Grain refinement and partitioning of impurities in the grain boundaries of a colloidal polycrystal

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Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 200X
DOI: 10.1039/b000000x

We study the crystallization of a colloidal model system in presence of secondary nanoparticles acting as impurities. Using confocal microscopy, we show that the nanoparticles segregate in the grain boundaries of the colloidal polycrystal. We demonstrate that the texture of the polycrystal can be tuned by varying independently the nanoparticle volume fraction and the crystallization rate, and quantify our findings using standard models for the nucleation and growth of crystalline materials. Remarkably, we find that the efficiency of the segregation of the nanoparticles in the grain-boundaries is determined solely by the typical size of the crystalline grains.

1 Introduction

Impurities affect drastically crystal nucleation, growth and texture and understanding the role they play during the solidification processes is of great interest in material science and engineering, pharmaceutical industry, mineralogy, protein crystallization and life science. Moreover, the control of the texture by addition of solutes is important for tailoring the mechanical properties of crystals.

Relevant progress in understanding crystallization of mono and bidisperse systems has been achieved using colloids, that are often regarded as an analog to atoms on larger length and time scales, enabling real-time studies by direct visualization of processes of importance and interest in condensed matter physics. Crystallization of nano- and micro-spheres have been widely investigated numerically and experimentally, including in bi-component systems. Binary mixtures of colloids where the volume fraction of the two species is not too unbalanced (up to a factor of 7, but most typically by a factor of 2) exhibit a great variety of crystalline superlattice structures similar to atomic systems. By contrast, the addition of a very small amounts of a dopant in a solidifying matrix does not change the crystalline unit cell, but can modify the nucleation, and induce crystal growth frustration, local defect formation and local fractionation, depending on the volume fraction and size of the dopants.

In this article we present a novel strategy for the control of the texture of colloidal polycrystals, based on the addition of small amounts of nanoparticles (NPs) as dopants to a solidifying matrix. We achieve the segregation of NPs in a network of thin sheets that is the colloidal counterpart of the texture of grain boundaries formed during the solidification of crystalline metallic alloys and other molecular materials doped with impurities. By varying the NP volume fraction and the rate at which the background matrix is solidified, both the typical mesh size of the dopant network and the efficiency of the partitioning of the NPs between the matrix and the grain boundaries are tuned. In the framework of the classical nucleation theory, we show quantitatively for the first time how both the nucleation and the growth of colloidal crystallites are influenced by the NP volume fraction and the crystallization rate, determining the final grain size.

2 Materials and methods

The colloidal polycrystal is composed of an aqueous solution of Pluronic F108, a commercial PEO-PPO-PEO triblock copolymer (Serva Electrophoresis GmbH), where PEO and PPO denote polyethylene oxide and polypropylene oxide, respectively. The co-polymer (concentration of 34% w/w) is fully dissolved at T ≈ 0 °C. Upon increasing T, it self-assembles into spherical micelles of diameter d ∼ 22 nm, due to the increased hydrophobicity of the PPO block. The volume fraction, φ, of the micelles increases with T, until crystallization occurs due to micelle crowding. Differential scanning calorimetry and rheology show that crystallization occurs be-
between 15 °C and 16 °C, depending on the heating rate.31 We emphasize that, unlike conventional colloidal systems where controlling precisely and changing in situ the volume fraction is a difficult task, our system allows crystallization to be induced at the desired rate simply by varying \( T \), in analogy with molecular materials.

In order to analyze in a quantitative way the crystallization process, as it will be discussed in Sec. 3, it is convenient to map our micellar system onto a hard sphere suspension, by determining the relation between \( T \) and \( \phi \). The soundness of this approach is supported by previous work22 showing that the static structure factor of a similar micellar system could be mapped onto that of hard spheres using an affine relation between \( T \) and \( \phi \). In our case, we determine \( \phi(T) \) by comparing the temperature dependence of the sample viscosity in the micellar fluid phase to the volume fraction dependence of the viscosity of hard-spheres suspensions33. The mapping thus determined is \( \phi = \alpha \times (T - T_0) \) with \( T_0 = 4.2 \) °C and \( \alpha \approx 0.045 \, \text{°C}^{-1} \). With this mapping, rheology measurements in the regime where the sample is solidified very slowly so as to avoid any significant undercooling show that the onset of crystallization occurs at \( \phi = \phi_{\text{cryst}} \approx 0.5136 \), a value compatible with that expected for slightly polydisperse hard spheres.

