The phase behavior of a weakly attractive colloidal system
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6.1 Introduction

Colloidal crystals are ordered, periodic structures of colloidal particles suspended in a fluid. It is well known that the phase behavior of a colloidal system is analogous to what is observed in atomic and molecular systems\cite{8, 16}. Studies of the crystallization of colloids benefit from the convenient length and time scales. The typical range of sizes of colloidal particles (50nm - 1000nm) means that the length scales can be probed using light scattering techniques and microscopy. The time scale for crystallization is long enough to allow for a detailed investigation. Crystallization, the disorder-order transition, from a metastable fluid to a crystalline solid has been observed in a variety of systems such as dilute charge stabilized suspensions that form bcc crystals similar to a Wigner crystals, more concentrated charge stabilized particle suspensions that form fcc crystals, crystallization to close packed structures driven by attractive depletion, flocculation and sterically stabilized particle suspensions that exhibit ”hard sphere”crystallization\cite{16}. When excluded volume interaction is the only interaction between the particles, as for hard spheres, colloidal crystals can be formed through self-assembly by controlling the volume fraction of particles\cite{121, 122}. Colloidal crystals can also be formed when a long-range repulsive interaction is present, with other crystalline structures as a result\cite{123, 124}. Still other colloidal crystals are formed when a weak attractive interaction is induced between the particles through the addition of polymers or small particles by depletion.
interaction[2]. In addition, binary alloys of colloidal crystals can be formed when two sets of different sized particles are mixed together. In this case, also packing considerations determine the nature of the crystals that are formed. Crystallization kinetics is studied as well, particularly on the hard-sphere system. Notwithstanding the apparent simplicity of these systems, the results from independent experiments on samples made from different particles do not always agree quantitatively[125–129]. It has been suggested that some of the differences are due to the effects of gravitational settling. The colloidal crystals are typically higher in volume fraction, and hence denser than the surrounding suspension; the sedimentation will disturb the nucleation and growth of crystal at an early stage[130]. The study of colloidal crystallization has even been performed in the microgravity environment of the Space shuttle as an alternative way to escape the sedimentation effect[131].

From computer simulations, theory and experiment, we know that polydispersity has a significant influence on crystallization kinetics[132–134]. In a Monte Carlo simulation, Kofke and Bolhuis[135] concluded a solid crystalline phase of polydispersity exceeding 5.7% of the average sphere diameter cannot be precipitated from a fluid phase, indicating the presence of an upper limit to the polydispersity tolerance in a single hard-sphere crystal.

In this chapter we present a time-resolved scattering study of the crystallization kinetics of colloidal particles in a binary liquid mixture. The density of the particles closely matches with that of solvent at the crystallization temperature, offering the microgravity condition to study the kinetics of crystallization and avoiding the influence of gravity. Another advantage of this system is that we can study the crystallization with temperature as a control parameter. Hence the freezing and melting are both accessible to study. The polydispersity determined by the form factor is around 2.1% and 3.4%, which is quite monodisperse below the upper limit found by Bolhuis. Ten Wolde and Frenkel suggest that near the critical point the system will display large density fluctuations[136]. As the high-density regions created by these fluctuations are at a larger supersaturation for crystal nucleation and will have a low solid/liquid surface tension, the rate of crystal nucleation will be enhanced. While nucleating rapidly, crystals will grow at a rate determined by the average density and thus will be more highly ordered. In our system, the growth of peaks in the structure factor over time was analyzed to yield the crystallinity, the average linear crystal dimension, the number of crystals and volume fraction of the crystal phase. The glass phase also was observed instead of formation of crystal due to the fast quench rate similar to that of molecular glass. The result is very similar to what is found by Chaikin et al.in an experiment performed in the Space Shuttle[131]. This study shed new light on the kinetics of crystallization charged colloidal systems,
since there are less experimental results to date.

6.2 Experiments

6.2.1 Sample preparation and time-resolved scattering measurements
The particle suspensions used in this study consist of charge stabilized polystyrene particles dispersed in the binary liquid mixture 3MP/water/heavy water. The detailed characterization of particles is presented in chapter 2. The function of adding heavy water is to match the particle and solvent density. It offers the opportunity to study the crystallization as close as possible to the microgravity conditions in space. The mean particle radius and polydispersity were determined by the analysis of the measurement of the form factor (see chapter 2). At the freezing temperature, time-resolved small-angle x-ray scattering measurements were performed to study the kinetics of the crystallization. The intensity profiles were recorded every 20 seconds. From this the structure factor is obtained after substraction of the solvent background and division by the form factor. Two samples with initial volume fractions of 0.015 and 0.050 were used to investigate the crystallization. The properties of the sample are shown in table 6.1.

