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コロイド結晶の核生成

Nucleation of Colloidal Crystals

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1. Introduction

Monodispersed colloidal particles accumulated in a crystalline ordered structure are called colloidal crystals. Colloidal crystals using latex particles or silica particles with a diameter of several tens of nm ~ several μm are well known. When the single-dispersion colloidal particles crystallize, the cloudy dispersion exhibits a pronounced opal-like luster. The volume of the cloudy disorderly dispersed phase decreases over time, and the entire dispersion crystallizes beautifully. Since such ordering of colloidal particles is easy to observe by optical methods such as direct observation under a microscope or spectroscopy, it is regarded as a model system for general nucleation and crystal growth, and analogical research has been pursued[1].

While the ordering of colloidal particles is regarded as an analogy of atomic and molecular crystals, it should not be forgotten that it has a special aspect unique to colloids, which is that ordinary colloidal particles have the property of being negatively charged and exhibit behavior in which each particle interacts repulsively at the distance of the Deby length[2]. In this paper, we explain that the classical nucleation theory governed by a free energy barrier formulated by surface tension is valid as a phenomenological model even in a huge colloidal particle system governed by repulsive force interactions[3-6].

2. The Avrami-type nucleation and growth model

The phase transition from uniformly dispersed colloidal suspension to the crystalline phase proceeds as follows: When the conditions are abruptly changed (quenched) across the phase transition point, a new stable phase nucleus (critical nucleus) occurs at various places in the uniform bulk that is the metastable phase, and thereafter the nucleus grows so that particles surrounding it are incorporated into the crystalline phase. In parallel with that, nucleation occurs elsewhere, and as they grow, they come into contact with each other. Such nucleation and growth processes are known as the Avrami-type model[7]. In the early stages of nucleation, critical nuclei occupying a certain volume v_0 are produced by the nucleation rate $J(t)$ which determine how many critical nuclei per unit volume are produced per unit time and unit volume. Then, the temporal change in the volume $V(t)$ occupied by the crystalline phase in the total volume V_0 of the colloidal dispersion system is formulated as follows.

$$\frac{\mathrm{d}V(t)}{\mathrm{d}t} = v_0 J(t)[V_0 - V(t)] \tag{1}$$

Divide both sides by V_0 and replace them with the volume fraction of the crystalline phase $P(t)$ to obtain the following equation.

$$\frac{\mathrm{d}\,P(t)}{\mathrm{d}t} = v_0 J(t)[1 - P(t)] \tag{2}$$

3. The classical nucleation theory

Colloidal particles uniformly dispersed in the dispersion medium by stirring form clusters (aggregates), in which two adjacent particles are in close proximity, then particles form clusters of three particles, and gradually form large clusters, as follows:

$$A_1 + A_1 = A_2, \cdots, A_{i-1} + A_1 = A_i, A_i + A_1 = A_{i+1}, \cdots$$

Such an ordering process of colloidal particles can be formulated by the classical nucleation theory. The classical nucleation theory formulates the process in which a microscopic cluster called a critical nucleus A_{i^*} in a metastable phase is directed to a stable ordered phase (crystalline phase). The critical nucleus is described as the smallest unit that exists as a crystalline phase. Nucleation requires free energy that exceeds the activated free energy ΔG^*, expressed by the following equation using the driving force $\Delta\mu$ of crystallization[8].

$$\Delta G^* = \frac{16\pi}{3}\frac{\gamma^3 a^2}{\Delta\mu^2} \tag{3}$$

$$\Delta\mu = k_\mathrm{B}T\ln\frac{\emptyset}{\emptyset_\mathrm{e}} \tag{4}$$

Where γ is the surface tension of the critical nucleus, a is the volume of the colloidal particles, k_B is the Boltzmann constant, T is the absolute temperature, and $\emptyset$ is the particle concentration of the colloidal dispersion in the supersaturated state, and $\emptyset_\mathrm{e}$ the particle concentration of the colloidal dispersion in a saturated state where colloidal crystal growth is not seen. At this time, the nucleation frequency $J(t)$ is derived by examining in detail the process of association reaction between the monomer particles described above and higher-order clusters. Assuming partial equilibrium at each step of cluster formation, the steady state nucleation frequency J_st is expressed by the following equation.

