

Novel Crystallization in Dilute Ionic Colloids

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Abstract: The crystallization process in an electrostatically stabilized dilute silica colloid dispersion was studied experimentally in an order-disorder coexistence regime. In shear melted homogeneous disordered dispersions, space-filling grains of body-centered cubic lattice were first formed by a conventional nucleation and growth process, which was followed by a lattice contraction resulting in a "Swiss cheese-like" structure of coexisting ordered and disordered regions. The result reveal an important role of the net attractive interaction.

Introduction

Aqueous dispersions of electrostatically stabilized colloidal particles are known to undergo order-disorder transitions.¹⁻¹¹ In deionized conditions, the order-disorder transitions were found to take place at very low particle volume fractions (ϕ). Further studies have revealed the existence of a biphasic regime, where the ordered and disordered regions coexist.^{7,9,10} To account for these findings, two contradictory explanations have been advanced. One is an "effective" hard sphere model.¹⁰⁻¹² In this assumption, the particle size is enlarged by adding the thickness of surrounding counterion clouds to its bare radius, which enables to explain the phase behavior entropically. Another much straightforward explanation is to assume presence of a long-range electrostatic attraction among the particles in addition to the widely accepted Yukawa type repulsive interaction. The existence of such a long-range attraction has recently been demonstrated experimentally^{1-8,12-17} and also studied theoretically.¹⁸⁻²³ In the present report, a novel observation in the crystallization process in the biphasic regime, which may reveal that the latter explanation employing the long-range attraction is more appropriate, will be discussed.

Experimental

Aqueous dispersions of colloidal silica particles (radius: 0.053 μm , effective surface charge density: 0.25 $\mu\text{C}/\text{cm}^2$) were used. All experiments were performed under deionized conditions (ionic strength 1 ~ 3 μM), in which the particles were in their protonated form.

The internal structure of the dispersions were determined by a confocal laser scanning microscopy (CLSM)²⁴ utilizing LSM 410 (Carl-Zeiss, Germany) and by an ultra-small-angle X-ray scattering analysis (USAXS).^{25,26} Under the present conditions, with increasing ϕ , the dispersion was found to change from a disordered structure to the order-disorder coexistence at $\phi = 0.006$ and then to a volume filling ordered structure at $\phi = 0.050$.

Results and Discussion

In figure 1, typical CLSM images of the order-disorder coexistence structure observed in the internal region of the dispersion (200 μm inside from the coverslip) at $\phi_o = 0.018$ are presented. These micrographs were taken at evolution time $t = 1$ day after homogenizing the dispersion by shear-melting the existing structure. Figure 1 (b) clearly shows ordered lattices coexist with the disordered regions. The USAXS measurement revealed that the particles in the ordered grains are arranged in body-centered cubic (BCC) lattices. The lattice constant a was 0.376 μm , which was smaller than that calculated assuming homogeneous particle distribution ($a_o = 0.408 \mu\text{m}$). The observed inequality $a < a_o$ indicates that the crystalline grains had a higher particle concentration than that of the coexisting disordered regions. It should be noted that this inequality has already been reported for various kinds of ionic colloidal dispersions and has been attributed to an electrostatic long-range attraction between the charged particles.¹⁻⁶

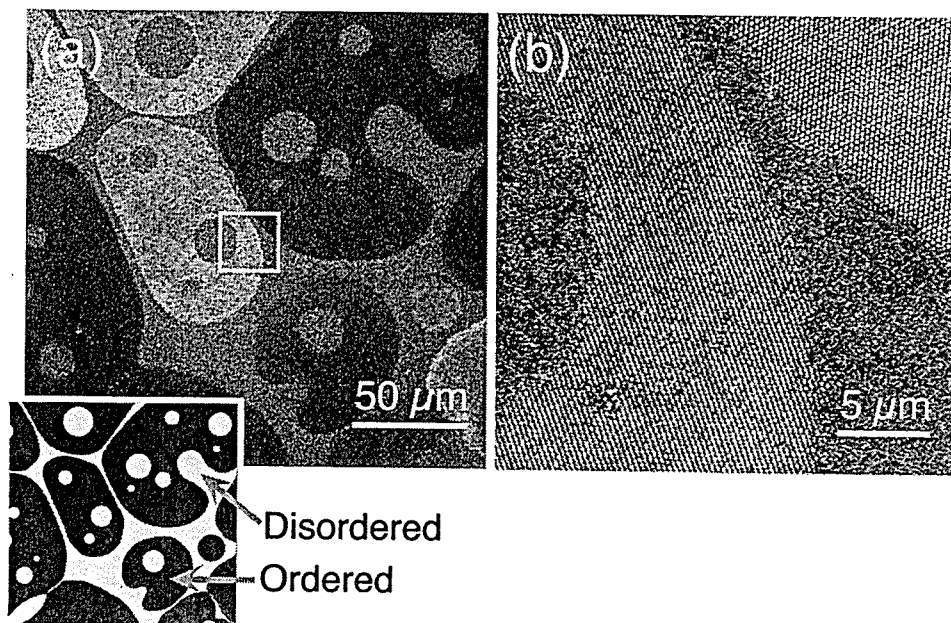


Figure 1. CLSM images showing the order-disorder coexistence in a silica colloid dispersion at (a) low and (b) high magnifications at $t = 1$ day. Micrograph (b) was obtained by zooming into the white square region shown in micrograph (a).

