THE CALL IT "FREE ENERGY" SO, HEY, WHY PAY?

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Nucleation is the seminal process in the formation of ordered structures ranging from simple inorganic crystals to macromolecular matrices. Observations over the past fifteen years have revealed a rich set of hierarchical nucleation pathways involving higher-order species ranging from multi-ion clusters to dense liquid droplets, as well as transient crystalline or amorphous phases. Despite their complexity, a holistic framework for understanding particle-based pathways to crystallization 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 [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 results show that 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.

The findings from these studies 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 et al., Science 349 (2015) aaa6760.