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Crystallization in Polydisperse Binary Colloidal Suspensions

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We present results from recent crystallization studies on marginal binary suspensions of colloidal particles. As small amounts of the second component are added, crystallization slows, and in some cases may cease altogether. The results support a growth mechanism whereby crystallization occurs in conjunction with a local fractionation process near the crystal-fluid interface, significantly altering the kinetics of crystallite nucleation and growth.

1. Introduction

It is well known that single component hard spheres begin to crystallize at volume fractions beyond 0.494. Between 0.494 and 0.545 there is a crystal-fluid coexistence region, and above 0.545 the entire system will crystallize. The crystals take the form of close-packed hexagonal layers, and can be Face-Centered Cubic FCC (an ABCABC stacking sequence), Hexagonal Close Packed HCP (an ABAB stacking sequence), or random hexagonal close packed (RHCP), which consists of a mixture of FCC and HCP with random registration of planes. This latter form is observed experimentally in single component hard sphere colloidal systems crystallized from the melt [1, 2]. The application of shear can induce more FCC-like stacking [3], while some binary mixtures exhibit superlattice formation [4].

However, colloidal particles are inherently polydisperse, and theory, simulation and experiment show that polydispersity causes a slowing in the crystallization process, and may be accompanied by local partitioning or segregation of particle sizes [5,6].

We recently demonstrated [7, 8] that particles with a negatively skewed polydispersity can exhibit a smectic-like crystalline structure consisting of close-packed layers with no registration of planes. We also showed that for these particles, the onset of nucleation was delayed by up to an order of magnitude, and they displayed qualitatively different growth behaviour compared to particles with a more symmetric size distribution. We proposed a growth mechanism whereby local size-based fractionation of particles near the crystal-fluid interface accompanies growth. This completely alters the kinetics of crystal nucleation and growth, and becomes more significant as polydispersity or skewness increases.

In this paper marginal binary mixtures are used to further examine these ideas.

2. Methods

The methods and analysis used here have been described in detail previously [7-11] and will be summarized only briefly. The particles behave as hard spheres in the suspending solvent, cis-decalin and are index matched to allow light scattering measurements [9].

The mean particle radius and polydispersity were determined by light scattering [10]. Measurements of the crystal growth parameters were obtained from time resolved measurement of the Bragg reflections scattered from the growing crystallites, analogous to X-ray powder crystallography [11]. The parameters measured from the main reflection are: the relative amount of crystal present in the sample, the crystallinity $X(t)$, measured from the peak area; and the average crystallite size $L(t)$, measured from the peak width.

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3. Results

The structure factors as functions of volume fraction and composition are shown in figure 1. The single component samples (X1 and W1) exhibit quite different crystal structures – latex X exhibits the three peaks indicative of RHCP structure, while latex W (which has a polydispersity highly skewed towards smaller than average particles) shows a single peak at higher angles that is identified as being indicative of close-packed layers with no registration of planes [7].

At a volume fraction of 0.53, the addition of small amounts of latex W (smaller particles), causes the peaks to broaden, implying smaller crystal sizes. However, the nature of the crystal packing (RHCP) does not change, even with 10% latex W. At higher volume fractions (0.54 and 0.55), the addition of even a small amount of latex W completely disrupts crystallization, and the samples remain amorphous over all time scales. The amorphous structure factors are, however, different from the initial metastable fluid, implying that there has been some structural rearrangement.

By contrast, the addition of small amounts of the larger particles to latex W (W2) does not inhibit crystallization. The samples still crystallize, and in the case of a volume fraction of 0.55, the crystallization is enhanced.

