

## Formation and surface melting of nanoparticle superlattices in a solution

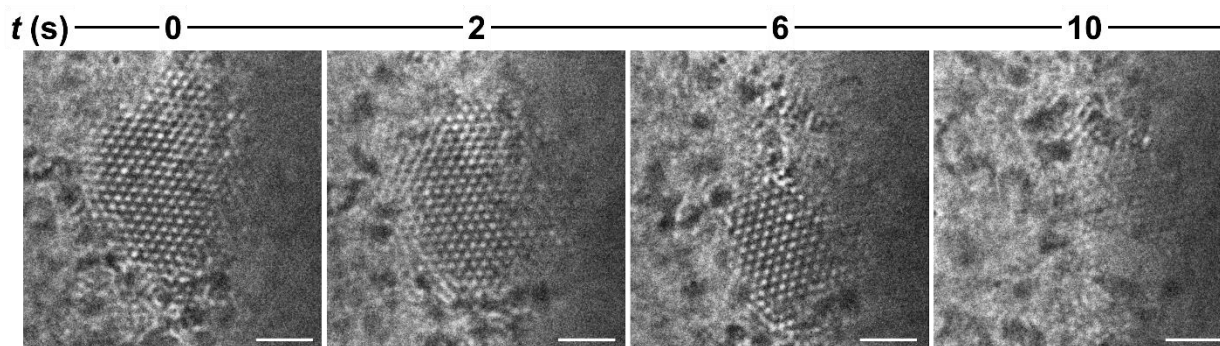
Ahyoung Kim<sup>1</sup>, Chang Liu<sup>1</sup>, Erik Luijten<sup>2</sup> and Qian Chen<sup>3</sup>

<sup>1</sup>University of Illinois at Urbana-Champaign, United States, <sup>2</sup>Northwestern University, United States, <sup>3</sup>University of Illinois at Urbana-Champaign, Urbana, Illinois, United States

The wisdom in the saying of “There are no two snowflakes alike” lies in the importance of history or kinetic pathways in the phase transitions of solids. Likewise, “artificial solids,” namely superlattices consisting of functional nanoparticles, have lattice size, surface morphology, crystallinity, symmetry, and structural reconfiguration (for example, transition into a disordered state) highly dependent on the kinetic pathways as the nanoparticles interact with each other in solution [1]. Great progresses have been made in understanding the formation pathways of superlattices using liquid-phase transmission electron microscopy (TEM) [2-4]. For example, by tracking single nanoparticle’s trajectories, especially aided by U-net neural network-based machine learning, previous studies mapped the fundamental nanoparticle interactions at nanometer resolution [5]. Nonclassical, two-step nucleation pathway has also been elucidated in the system of nanoprisms, by optimizing protocols such as loading nanoparticle suspensions over the supersaturation threshold and minimizing particle–substrate interaction [2]. Surface morphologies or exposed facets of superlattices have been shown to follow the principles of Wulff construction rule, where the facet-dependent surface energy can be measured based on the capillary wave theory [4]. However, the reverse process of crystallization of superlattices, the conversion from crystalline to disordered state, has been much less explored. On one hand, the melting of nanoparticle superlattices can provide a preferred pathway to induce structural reorganization or shuffling of building blocks for them to transform into different types of crystal structures. On the other hand, understanding nanoscale superlattice melting and comparing such behaviors with the prevailing surface melting theories developed for atomic/molecular solids can provide a potent way to engineer phase transitions of supra- and hierarchical structures constructed from nanoscale entities (e.g., DNA-coated nanoparticles, proteins), for their applications in reprogrammable and switchable materials with multifunctional properties [6, 7]. The experimental challenges to observe melting of superlattices are twofold. Practically it is difficult to load the initial superlattice form, in an intact manner, into the highly confined liquid-phase TEM chamber for in-situ observation. The triggering of melting also needs meticulous manipulation of nanoparticle concentration, interparticle interaction, and solution environment.

Here we used the Hitachi 9500 Environmental TEM at 200 kV, a Hummingbird liquid flow holder at dose rates below  $10 \text{ e}^{-}\text{\AA}^{-2}\text{s}^{-1}$ , and obtained preliminary observations on the melting of a nanoparticle superlattice composed of gold nanospheres in solution. Instead of loading a suspension of preformed nanoparticle superlattices into the  $\text{SiN}_x$ -membraned liquid chamber, we loaded an aqueous solution of gold nanospheres, and triggered the formation of crystal upon flowing a phosphate-buffered saline solution following our previous protocol [2]. Followed by growth of the superlattices, the melting was then triggered *in situ* by lowering the ionic strength of the solution and subsequent increase of the electrostatic repulsion of the nanospheres. As shown in the time series of liquid-phase TEM snapshots in Figure 1, we revealed an intriguing surface melting process where nanospheres at the surface of the lattice are effectively peeled gradually. The particles inside the lattice, in comparison, remain crystalline ordered. We expect further analysis of this gradual and heterogeneous loss of structural order to reveal the thermodynamic origin as well as providing kinetic insights in polymorph engineering. Our observation is

reminiscent of the surface melting in ice, where the existence of thin quasi-liquid water layer wetting the surface of ice crystals below the melting temperature [8, 9].



**Figure 1.** Figure 1: Snapshots of the melting of superlattice composed of gold nanospheres in a continuous liquid-phase TEM movie. Scale bars: 500 nm.

#### References

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