6.2.2 Data analysis
From the peak $S(q, t)$, the position $q_m(t)$ of its maximum, and its width $\Delta q(t)$ at half maximum, the following quantities are obtained. Firstly, the crystallinity $X(t)$ of the sample converted from fluid to crystal is calculated from[137, 138]:

$$X(t) = c \int_{q_1}^{q_2} s(q, t) dq,$$  \hspace{1cm} (6.1)

where the constant $c$ is chosen such that $X(t \to \infty) = 1$.

Secondly, the average linear crystal dimension (in units of the particle diameter $2R$) is given by[139]

$$L(t) = \pi k/\delta(t)R,$$  \hspace{1cm} (6.2)
where $K = 1.155$ is the Scherrer constant for a crystal of cubic shape.

Thirdly, the number density of (average-sized) crystal is

$$N(t) = X(t)/L^3(t),$$

(6.3)

The rate of addition of crystals, which we shall identify as the nucleation rate, is given by $R_c = dN_c(t)/dt$.

Fourthly, the volume fraction $\phi(t)$ of an fcc crystal is related to the location $q_m(t)$ of the (111) reflection as follows:

$$\phi(t) = \frac{2}{9\pi^2\sqrt{3}}(q_m(t)R)^3.$$

(6.4)

Since the volume fraction of the structure of the close-packed plane is independent of the stacking arrangement, we interpret $\phi(t)$ as average volume fraction of the crystal phase.

### 6.3 Results

First of all, we will address the gravitational influence. The particle Peclet number is given by $Pe = \tau_s/\tau_b$, where $\tau_s$ is the time for a free particle to sediment one radius, $\tau_s = U_0/R$, where $U_0$ is the dilute sedimentation velocity given by:

$$U_0 = \frac{2\Delta\rho R^2g}{9\eta},$$

(6.5)

where $\Delta\rho$ is the difference in density between particle and solvent, $g$ is acceleration due to gravity, and $\eta$ is the solvent viscosity. The Brownian time is $\tau_b = R^2/D_0$, where $R$ is the average radius of the particle, and $D_0$ is the free particle diffusion coefficient. The Peclet value of PS0 and PS1 is $3.7 \times 10^{-6}$. This value suggested that the effects of gravity are negligible compared to the dynamics of the particles, so we can consider the crystallization process in the microgravity condition.

Fig.6.1 shows the intensities $I(q,t)$ measured by SAXS during the process of crystallization for a suspension at the fluid/crystal coexistence region. The data are from the sample PS1, where the liquid and solid transition occurs at the temperature $T = 59.5^\circ C$. The crystalline features are clearly present in the structure factor $S(q,t)$ after subtracting the solvent background and division by the form factor (Fig.6.2).

We observe the pronounced peaks at the $q$-range from $0 - 0.3nm^{-1}$. The curve can be fitted with the structure factor calculated for face centered cubic (fcc) crystals. The amplitude of peak $S(q_m)$ at the two peak positions $q = 0.058$ and $q = 0.131$ are displayed in Fig.6.4. The two peaks behave qualitatively similar. Two distinct stages appear during the crystallization process: slow mode and fast mode.
Fig. 6.5 shows the quantities that characterize the process of the crystallization determined using equations 6.1-6.4. From the crystallinity $X(t)$ as function of time, we can identify two stages: an initial relaxation stage with increasing suspension concentration from $t = 20$ s to about 260 s, and a fast mode associated with nucleation and growth for $t > 280$ s.

When we plot $S(0)$ as function of time during the crystallization process (Fig. 6.3), we observe a continuous change over the whole time span, no sudden jump occurs. It suggests that the particles remain in the same state. The rapid crystallization process can be described by power law, $X(t) \sim t^\alpha$. The growth exponent $\alpha = 1$, indicates that interface limited growth is controlling this crystallization process. One unexpected feature during the growth process is the jump from solid back to liquid at $t = 420$ s. Although at odds with the continuous change of the compressibility, a similar observation was reported by Chaikin et al. in their measurements on hard sphere systems in space[131]. They proposed the idea of interaction between crystallites: growth and coarsening at the same time. It is opposed to the classical theory for crystallization that assumes that growth and coarsening are independent stages, one after the other. In Fig. 6.5b, we see that from $t = 260$ s to 420 s and $t = 520$ s to 640 s, the size of the crystallites increases linearly, while the crystallinity $X$ over this
Figure 6.2: Structure factors as function of q vector for the corresponding intensity in Fig.6.1.

