Growth Dynamics For DNA Guided Nanoparticle Crystallization

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Here, we give the details of the simulation methods, the technique for the superlattice spacing measurement and melting temperature of SNA polycrystals, the crystallite tracking algorithm we developed, and the calculation of the misorientation angle between two crystallites. The dynamics of the crystallite growth presented in the main article has been collected from the following two types of simulations varying the length scales of the DNA and Au core.

We begin by enclosing two movies that show the nucleation and growth of the crystallites. The file **SP_growth** shows crystallite growth in a gas of SNA particles. The file **SP_coalescence** shows the binary coalescence of two crystallites with the SNA occupying lattice sites of a bcc crystal. The length scales of the SNA used in each movie are listed below.

Movie **SP_growth**: Animation showing the assembly of bcc superlattice simulations. Pink beads: SNA type A, cyan beads: SNA type B ($L = 16.3$ nm, $R = 9.3$ nm, $l = 3.0$ nm, at $T = 0.96T_m$).

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Movie **SP_coalescence**: Simulation of coalescence of two isolated bcc crystallites. Pink beads: SNA type A, cyan beads: SNA type B ($L = 16.3$ nm, $R = 9.3$ nm, $l = 3.0$ nm, at $T = 0.96T_m$).

Interparticle distance

First, we compute the radial distribution function of the SNA inside a simulation cell. We show a plot of the radial distribution function for different NP sizes in Fig.1. For clarity we truncate the curves at the second peak or next-nearest neighbor. The bcc lattice spacing in Figure 2(a) of the main article is computed from these radial distributions. The orientation of the crystallite's bcc lattice is calculated from the lattice vector of the next-nearest neighbor shell.

Figure 1: (a) SNA separation for different σ with fixed $L = 9.3$ nm in a bcc superlattice.

Bond-order parameter and the melting temperature T_m

Superlattices are characterized by long-range positional order of the SNA. In this section, we provide the measure of the bond order parameter to characterize the crystalline order of the SNA in each crystallite as a function of the temperature below the melting temperature T_m or sub-cooling.

Figure 2: Snapshots at different temperatures after $10^7\tau$ time steps during MD simulations. Two types of SNAs are shown with different colors (cyan and pink). Upon cooling from higher temperature, there is an abrupt transition from liquid state to the crystalline state at $T = 1.10T_m$ for $\sigma = 6.0$ nm, $L = 9.3$ nm, and $l = 3.0$ nm.

As introduced in the Ref.,¹ the bond order parameter in three spatial dimensions is defined as

$$Q_{lm}(i) = \frac{1}{nn(i)} \sum_{j=1}^{nn(i)} Y_{lm}(r_{ij}), \quad (1)$$

where $Y_{lm}(r_{ij})$ are the spherical harmonics of l^{th} order, r_{ij} is the position vector between two bonded SNAs, and $nn(i)$ is the total number of nearest neighbors for the i^{th} SNA. In order to measure the bond order, we first evaluate the radial distribution function described in the previous section. The position of the first peak in the radial distribution function provides the selection criteria to distinguish the SNA participating in the bond formation. These calculations provide two opportunities. First, it allows us to follow the melting transition of SNA crystallites. Secondly, it enables us to count the number of superlattice orientations in the simulations. Fig. 2 shows snapshots of the superlattice growth at different temperatures relative to T_m . Fig. 3(a, b) show the bond order Q_6 in Eq. 1 as a function of temperatures for five NP sizes σ and DNA lengths L , respectively. The profiles in Fig. 2 provide evidence for the expected nucleation and growth (first-order phase transition), though the order parameters are continuous due to finite size of the simulations. These simulations further reveal two design rules to the experiments; (i) increasing L increases the stability of the lattices, and (ii) increasing σ destabilizes the superlattice as discussed in the text in the main article. The melting temperature curves shown in Fig. 2(b) of the main text are calculated from Fig. 3.

We note that the order parameters shown in Fig. 3 are less than 0.58, as one expects for a single crystalline bcc lattice. This reduction in the order parameter is associated mainly to the interaction between the grain-boundaries present in the superlattices [see Fig. 2 (a-c)], and in part because we average the order parameter over all SNA while some of them are free without any bonding (background SNA). Nevertheless, the distribution of Q_6 parameter is peaked at 0.58, as expected [see Fig.4]. Further, the increased order parameter for $T \rightarrow T_m$ provides a strong evidence of gradual melting of the grain boundaries or the coalescence of the grains. We simulate a large number of systems with varying DNA length and SNA size; however, we did not find any signature of a phase of the intermediate order between the bcc crystals and the liquid state.

Figure 3: (a) Plots the bond orientational order parameter (Q_6) averaged over all SNA in the ensemble as function of reduced temperatures for increasing Au-NP size σ . (b) Bond order parameter (Q_6) as function of reduced temperatures for five DNA lengths L . In either cases, the difference $\Delta Q_6 = Q_6(II) - Q_6(I) \approx 0.50$, where I and II refers to the disorder and ordered phases, respectively. The abrupt transition is clear evidence a first-order transition.

Figure 4: Histogram of local Q_6 parameter of an individual SNA SNA in a typical simulation below the melting transition.

Grain tracking algorithm

Figure 5: Comparison showing the number of grains in superlattice growth in our method with DXA algorithm.²

Superlattices in the simulations were analyzed by the different methods: orientation analysis, distance analysis, common neighbor analysis (CNA), Dislocation Extraction Algorithm (DXA),² and also by measuring the orientational order parameter. Each of these methods produces identical results. Here, we present the simplest algorithm to track superlattice grains by distance analysis. The algorithm is as follows:

(i) We first measure the lattice constant d from the position of the first peak of the radial distribution function $g(r)$ as illustrated in Fig.1.