We dope the micellar crystal with small amounts (at most 1\% v/v) of green-yellow fluorescent carboxylated polystyrene nanoparticles purchased from Invitrogen, with diameter \( \sigma = 20, 36 \) and 100 nm. Neutron scattering measurements show that the microscopic crystalline structure (face-centered cubic, with lattice parameter 30 nm) is preserved upon addition of up to 2\% v/v of NPs, twice than the highest concentration used here. For confocal microscopy imaging, samples are introduced in chambers of thickness 250 \( \mu \text{m} \) and solidified by raising the temperature from 33 °C to 23 °C at a controlled rate, \( \dot{T} \), and visualized at least 20 \( \mu \text{m} \) from the walls.

### 3 Results and Discussions

We show in Figs. 1A-C representative images of colloidal samples doped with NPs with diameter \( \sigma = 36 \) nm. All samples are solidified at the same rate, \( \dot{T} = 7 \times 10^{-3} \, \text{°C min}^{-1} \), and the average NP volume fraction \( c_0 \) is varied between 0.05\% and 1\%. Images exhibit fluorescent (clear) connected thin lines that separate featureless (dark) zones. Confocal scans through the material show that the clear lines are in fact 2-D sections of a network of grain boundaries enriched in NPs that delimitate grains with different crystalline orientations. A 3-D reconstruction of sample with \( c_0 = 0.5\% \) is reported in Fig. 1D, where different false colors indicate different grains. Figures 1A-C clearly show that the grain size decreases by increasing the amount of NPs. To quantify the influence of NPs, we calculate the cross section area of the grains, \( S \). The frequency distribution of \( S \) for various \( c_0 \) is reported in Fig. 1E: [about 800 cross sections, taken in distinct positions on both sides of the chamber are measured for each experimental condition]. The peak of the distribution moves to smaller values with increasing \( c_0 \), demonstrating grain refinement at larger impurity content.

![Fig. 1 Color online. (A-C) Confocal microscopy images of three samples prepared at different impurities (NP) volume fraction \( c_0 \). The clear lines are sections in the observation plane of the grain boundaries, where the NPs accumulate. The temperature ramp is \( \dot{T} = 7 \times 10^{-3} \, \text{°C min}^{-1} \). (D) 3-D reconstruction of a sample with \( c_0 = 0.5\% \). The size of the reconstructed region is 35×30×53 \( \mu \text{m}^3 \). (E) Frequency distribution of the cross section of the grains, for samples with various \( c_0 \) prepared at a constant \( \dot{T} = 7 \times 10^{-3} \, \text{°C min}^{-1} \). Inset: same data as in the main plot but scaled by the average cross section \( S \). Impurities are fluorescently labeled polystyrene NPs with diameter 36 nm.

In analogy to atomic crystals and other materials,35 we find that the rate at which temperature is changed during solidification has also a crucial influence on the final grain size, slower ramps leading to a coarser texture. This is demonstrated for samples with a fixed NP volume fraction (\( c_0 = 0.5\% \)) and prepared with various temperature ramps, as in the images in Figs. 2A-C and in figure 2D where the size distributions of the cross section area of the grains, spanning two decades, are reported. In all cases, the distributions are relatively narrow, their standard deviation normalized by the average being 0.7 ± 0.2. Remarkably, we find that the shape of the distributions is almost independent of the NPs volume fraction and of the temperature ramp, as demonstrated by the inset of Fig. 1E: (resp. Fig. 2D), where curves for various \( c_0 \) (resp. \( \dot{T} \)) are col-
lapsed by normalizing the $S$ with respect to its mean value, $\bar{S}$. In the insets, the right tails of the distributions are approximately straight lines in a semi-logarithmic plot, indicating exponential tails.

To quantitatively analyze our experimental findings, we use classical models for the nucleation and growth of crystalline grains. We first recall how an average grain size can be computed, using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory, which assumes that nucleation occurs randomly and homogeneously, and that the growth velocity of the crystallites, $v_g$, does not depend on the extent of the crystallization process and is isotropic. Following JMAK, the extended volume fraction of the sample that has crystallized at time $t$, $X_c(t)$, reads:

$$X_c(t) = \frac{4\pi}{3} \int_0^t I(\tau) \left[ \int_\tau^t e^{\kappa(\tau')} d\tau' \right]^3 d\tau$$

where $I(\tau)$ is the nucleation rate per unit volume at time $\tau$. The extended volume fraction does not take into account that as crystallization proceeds less fluid phase is available for nucleating new crystallites. Moreover, it doesn’t account for the fact that crystallites stop growing when they impinge into each other. As shown by Kolmogorov and Avrami, these effects can be accounted for by calculating the actual volume fraction that has crystallized, $X_a(t)$, according to:

$$X_a(t) = 1 - \exp[-X_c(t)]$$

The expected grain radius $R$ can be calculated from the grain number density at the end of the crystallization process, yielding

$$R = \left( \frac{4\pi}{3} \int_0^\infty I_a(\tau) d\tau \right)^{-1/3}$$

where $I_a$ is the actual nucleation rate:

$$I_a(\tau) = [1 - X_a(\tau)] I(\tau)$$

Note that the nucleation rate, $I$, and growth rate, $v_g$, are in general time-dependent quantities. This is indeed the case in our experiments, where crystallization occurs while the sample is submitted to a continuous increase of temperature, leading to a continuous increase of the micelle volume fraction. In the following, we aim at calculating $R$ using Eqs. (1-3) in order to compare it to the experimental results of Fig. 3A-B. To this end, explicit expressions are required for $I$ and $v_g$. We start by discussing the growth velocity and assume that $v_g$ is given by the Wilson-Frenkel law:

$$v_g = \frac{D_r}{k_B} \left[ 1 - \exp\left(-|\Delta\mu|/k_BT\right) \right]$$

where $k_B$ is Boltzmann’s constant, $\Delta\mu$ is the difference in chemical potential between the solid and the liquid phases, since $S$ is the grain cross section obtained by a random slicing, not the maximal cross section. However, we expect the difference to be relatively small: for an isolated sphere, e.g., the average radius of a random cross section differs from the actual sphere radius by less than 20%.

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Note that strictly speaking $R$ is smaller than the actual average grain radius, with a clear influence of both NP content and temperature ramp. In A and B the bars are the standard deviation of the size distributions.
$D_s$ is the self-diffusion coefficient of the micelles in the liquid phase, and $\lambda$ is a typical distance over which diffusion occurs when a micelle in the fluid phase is incorporated in the growing crystallite.

To evaluate $\Delta \mu$, we take advantage of numerical and experimental results on the crystallization of hard spheres (HS) suspensions, assuming that micelles in first approximation behave as HS and using the $\phi(T)$ mapping discussed in Sec. 2. We evaluate $\Delta \mu$ from numerical simulations of HS colloids, where data can be well fitted by

$$\Delta \mu = A_\mu k_BT (\phi_{\text{cryst}} - \phi)$$

with $\phi_{\text{cryst}} \approx 0.5$ and $A_\mu \approx 15$. In the following, we take $\phi_{\text{cryst}} = 0.5136$ as discussed in Sec. 2 while $A_\mu$ is treated as an adjustable parameter. The volume fraction dependence of $D_s$ for the micelles is estimated from experimental data on the structural relaxation time associated with self-diffusion in suspensions of HS colloids, assuming that the diffusion coefficient is inversely proportional to the structural relaxation time. We use the empirical formula $D_s = D_0 \times \left[1 - 2.5\phi + 1.36\phi^2 - (1 - \frac{\phi}{\phi_0}) + 144.57\phi^2 \left(1 - \frac{\phi}{\phi_0}\right)^{-2.5}\right]$, which reproduces very well the experimental data in the range $0 \leq \phi \leq 0.59$, and use $D_0 = \frac{k_BT}{3\eta_0\pi d^2} = 6 \times 10^{-14} \text{m}^2/\text{s}$ as the diffusion coefficient of a micelle in the dilute regime, where $\eta_0 = 0.32 \text{ Pa s}$ is the solvent viscosity. The quantity $\lambda$ is expected to be of the order of the micelle diameter, $d$, although significant differences between simulations and experiments have been reported. We set $\lambda = A_\lambda d$ with $A_\lambda$ an adjustable parameter.

We now turn to the nucleation rate $I$. Classical nucleation theory (CNT) predicts

$$I = \Gamma \exp[-\Delta G^*/k_BT] \tag{6}$$

where $\Delta G^*$ is the nucleation barrier in the Gibbs free energy to be overcome in order to form a stable nucleus, and the kinetic prefactor $\Gamma = \left(\frac{1}{6\sigma_d N_c d^6} |\Delta \mu|\right)^{1/2} \rho_s^{2/3} d^{2/3}$. Here $N_c$ is the number of micelles in the critical cluster, and $\rho_s = 6\phi_0/\pi d^3$ is the number density of the micelles in the liquid phase. According to CNT, $\Delta G^*$ is the maximum in the Gibbs free energy, which is the sum of a surface free energy term, $\Delta G_s = 4\pi r^2 \gamma_0$, and a volume term, $\Delta G_v = \frac{-4\pi r^3}{3} \rho_s |\Delta \mu|$. Here $r$ is the radius of a nucleus, $\gamma_0$ is the surface free energy density of the fluid-crystal interface and $\rho_s$ is the number density of micelles in the solid phase ($\rho_s = 6\phi_0/\pi d^3$ with $\phi_0 \approx 0.5$). One readily finds

$$\Delta G^* = \frac{16\pi}{3} \frac{\gamma_0^3}{\rho_s |\Delta \mu|} \tag{7}$$

For the surface free energy density, we use $\gamma_0 = k_BT A_\gamma/a^2$ with $A_\gamma$ an adjustable parameter expected to be of order 1. Numerical simulations of HS colloids show that $N_c$ the number of colloids in the critical nucleus is of order 100 and depends only weakly on the volume fraction; accordingly, we take $N_c = 100$ independent of $\phi$.