Figure 6.3: S(0) as function of time during the crystallization. S(0) is related to the osmotic compressibility.

interval increases at a rate less than $L^3$. The number of crystallites decreases during this period. The process can be described as “simultaneous coarsening and growth”. The small crystallites shrink and eventually disappear. As a result, the number of
Figure 6.4: The amplitude of structure factor changes during the crystallization at different \( q \) vector with respect to (111) and (202) plane. Slow mode and fast mode are observed in the crystallization.

Figure 6.5: Extracted parameters from the data shown in Fig. 6.2. (a) Crystallinity. (b) Average crystal size \( L \). (c) Number density of crystal. (d) Volume fraction of crystal.
crystallites decreases, while large crystallites keep growing, and the measured average crystallite size still increases with time[131]. Although the reproducibility of the phenomena we report here should be tested in future work, the preliminary result is promising to shed the light to understand the true mechanism of crystallization. The volume fraction of the solid remains 0.43 during the crystallization process. For charged particles, the freezing volume fraction of 0.43 is in reasonable agreement with the prediction from simulation[133].

Figure 6.6: The structure factor evolution during crystallization at a volume fraction of 0.015, T=51.3°C.

For the sample PS0, we observe the gas to solid instead of the fluid to solid transition for PS1. The process of crystallization is completely different. In Fig.6.6 we show the evolution of the structure factor $S(q)$ with time. The initial volume fraction is $\phi = 0.015$ and the structure factor is unity over the whole $q$-range at the room temperature. The same analysis was carried out as before to present the quantities that characterize the kinetics of the crystallization. In Fig.6.7, the initial fast stage results from the nucleation and growth. The crystal size $L \approx 20$ (b) remains constant over time, although $X(t)$ increases rapidly. This suggests that crystallization is dominated by nucleation. Indeed, the number of crystallites increases at this stage as can be seen in Fig.6.7(c). The slow stage at the long time results from the coarsening of large crystals at the expense of the small crystals. The volume fraction of crystal
Figure 6.7: Extracted parameters from the data shown in Fig.6.6: (a) crystallinity, (b) average crystal size \( L \), (c) number density of crystal, (d) volume fraction of crystal.

Increases from 0.365 to 0.385. The value is smaller than that of crystal formed from liquid to solid.

As we mentioned before, there is initial relaxation period at the first stage to rearrange the structure. The new experiment was performed to study the crystallization at the deep quench. The measurement has been done with temperature increase in steps of 0.5 K instead of 0.05 K, which corresponds to an average heating rate of \( 10^{-3} \) C/s instead of \( 10^{-4} \) C/s. The structure factors of the samples obtained with both heating rates and measured at the same temperature are shown in Fig.6.8. We found structure factor (A) at the higher heating rate, which does not show the characteristic crystal peaks, but shows the signature of a glass: The height of the first peak is 2.6, and the higher order reflections are less pronounced except the second peak. Both structure factors remained constant in time when we stopped the temperature rise. We conclude that at this higher heating rate, the system is "quenched" into a glassy state, analogous to glass formation in a molecular system. The reason for
the glass formation could be, at the first stage, the initial relaxation stage is essential because the concentration of suspension increases slowly to relax and dissipation of any strongly asymmetric and thermodynamically unstable structure. If the system are quenched very fast to neglect this relaxation time, the structure appear to form the irregularly shape, which is characterized as glass phase[2].

Figure 6.8: The structure factor $S(q)$ obtained with the different step of increase the temperature $T = 56.0^\circ$C. $\phi = 0.015$, Curve A: quenching rate: $10^{-4}$C/s, Curve B $10^{-3}$C/s.

6.4 Conclusion

The dynamics of crystallization were studied by time-resolved structure factor measurements, from which we calculated the amount of sample converted to solid, the average linear crystal size, the number of crystals and the average volume fraction of the crystal phases as function of time. Both gas to solid and liquid to solid transitions are investigated. The two transitions show different scenarios for the crystallization process:

For the liquid to solid transition, there is initial relaxation stage with slow increase of suspension concentration. It is followed by a fast stage of nucleation and growth, the growth is described in the linear of the elapsed time (interface limited growth). Both coarsening and growth proceed spontaneously, in contrast to the classic theory of the nucleation and growth of isolated crystallites. The average volume fraction of crystal remains 0.43 in the crystallization process. For the gas to solid transition, there is no initial relaxation stage, the fast conversion immediately occurs at the early
stage, although the size of crystal does not increase at the fast conversion time, the number of crystal increases at this stage. It suggested the process is dominated by the nucleation. The coarsening stage at the longer time. The average volume fraction of crystal slightly increases from 0.365 to 0.385. We also observe that a deep quench from the gas phase leads to the formation of a glass, not a regular crystal.

We demonstrated the dynamics of crystallization in charged colloidal system using the temperature as a control parameter. The experiments, restricted in number, indicate that interesting physics can be done and unexplained behavior can be explored in future.