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Colloidal crystal growth monitored by Bragg diffraction interference fringes

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ABSTRACT

We monitored the crystal growth kinetics of crystallization of a shear melted crystalline colloidal array (CCA). The fcc CCA heterogeneously nucleates at the flow cell wall surface. We examined the evolution of the (1 1 1) Bragg diffraction peak, and, for the first time, quantitatively monitored growth by measuring the temporal evolution of the Bragg diffraction interference fringes. Modeling of the evolution of the fringe patterns exposes the time dependence of the increasing crystal thickness. The initial diffusion-driven linear growth is followed by ripening-driven growth. Between 80 and 90 μM NaCl concentrations the fcc crystals first linearly grow at rates between 1.9 and 4.2 μm/s until they contact homogeneously nucleated crystals in the bulk. At lower salt concentrations interference fringes are not visible because the strong electrostatic interactions between particles result in high activation barriers, preventing defect annealing and leading to a lower crystal quality. The fcc crystals melt to a liquid phase at >90 μM NaCl concentrations. Increasing NaCl concentrations slow the fcc CCA growth rate consistent with the expectation of the classical Wilson–Frenkel growth theory. The final thickness of wall-nucleated CCA, that is determined by the competition between growth of heterogeneously and homogenously nucleated CCA, increases with higher NaCl concentrations.

1. Introduction

Charged, monodisperse colloidal particles suspended in relatively pure water can form randomly dispersed suspensions, crystalline colloidal arrays (CCA), or glassy structures [1–9]. Surface-charged monodisperse colloidal particle suspensions will crystallize into non-close-packed CCA with fcc or bcc structures over wide ranges of particle concentrations, surface charge densities, and salt concentrations [5,6]. The samples can be polycrystalline or they can form large single crystal domains [10–15]. The degree of CCA ordering depends on the colloidal particle size and charge, as well as the particle size and charge monodispersity, the average spacing between particles, and the solution ionic strength, the temperature, and the medium dielectric constant, all of which impact the electrostatic interactions between particles [16–20].

Very low particle charge and/or very high charge screening can result in particle repulsive interactions so small that the thermal kinetic energy of the particles exceeds their primary interparticle repulsive energy barriers. This allows the attractive van der Waals forces to dominate, which results in irreversible particle flocculation [21,22].

Increasing particle charge will electrostatically stabilize colloidal particle dispersions, preventing particle flocculation. For modest electrostatic stabilization the colloidal particles will not show long-range order and, thus, adopt a liquid-like phase with short range ordering [1,2,13,23,24]. At larger electrostatic interactions the particles can self-assemble into well-ordered CCA [1,13,14,25]. The equilibrium particle ordering in this case is generally in an fcc or bcc structure.

Further increases in particle electrostatic interactions can create systems where the interparticle repulsive interactions are too large for the particles to crystallize into highly ordered crystalline states [4]. This is because the electrostatic interactions are too large to allow the particle motion and density fluctuations which enable crystal annealing. The system in this case forms a vitreous glass or an amorphous solid [4,7,9,26–28].

The kinetics of ordering of these glassy and amorphous solid systems can be very slow to nonexistent [4,7,26,27]. However, these systems can be induced to order by applying mechanical perturbations such as shear forces parallel to the container walls that induce particle layer assembly parallel to the walls; the shear forces overcome the activation barriers for particle motion [9,13,14,29–34].

Previous studies of colloidal crystal growth in strongly electrostatically repelling colloidal suspensions show two regimes: linear growth followed by growth by ripening. In the linear crystal growth regime the growth kinetics are controlled by particle diffusion from the melt to the growing colloidal crystal surface. The growth rates of homogeneously nucleated crystals have been measured over a large range of colloidal particle volume fractions as well as increasing salt concentrations at constant colloidal particle volume fractions [13,30–32,35].

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The growth rates of bcc CCA heterogeneously nucleated at the container cell wall have been measured and found to vary between 0.1 and 10 μm/s for colloidal suspensions of 102 nm diameter particles and 450 charges [36,37]. Increasing the volume fraction of these colloidal particles from 0.0013 to 0.0024 increases the growth rate 1000-fold from 0.01 to 10 μm/s. Increasing the NaCl concentration from 0 to 1.2 μM while holding the colloidal particle volume fraction fixed decreases the colloidal crystal growth rate from 10 to 0.01 μm/s.

From these studies it appears that both homogeneously and heterogeneously nucleated colloidal crystal growth rates follow the Wilson–Frenkel growth law [13,30,35,36,38,39]. There are fewer studies of the growth rates of more strongly electrostatically interacting particles that commonly form fcc CCA.

An understanding of the crystal growth mechanisms of CCA is important for optimizing this growth to form large single domain crystals for use as photonic crystals [11,40–44]. Thin films of these crystals can be used to reject narrow bandwidths of light from the UV to near-IR spectral regions [11,10].

Numerous methods have been used to study the degree of ordering of CCA. Methods utilizing confocal and visual microscopy are able to image colloidal particles in the first few layers of a colloidal crystal [36,45–48].

The CCA Bragg diffraction intensities and bandwidths can provide information on the crystal ordering [48–53]. In the thick crystal limit a decreasing crystal ordering results in a decrease in the Bragg peak intensity and an increase in the angular width. For example, Colvin and co-workers showed that the Bragg-diffracted intensities decrease for close-packed CCA fabricated with increasing colloidal particle size polydispersities [48]. Norris et al. demonstrated for solid close-packed CCA that the interference fringe modulation depths decrease with increasing disorder [54].

