

Heterogeneous two-step crystallization from colloid suspensions: surface geometry and confinement effects on mechanisms and rates

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Classical nucleation theory predicts an increase in the rates of crystallization at surfaces—compared to crystallization in the bulk—due to a reduction in the interfacial free energy arising from interactions of the crystal embryo with the surface. Our recent work on NaCl [1] nucleation indicates that, at sufficiently high supersaturations, a two-step pathway dominates the assembly of ions into crystals, where dense liquid-like intermediates first form before an ordered lattice emerges in the condensed phase. The presence of carbon surfaces catalyses the formation of liquid-like monomer clusters and likely makes the two-step pathway, with lower overall energy barriers to crystals in this regime, more accessible than in the bulk case. [2] Our hypothesis, therefore, is that surfaces not only affect the interfacial free energies of critical clusters but also direct crystallization towards a two-step pathway.

How the surface geometry and surface-induced confinement promote crystal nucleation is still not clear. In this presentation, we explore these questions using simulations of a single-component colloid suspension which undergoes two-step crystal nucleation. [3] We explore ‘ideal surface’ features with defined geometries such as planar surfaces, concave wedges with varying angles, hemispherical and conical surfaces.

Our results indicate that, in the absence of chemical control or epitaxial matching, surfaces do indeed promote the formation of a microscopic dense liquid which subsequently transforms into a nanocrystal. Correlation between the crystallisation rates (evaluated using Markov State Models) and confinement is linked to the droplet size to infer how the geometry promotes liquid droplets. Furthermore, by exploring ‘non-ideal surfaces’ from polymorph-selective nucleants adopted in experiments, the structures for which are elucidated by electron tomography, we can identify changes to the mobilities of monomers in liquid intermediate phases trapped in the most confined regions of these surfaces, e.g., in crevices, and discuss how these particularly rough features can promote crystallisation by affecting the dynamics for the liquid-to-crystal transition. Generally, our results provide a useful appraisal of how surfaces control crystallisation, which we discuss in the context of classical nucleation theory and theories for two-step crystal nucleation.

References

- [1] A. R. Finney and M. Salvalaglio, Multiple pathways in NaCl homogeneous crystal nucleation, *Farad. Discuss.*, 2022, **235**, 56-80.
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- [3] A. R. Finney and M. Salvalaglio, A Variational Approach to Assess Reaction Coordinates for Two-Step Crystallisation, <https://arxiv.org/abs/2212.12486>.