$$J_\mathrm{st} = \alpha^* n_1 q_\mathrm{rep}\left(\frac{\lambda}{2\pi k_\mathrm{B}T}\right)^{\frac{1}{2}}\exp\left(-\frac{\Delta G^*}{k_\mathrm{B}T}\right) \tag{5}$$

Where α^* is the rate constant at which a single particle adheres to the critical cluster, and n_1 is the number of particles per unit volume of the monomer particle contributing to the association reaction ($= \emptyset - \emptyset_e$). q_{rep} is the exchange partition function of the freely moving clusters in the unit volume of the colloidal dispersion using $\lambda = -\left(\frac{\mathrm{d}^2\Delta G}{\mathrm{d}i^2}\right)_{i=i^*}$, and the detailed derivation of equation (5) is described in Mutaftschiev[9].

Equations (3) and (4) are substituted into equation (5) to obtain equation (6).

$$\ln\left(\frac{J_\mathrm{st}}{\emptyset - \emptyset_\mathrm{e}}\right) = -\frac{16\pi}{3}\frac{\gamma^3 a^2}{k_\mathrm{B}{}^3 T^3}\left(\ln\frac{\emptyset}{\emptyset_\mathrm{e}}\right)^{-2} + \ln\left(\alpha^* q_\mathrm{rep}\sqrt{\frac{\lambda}{2\pi k_\mathrm{B}T}}\right) \tag{6}$$

Equation (6) represents the relationship between the frequency of steady state nucleation and the degree of supersaturation, and can be verified by experimentally measuring J_st.

Equation (2) is substituted with equation (7) representing the time-dependent nucleation frequency[9], and the obtained equation (8) is integrated with respect to time to obtain equation (9).

$$J(t) = J_{st}\left[1 + 2\sum_{k=1}^{\infty}(-1)^k \exp\left(-\frac{k^2 t}{\tau}\right)\right] \tag{7}$$

$$\int_0^t \frac{dP(t)}{[1-P(t)]} = \int_0^t v_0 J_{st}\left[1 + 2\sum_{k=1}^{\infty}(-1)^k \exp\left(-\frac{k^2 t}{\tau}\right)\right]dt \tag{8}$$

$$\ln[1-P(t)] = v_0 J_{st}\left[t - \frac{\tau\pi^2}{6} - 2\sum_{k=1}^{\infty}\frac{(-1)^k \tau}{k^2}\exp\left(-\frac{k^2 t}{\tau}\right)\right] \approx v_0 J_{st}\left(t - \frac{\tau\pi^2}{6}\right) \tag{9}$$

Where τ is the delay time (also called induction time) required for nucleation to a steady state, and is expressed by $\tau = \frac{8k_B T}{\pi\lambda\alpha^* n_1}$. The transition to a steady state is proportional to the reciprocal of the particle concentration surrounding the cluster, the larger the particle concentration, the faster it becomes, and the smaller the particle concentration the slower.

In nucleation experiments of colloidal dispersions, since the gravitational sedimentation of colloidal clusters cannot be ignored, microgravity experiments are required for the measurement of J_{st}. Ishikawa and Okubo[10] conducted microgravity experiments using aircraft and measured the temporal change of the volume fraction $P(t)$ from the Bragg reflection spectral intensity of colloidal crystals according to equation (9). They showed that there is a linear relationship of $\ln\left(\frac{J_{st}}{\emptyset - \emptyset_e}\right)$ with respect to $\left(\ln\frac{\emptyset}{\emptyset_e}\right)^{-2}$, to verify that the appearance of ordered phases in the early stages of colloidal crystallization follows the classical nucleation theory. Furthermore, it was confirmed that the delay time τ obtained from the experiment by equation (9) is proportional to the reciprocal of the colloidal particle concentration $\frac{1}{\emptyset - \emptyset_e}$. These results showed that the formation of critical nuclei and the classical nucleation theory are valid in colloidal nucleation.