(ii) We then find the number of nearest neighbor for each SNA in the lattice using this cut off distance. For bcc, the number of first and next-nearest neighbors should be respectively 8 and 14 respectively. This allows us to identify the crystalline SNA in the superlattice. The rest of the

matrix consists of the surface SNA, grain boundary SNA, background SNA.

(iii) Step 2 produces a configurations of bcc grains, the distance between any two crystallites is greater than R_{cut} . We write a code to iteratively count those disconnected cluster and report it as N_G in the main article.

(iv) The surface SNA are those which are adsorbed to the surface of the crystallite.

(v) From the set of the surface SNA, we identify the subset of the grain boundary SNA by distinguishing those SNA which connects two crystallites. The connectivity sequence of GB SNA is like:

One layer : C_A (bcc SNA from crystallite A) $\leftrightarrow$ GB SNA $\leftrightarrow$ C_B (bcc SNA from crystallite B).

Two layers: $C_A \leftrightarrow$ GB SNA $\leftrightarrow$ GB SNA $\leftrightarrow$ C_B .

Three layers: $C_A \leftrightarrow$ GB SNA $\leftrightarrow$ GB SNA $\leftrightarrow$ GB SNA $\leftrightarrow$ C_B and so on.

We consider the possibility of multiple layers in our analysis, however, in most of the simulations the grain boundary extends only up to 1-2 layers of SNA.

(vi) The remaining SNA in the bulk are considered as the background SNA.

It should be noted that care must be taken when adopting this analysis for other systems. For example, the coexistence of the hcp, and fcc SNA cannot be distinguished by this simple analysis. To check the correctness of this method, we analyzed the problem by tracking the orientation of the grains, and CNA analysis. For comparison, we present the results of DXA algorithm² with our analysis in Fig. 5. In this plot, we plot the number of grains as function of time and the results agree well.

In Fig. 7(a, b) in the main article, we show how the orientation order between the grains are distributed and relax with time. In collecting this data, we take the average over many runs (≈ 300), each starting from different initial configurations and we take an average of the relaxation time. A few of these calculations are shown in Fig. 6.

Figure 6: Evolution of the grain boundary angle with time in a number of independent simulations for $a_0 = 229.25$ nm, $\sigma = 10$ nm, and $L = 9.3$ nm.

Catenoid Shape

We measure the center-to-center distance between the grains as function of time as shown in Fig. 7(a) to estimate the mean free time of coalescence (τ_m) as well as the time when grain coalescence starts. The coalescence time is diffusion limited since it increases linearly when the temperature is increased [Fig. 7(a) inset]. Once the neck develops between adjacent grains, it coarsens, as il-

Figure 7: (a) Center-to-center distance z between two grains as a function of time during the coalescence of two bcc grains of diameter ($a_0 \approx 160$ nm). In inset, we show the mean free time of coalescence (τ_m) at different temperatures. (b) Scaled radius of the neck as function of scaled distance from the centers of the grains at different stages of the coalescence. The solid lines show $2R_{min}/a_0$ as function of the distance from the center for a catenoid with waist radius c measured from simulations. These simulations correspond to SNA systems of $R = 14.3$ nm, $L = 9.3$ nm and $l = 3.0$ nm. The neck formation between a pair of coalescing grains can be modeled as a minimal surface. (c) The minimal surface formed in our simulations can be approximated as a catenoid. We track the evolution of the catenoid radius R_{min} as the neck region coarsens.

lustrated in Fig. 6 of the main paper, in order to decrease the interfacial energy. We calculate the neck radius profile at different time steps to show its growth. This is illustrated in Fig. 7(b), where we plot the scaled radius R_{min} as function of scaled distance from the centers of the coalescing grains. As a simple test, we compare the radius of the neck in simulations with that of an equivalent catenoid, which is determined by measuring the radius of the waist c from the simulations and comparing it to the catenoid equivalent. It should be noted that the catenoid is represented in the parametric form as $(c \cosh \frac{z}{c} \cos u, c \sinh \frac{z}{c} \sin u, z)$, with $u \in (0, 2\pi)$ and $z \in (-1, 1)$ shown in Fig. 7(c). From this parametric form, one can easily calculate the radius as $r(z) = \sqrt{c^2 + 2v^2 + c^2 \cosh \frac{2z}{c}}$. The solid lines plot the radius of a catenoid as function of distance from the waist z . It is clear that

the shape of neck follows the catenoid minimal surface, at least in the initial stage.

Figure 8: (a) Mean square displacement (MSD) of freely diffusing bulk **b** SNA for three nanoparticle radii ($R = 12.3$, $R = 16.3$, $R = 20.3$ nm). As the SNA grow the diffusion becomes sub-linear. The maximum diffusivity D_b is shown in dashed. (b) The MSD for the surface bound **s** SNA are comparatively shown for the same three nanoparticle sizes. The surface diffusivity D_s for larger SNA does not slow at the same rate as D_b due to the increased coalescence. The length and binding region of the DNA in these simulations were fixed at $L = 9.3$ nm and $l = 3.0$ nm, respectively.

Bulk and Surface SNA Diffusion

In Fig. 8(a,b) we show the dependence of MSD on SNA size (with SNA radius $R = 12.3$ nm, $R = 16.3$ nm and $R = 20.3$ nm) for bulk (**b** type) and surface bound (**s** type) SNA, respectively. These results further demonstrate that the surface diffusion is faster for SNA's with larger R , especially between $R = 16.3$ and $R = 20.3$ nm, until a cross-over occurs at later times likely due to slower GB coalescence. However, bulk diffusion, which is slower for larger SNAs, also contribute to material transport to reduce the interfacial energy during neck growth.

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