In the work here, we examine the growth kinetics of CCA formed from highly charged colloidal particles in suspensions containing different NaCl concentrations. We observe for the first time Bragg diffraction fringes from non-close-packed liquid CCA samples. We use these interference fringes to monitor the growth of the CCA out from the wall where they heterogeneously nucleate.

2. Materials and methods

Our CCA are composed of 200 ± 3 nm diameter polystyrene colloidal particles (2.52×10^{13} particles/cm^3) which each possess 33 000 surface sulfonate groups. We added NaCl to the particle dispersions to partially screen the electrostatic interactions in order to achieve ordering kinetics in the seconds time frame, which is easily studied.

We previously characterized the structure of our CCA without adding NaCl and found them to be fcc [55]. Since the (1 1 1) plane diffraction wavelength did not change with NaCl addition no transition to a bcc structure occurred, indicating that the samples studied here are all in an fcc structure; if an fcc to bcc phase transition occurred due to the NaCl-induced decrease in the electrostatic repulsions between particles the Bragg peak wavelength would have blue-shifted ~25 nm.

We monitored the ordering and growth of CCA from the wall by measuring the relative intensities of the Bragg fcc (1 1 1) diffraction peaks and the interference fringes in the wings of these Bragg diffraction peaks. The fringe spacings are known to depend on the crystal thickness [54,56]. Thus, measurements of the fringe spacings directly indicate the thickness of the growing CCA crystals. As far as we know this is the first report to observe these fringes in liquid CCA samples and the first to utilize their time-dependent spacings to monitor CCA growth kinetics.

Fig. 1 shows the reflection spectrum of an fcc CCA sample of 200 ± 3 nm diameter polystyrene colloidal particles containing 30 μM NaCl illuminated with a collimated white light beam normal to the flow cell container wall, where the light was collected in a backscattering geometry.

We mechanically perturbed this sample by inducing shear flow and then tapped on the container to mechanically disturb the CCA to speed up its crystallization. The peak centered at $\lambda_B = 861$ nm derives from first-order Bragg diffraction from the fcc CCA (1 1 1) planes.

On both sides of the first-order Bragg diffraction reflection peak we observe intensity oscillations which damp off at wavelengths away from the Bragg maximum [49,55,57–59]. These fringes result from the partial constructive interference for light which is backscattered from the (1 1 1) planes within the crystal [57].

The highest particle density fcc (1 1 1) planes orient parallel to the sample cell wall, such that normally incident light travels along the normal to the (1 1 1) planes [2]. The (1 1 1) plane diffraction occurs at $\lambda_B = 2d_{111}n_{avg}\sin\theta$, where λ_B is the wavelength of light in vacuum, n_{avg} is the CCA average refractive index, d_{111} is the (1 1 1) plane spacing, and θ is the glancing angle, that for normal incidence is $\pi/2$ giving $\lambda_B = 2d_{111}n_{avg}$. We calculate a volume-averaged CCA refractive index, $n_{avg} = \varphi_{H_2O}n_{H_2O} + \varphi_{Pst}n_{Pst} = 1.357$, where φ_{H_2O} is the volume fraction and n_{H_2O} is the refractive index of water. φ_{Pst} is the volume fraction and n_{Pst} is the refractive index of polystyrene. We calculate a lattice plane spacing of $d_{111} = 321$ nm.

This fringe pattern can be used to determine the thickness of the CCA fcc crystal. We search for the crystal thickness which gives the best match between the calculated and the observed fringe patterns. We model the CCA diffraction as if it results from a 1-D stack of bilayer dielectric slabs which have periodicities and an overall average refractive index that is identical to those of the CCA [59]. We determined the thicknesses and refractive indices of the dielectric slab bilayers by requiring them to show the same reflectance as that of a single CCA fcc (1 1 1) layer calculated in the kinematic single scattering approximation [59]. Our modeling of Fig. 1 data indicates a total of 90 (1 1 1) layers which yields a 29 ± 0.5 μm CCA thickness.

We examined the time dependence of ordering of a CCA sample within a rectangular 700 μm flow cell. We used a syringe to inject

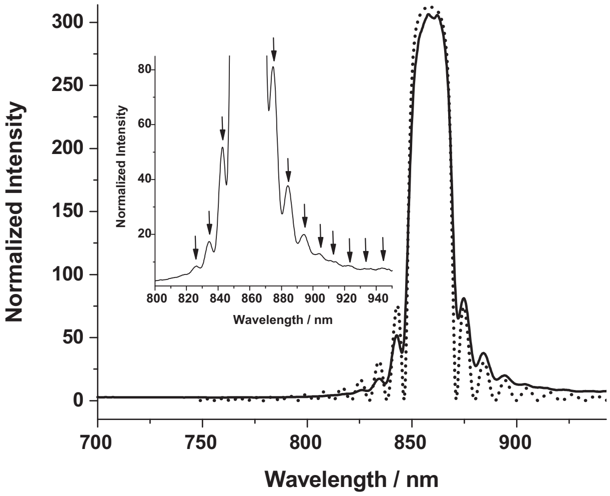

Fig. 1. Normal incidence reflection spectrum from a CCA within a 700 μm thick flow cell. The CCA has a particle number density 23 μm^{-3} and consists of 200 ± 3 nm polystyrene particles in water containing 35 μM NaCl, where each particle contains ~33 000 surface sulfonates. The first-order Bragg diffraction peak at normal incidence from the (1 1 1) planes occurs at 869 nm. The inset shows an expanded region around the first-order Bragg diffraction peak. The dashed line shows the best fit modeling of the fringe pattern which indicates a 29 μm effective crystal thickness.