lambda_c{}^a$ (nm)	$\lambda_h{}^b$ (nm)
1	633 ± 3	634 ± 2
	($\phi = 0.271 \pm 0.005$)	($\phi = 0.270 \pm 0.003$)
5	567 ± 3	569 ± 2
	($\phi = 0.406 \pm 0.008$)	($\phi = 0.401 \pm 0.005$)
10	551 ± 2	551 ± 1
	($\phi = 0.454 \pm 0.007$)	($\phi = 0.454 \pm 0.003$)

^{a} λ_c is the Bragg wavelength at the ordered−disordered phase boundary in the centrifuged suspension. ^{b} λ_h is the Bragg wavelength measured from the homogeneous suspension at a two phase equilibrium.

shown in Figure 2, the Bragg wavelength at the boundary remains invariable (the fluctuation, ±3 nm) even if the boundary moves significantly. Namely, the particle concentration at the ordered−disordered phase boundary remains constant (the fluctuation, ±0.005), independent of time. Similar results were obtained under other centrifugation conditions, i.e., different rotation speeds and durations (results not shown). This strongly suggests that the phase equilibrium is locally attained even with the movement of the phase boundary.

To confirm whether the particle concentration at the boundary takes a value at a phase equilibrium, we compare the Bragg wavelength at the boundary obtained by the present method with that measured for a homogeneous suspension in a two phase coexistent state, that is, obtained by the conventional method. For the latter measurement, multiple dilution with a relatively large amount of a specimen is required.[8] Table 1 summarizes the comparison for various salt concentrations, where the critical particle concentrations calculated from the Bragg wavelengths[7] and the uncertainties originating from fluctuations among multiple measurements are included. These values are in good agreement. Therefore, it is concluded that the ordered−disordered phase boundary in the centrifuged suspension can be regarded to be at a phase equilibrium.

Although we regarded the salt concentration in the centrifuged suspension as homogeneous, it can be inhomogeneous to maintain thermodynamic balance with the biased distribution of charged colloidal particles, i.e., the Donnan effect. This effect would make the apparent critical particle concentration in the nonstationary sediment time-dependent and/or different from that in the homogeneous suspension. Since no such behavior was observed, the Donnan effect is considered to be negligible at least under the present experimental conditions. The Donnan effect should become relatively significant at lower salt concentrations.

The present findings enable the phase studies of colloidal crystallization with an extremely small amount of specimen. We can begin with a dilute suspension, which is particularly beneficial when the phase boundary lies at very high concentrations. The sample volume necessary in the present measurement was only 45 µL, and it can be further reduced by reducing the cell dimensions.

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(6) Under the present conditions, the structure of the colloidal crystal is face-centered cubic, as it is in most cases, although it can be body-centered cubic if the particle diameter and particle volume-fraction are reduced.

(7) Particle concentration ϕ can be determined from Bragg wavelength for the normal reflection λ by taking advantage of the Bragg condition $\lambda = 2nd_{111}$ and the crystallographic relation $\phi = (2\pi/9\sqrt{3}) \cdot (d/d_{111})^3$, where n is the refractive index of the colloidal crystal, d_{111} is the interplanar spacing of (111) planes, and d is the particle diameter. The refractive index n is assumed to be the volume-weighted average of the refractive indices of water ($n_w = 1.33$) and polystyrene ($n_p = 1.59$), $n = n_w(1 - \phi) + n_p\phi$.

(8) The concentrated colloidal crystal with a certain salt concentration was diluted in a vial step by step with water of the same salt concentration. At each dilution, after the suspension became homogeneous, the Bragg wavelength for normal reflection was measured. The Bragg wavelength increased with decreasing particle concentration, and finally, no Bragg reflection was detected. The longest Bragg wavelength thus obtained was for the ordered phase at the two phase equilibrium.

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