Keynote Lecture

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In situ views of classical vs non-classical pathways of nucleation

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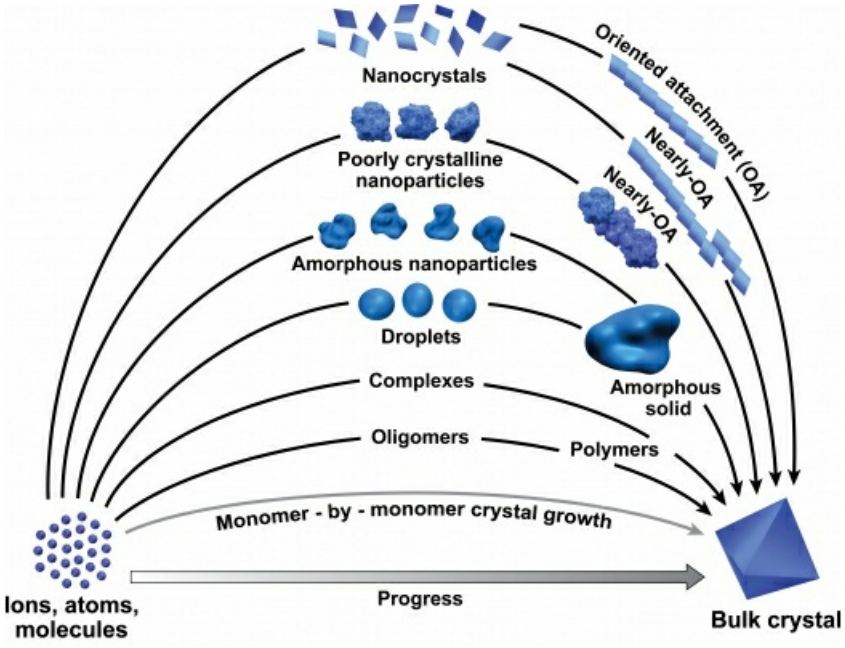
Field and laboratory observations show that crystals commonly form by the attachment of particles that range from multi-ion complexes to fully formed nanoparticles. These non-classical pathways to crystallization are diverse, in contrast to those of classical models that consider only the addition of monomeric chemical species. Despite their complexity, a holistic framework for understanding these particle-based pathways both during the nucleation and growth phase that extends classical concepts emerges when the coupled effects of complexity of free energy landscapes and the impact of dynamical factors that govern particle formation and interaction are considered (See Figure) [1].

Here I describe that framework and use a series of in situ TEM and AFM studies on inorganic, organic, and macromolecular systems to illustrate the evolution in nucleation and growth processes as these complexities and dynamical factors come into play. The introduction of either size-dependent phase stability associated with the high surface-to-volume ratios of nanoparticles, or high driving force coupled with the existence of metastable polymorphs leads to true two-step pathways characterized by the initial appearance of a bulk precursor phase. The creation of micro-states, which represent local minima in free energy stabilized by configurational factors, can also lead to hierarchical pathways, but the intermediates are transient states that do not appear on a bulk phase diagram. However, small changes in molecular structure can eliminate these transient states, leading to a direct pathway of nucleation. In either of these cases, reduction in molecular mobility, either through reduced temperature or introduction of ion-binding macromolecules, can freeze non-equilibrium states into place for dynamical reasons.

Even when energy landscapes are smooth, high driving force also creates a set of dynamic factors that lead to hierarchical crystallization through the post-nucleation interaction and assembly of nanoparticles. Some of these assembly pathways may involved oriented attachment of nanocrystals while others proceed via disordered aggregation followed by reorganization and coarsening. Many of these processes can occur concurrently or sequentially in a single system.

The results provide a common basis for understanding the development of order in systems as diverse as simple salt crystals, branched semiconductor nanowires, and microbial membranes.

[1] J.J. De Yoreo, P.U.P.A. Gilbert, N.A.J.M. Sommerdijk, R.L. Penn, S. Whitelam, et al., (2105). Science 349, aaa6760



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