It is important to note that the disordered regions exist not only in the interstitial regions between the crystalline grains but also inside the grains in Figure 1 (a). According to the conventional nucleation and growth process, it is difficult to account for the formation of such a structure. Therefore, to investigate the crystallization process, further studies were performed and the results are summarized in Figure 2. At the first stage, ordered grains were observed to form by a conventional nucleation and growth process. At $t = 40$ sec, the whole volume of the dispersion was occupied with the grains and there exist no disordered region. Unexpectedly, in the next stage, disordered regions were observed to develop inside the grains, resulted in a "Swiss cheese-like" structure ($t = 8$ min and later). First, at $t = 8$ min, many small disordered regions were found inside the crystalline grains. As time passed, the average size of these disordered regions increased while their number decreased. The disordered regions at positions close to the grain-grain interface were extruded from the grains and formed the interstitial disordered phase, while those in the internal regions of the grains formed spherical disordered phases. During this process, the somewhat squarish crystalline grains seen at $t = 40$ sec became rounded off to minimize the surface free energy of

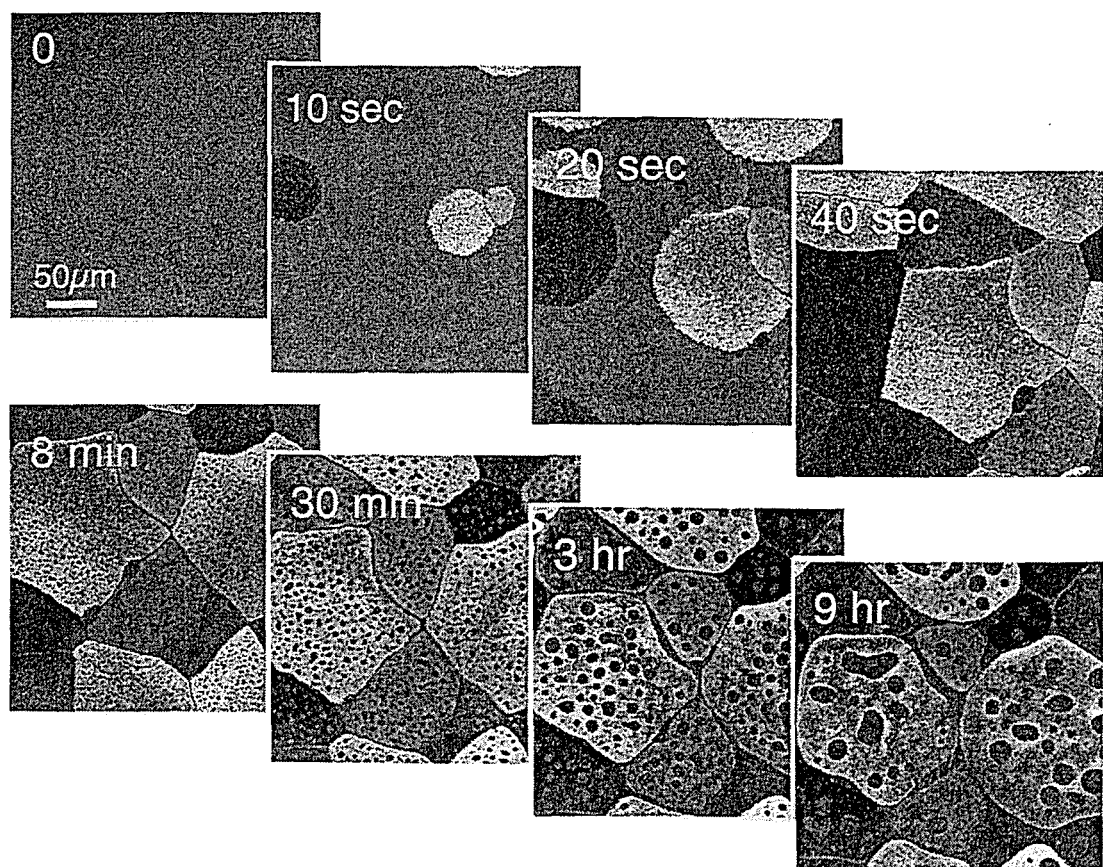


Figure 2 CLSM images showing the time evolution of the dispersion structure during the crystallization process.

the grains by minimizing their interfacial area. The structure at $t = 1$ day presented in Figure 1 was thus formed.

The evolution of lattice spacing during the crystallization process was also followed by CLSM and USAXS methods,²⁷ which revealed $a = 0.400 \mu\text{m}$ at $t = 40$ sec. On the other hand, at $t = 8$ min and later, a took a constant value of $0.376 \mu\text{m}$. These results imply that the lattice should be contracted between $t = 40$ sec and $t = 8$ min. The "empty" or less dense space formed during this process could develop as the disordered regions via a diffusion-coalescence mechanism.

As mentioned in the introduction, there are two models to account for the formation of the order-disorder coexistence structure. However, the relationship $a_o > a$ and the existence of a lattice contraction process seem to be only explained in terms of a net long-range attraction between the particles in addition to the widely accepted DLVO forces. In addition, it is worth mentioning that the small disordered regions observed in Figure 2 ($t = 8$ min) devolved to the larger ones with decrease in their number. In other words, the total free energy of the system favors the coexistence of defectless large crystalline grains and disordered regions, instead of having small disordered regions scattered inside the crystalline grains. This situation again testifies to the attractive interaction between the particles.

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