4. The non-classical behavior related to colloidal nucleation

The above discussion shows that the ordering of colloidal particles follows the general theory of nucleation and growth. However, compared to the nucleation of atomic and molecular crystals, colloidal particles are overwhelmingly large in size and the diffusion rate of particles is very small. Based on these characteristics, it is difficult to believe that the classical nucleation theory, which treats critical nuclei as a continuum and represents interfacial energy by surface tension, explains all the microscopic nucleation mechanisms of colloidal particles. It is natural to think that it remains within the scope of phenomenological explanations. Here, as an example of non-classical nucleation behavior seen in colloidal nucleation, the formation of percolation clusters in the process of colloidal crystal growth is introduced.

The study of colloidal crystals attracted attention because of the phenomenological interest in phase transitions in statistical mechanics. In the early 1950s, Kirkwood theoretically predicted a phase transition from liquid state to solid as particle density increased. Alder and Wainwright clarified through numerical experiments that rigid spheres undergo order-disorder transition at a certain pressure (hereafter Kirkwood-Alder transition). Hachisu et al. succeeded to draw a phase diagram of colloidal crystals using repulsive monodispersed latex particles and experimentally proved Kirkwood-Alder transition[3]. As an extension of these works, many simulation studies on the ordering of colloidal particles have advanced.

Phase transition studies of colloidal dispersion systems with large particle sizes are generally conducted using the Brownian dynamics method, in which individual particles that thermally move in a continuous fluid are described by the Langevin equation. Repulsive force interaction (Yukawa potential) is used for the potential acting between particles. The formation of clusters is determined by the Voronoi method. In the early stages of crystallization, ordered clusters appear discretely, but when clusters are formed at a certain density, a large-scale percolation cluster is observed, and the almost entire space becomes ordered. Showing the simulation result of the ordering process by the Brownian dynamics: the ratio p obtained by dividing the number of colloidal particles belonging to the largest cluster at each time by the total number of particles as a function of time in **Figure 1**. The change in cluster size showed an inflection point at 0.43, and the generation of a huge percolation cluster was confirmed[11]. The time dependence of the cluster size before and after the percolation cluster was obtained as a power law of $L \propto t^{0.31}$ was in good agreement with $L \propto t^{0.33 \pm 0.03}$ obtained by the microgravity experiment using TR-IA sounding rocket[12].
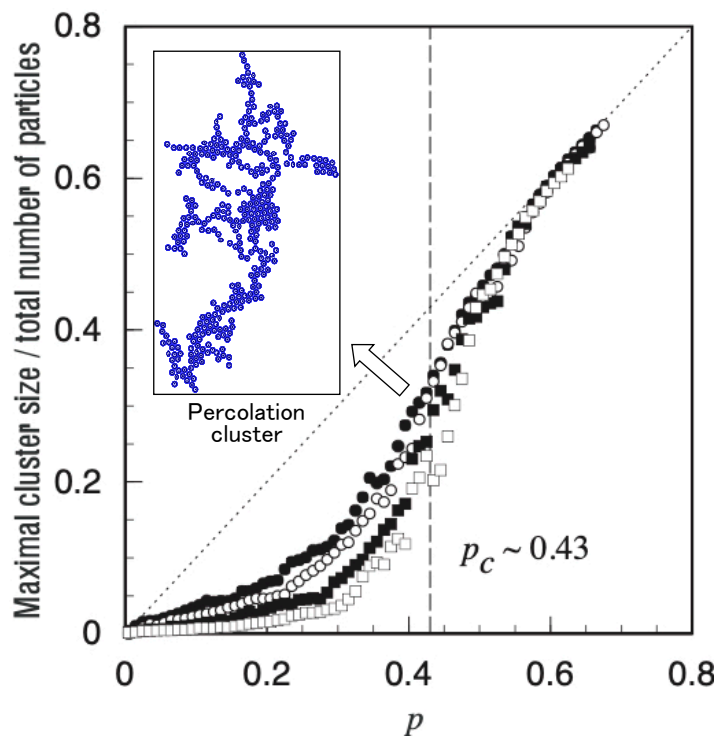

Figure 1. Computer simulation of ordering particles in a repulsive force system by Brownian dynamics method[11]. The symbol indicates the difference in the number of particles used in the calculations: ● = 196, ○ = 400, ■ = 784, □ = 1600. Ordering clusters appeared over time, and a huge percolation cluster observed at $p_c \sim 0.43$ in all the particle numbers examined.

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