In order to model the effect of the addition of NP, we need to modify the CNT expressions. We assume that the most relevant effect is a modification of the surface free energy term due to the accumulation of NP at the interface between the crystal and the liquid phase (see fig. 5), since slight variations of $\gamma_0$ are known to have a massive impact on nucleation rates. We thus neglect any dependence of $|\Delta \mu|$ on NP content, implying that both $v_g$ and the volume term $\Delta G_v$ are unchanged upon addition of NP, and propose that the presence of the NPs at the interface leads to a reduction of the surface free energy density. We assume that this reduction is proportional to the amount of NPs at the interface, which in turn is proportional to $n_p$, the amount of NPs initially available in the volume occupied by a crystallite. Hence, for a nucleus of radius $r$, the reduction of surface energy is proportional to $n_p = 8\pi^2 c_0/\sigma^3$, and to the cross-section of the NPs, $\pi \sigma^2/4$. The surface term then becomes $\Delta G_s = 4\pi r^2 \gamma_0 - \frac{2\pi r^3}{\pi \sigma^2} n_p$, with $F_p$ a proportionality constant. Note that the NP contribution, although physically due to a change of the surface term, formally can be incorporated in the volume term of $\Delta G$, because it scales with $r^3$. In the presence of NPs, the free energy barrier is then obtained by a suitable modification of the denominator of Eq. 7:

$$\Delta G^* = \frac{16\pi}{3} \frac{\gamma_0^3}{\rho_s |\Delta \mu| + \left(\frac{2}{3} \gamma_0 F_p c_0/\sigma^3\right)} \tag{8}$$

Using $A_\mu$, $A_\lambda$, $A_\gamma$ and $F_p$ as adjustable parameters, we fit the experimental $R$ using the modified CNT approach outlined above. Operationally, we take $t = 0$ as the time at which $\phi = \phi_{\text{cryst}}$ and, for a given $T$ and $c_0$, we calculate numerically $X_c(t)$ using Eq. 1 and $v_g(t)$ and $I(t)$ as given by Eqs. 5, 6, 8, where the latter quantities depend on time through $D_s$ and $\Delta \mu$. Equations 7-8 are then used to obtain $R$. We show in Fig. 3A-B the best fits as solid lines. While not perfect, the fits exhibit a reasonable quantitative agreement with the experimental data, especially given the order-of-magnitude variations of quantities related to colloidal crystallization often observed in the literature. The fitting parameters are: $A_\lambda = 0.14 \pm 0.05$, $A_\mu = 17 \pm 3$, $A_\gamma = 0.747 \pm 0.20$ and $F_p = 126 \pm 24$. The three fitting parameters that are independent of NP content and for which a comparison with previous works is possible are in good agreement with numerical results, for which $A_\lambda = 0.2 - 0.5$, $A_\mu \approx 15$, $A_\gamma = 0.64$. Furthermore, this simple model is able to capture the main experimental trends, in particular the roll-off of $R(T)$ at slow ramps, which is due to the presence of NPs (compare the continuous and dotted lines in Fig. 3B) . The discrepancy at high $c_0$ observed in Fig. 3A is presumably due to an over-evaluation of the effect of NPs on the surface tension, due to the fact that, as we shall show it in the following, as $c_0$ increases the fraction of NPs that are effectively expelled from a growing crystallite decreases. Although a qualitative relation between $\Delta G^*$ and the typical crystallite size has been reported for metals, our work is the
first quantitative analysis for colloids of the grain size using nucleation and growth theories.  

So far, we have shown that both the volume fraction of impurities and the crystallization rate determine the polycrystalline texture, thereby allowing for a fine control of the average grain size over almost one decade. We now turn to the investigation of the degree of confinement of NPs once the solidification process is completed. To better appreciate the spatial distribution of the NPs, we show in Figs. 4A-B confocal images of samples doped with particles large enough ($\sigma = 100 \text{ nm}$) to be individually resolved by confocal microscopy, at least for moderate volume fractions. The dopant volume fraction is kept fixed at $c_0 = 0.05\%$, while the effect of $T$ is investigated. 