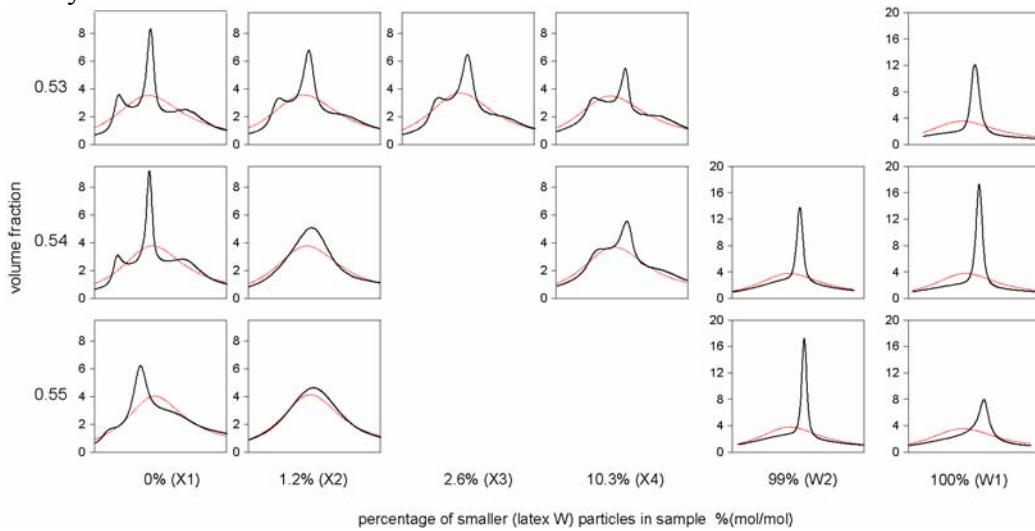


Fig. 1. Structure factors of the metastable fluid, taken immediately following tumbling (red) and after crystallization ceased (black). Vertical axes are intensity (arb. units) and horizontal axes are angle. Data are shown for 3 different volume fractions, and 6 different compositions.

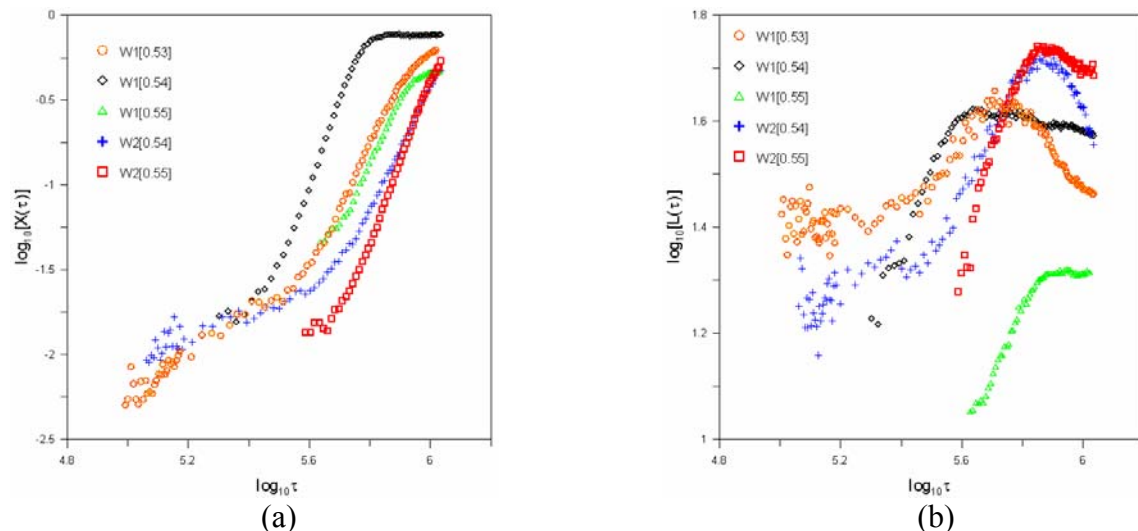


Fig. 2. (a) Log crystallinity vs. log time and (b) log average crystal size vs. log time.

Figure 2 shows the amount of crystal $X(t)$ and the average crystal size $L(t)$ as functions of time for samples W1 (pure latex W) and W2 (latex W with 1% larger particles). At each volume fraction the presence of 1% of the second component significantly delays the onset and speed of crystal growth (fig. 2a – note the log scale).

Figure 2b shows the average crystal size as a function of log time, and in all cases it rises to a maximum, then either plateaus or falls. For both 0.54 and 0.55, the addition of the second component increases the value of the maximum average crystal size. The presence of the larger particles therefore encourages larger crystals, consistent with figure 1.

4. Discussion and Conclusions

Changing the shape of the particle size distributions through the production of marginal binary mixtures has confirmed our previous results on polydisperse single component colloidal suspensions [7,8]. In the early part of the crystallization process, a number of nuclei form and begin to grow. In order to grow from the polydisperse suspension, there must be a local fractionation process, excluding the smaller particles from the crystal. At some point, the excluded layer of particles becomes sufficiently large that movement of correctly sized particles onto the crystal becomes exceedingly slow, and further growth effectively stops. In order for the sample to approach equilibrium, new nuclei must form elsewhere and begin to grow. At this point, the measured average crystal size begins to drop due to new smaller crystallites forming. The addition of smaller than average particles to the distribution therefore slows and/or disrupts crystallization (figure 1).

On the other hand, the addition of larger particles increases the distance between the planes and improves the ordering within the crystal lattice, allowing crystallization to proceed more easily (figure 2). A more extensive analysis of these results will be published elsewhere.

Acknowledgments

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