![Confocal images](image)

Fig. 4 Color online. (A-B) Confocal images of samples prepared with ramp rates $7 \times 10^{-3} \text{ °C min}^{-1}$ and $5 \times 10^{-4} \text{ °C min}^{-1}$, respectively. (C) Ratio $p$ of the volume fraction of NPs in the grain boundaries and inside the grains. The symbols are labeled by the particle diameter and their number density, $\rho$. (D) Same data as in (C) collapsed onto a master curve by plotting $p$ as a function of the average grain cross section. 

As shown in Fig. 4A, for polycrystals prepared using a relatively fast temperature ramp, an excess of NPs is observed in the grain boundaries, consistently with our previous observations with smaller dopants. However, large numbers of individual NPs are clearly visible also in the interior of the grains. By contrast, NPs are almost completely expelled from the grains in samples prepared using a slower ramp (Fig. 4B). We quantify the efficiency of the partitioning by evaluating the ratio, $p$, between the NP volume fraction in the grain boundaries and that in the interior of the grains, as obtained from fluorescence intensity measurements. Figure 4C shows that confinement in the grain boundaries becomes increasingly efficient as the temperature ramp slows down, similarly to observations in atomic systems, and that, quite generally, $p$ decreases when the average number density of impurities, $\rho$, increases. Thus, an increase of either $T$ or $\rho$ yields both a finer texture and a smaller degree of partitioning, suggesting that the degree of partitioning should correlate with the grain size. We note that the grain size, directly related to the number of successful nuclei, does not depend on the size of NPs but only on their quantity, signaling the absence of heterogeneous nucleation on the surface of NPs, as expected since the size of the NPs is comparable to the size of the micelles.

Remarkably, we find that all data for ramp rates spanning two decades, impurity number density spanning three decades, and for NP diameters ranging between 20 nm and 100 nm indeed collapse onto a master curve when plotting $p$ as a function of the average grain cross section (Fig. 4D). Interestingly, $p$ is close to unity and rather insensitive to $S$ until $S \approx 800 \mu m^2$, above which the degree of partitioning increases steeply.

To understand the origin of the correlation between grain size and degree of particle segregation, we analyze the growth of the crystallites during solidification, a quantity not accessible in metallic systems. This is illustrated in Fig. 5 and Supplementary movie S1. 

At low temperature, below the onset of crystallization, the images are homogeneously grey down to the smallest length scale that is accessible (1 pixel = 0.11 $\mu m$), revealing that the impurities are homogeneously distributed in the sample, which is still fully fluid. The nucleation and early stage growth can not be resolved in our confocal microscopy experiments, presumably because the partition of the fluorescent impurities is too weak (Fig. 5A). As solidification proceeds, however, the interface of the growing crystallites becomes increasingly visible, because the fluorescent NPs are expelled by the solid phase and accumulated in the fluid boundary layer (Fig. 5B-C). Eventually, the different grains that are growing touch each other and become faceted, resulting in the formation of a network of grain boundaries where the NPs are confined at a density larger than in the bulk (Fig. 5D). In Fig. 5E we report the normalized impurity volume fraction profiles, obtained from the fluorescent intensity, along the growth direction of one grain from its center: the height of the peak of NP volume fraction increases during the propagation of the solid-fluid interface, indicating that the amount of impurities rejected from the crystallite and accumulated at the interface increases steadily, until the grain stops growing when impinging on an adjacent growing crystallite. Thus, the larger a grain can grow, the higher the volume fraction of the impurities eventually trapped in the grain boundary, explaining the correlation between the grain size and the degree of partitioning shown in Fig. 4D. 

As a concluding remark, we note that we have successfully reproduced our experiments with a variety of NP of different kinds, thereby demonstrating that the system described here provides a powerful, robust and convenient way to study the crystallization of bi-disperse colloidal systems and to segregate NPs in thin sheets within a 3-D soft matrix. The colloidal
composite material investigated here, thanks to its softness and optical transparency, offers a unique opportunity to investigate in real time and by direct visualization the formation of a poly-crystalline texture and its response to an external perturbation. In particular, we are currently exploring the dynamics of the grain boundaries under a mechanical load.

Acknowledgments

We thank P. Olmsted for suggesting the effect of NP on the nucleation barrier, R. Piazza, M. Cloître, J.-L. Barrat, and D. Frenkel for insightful discussions and J. Lambert for the reconstruction of 3-D images. This work has been supported by ANR under Contract No. ANR-09-BLAN-0198 (COMET).

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