

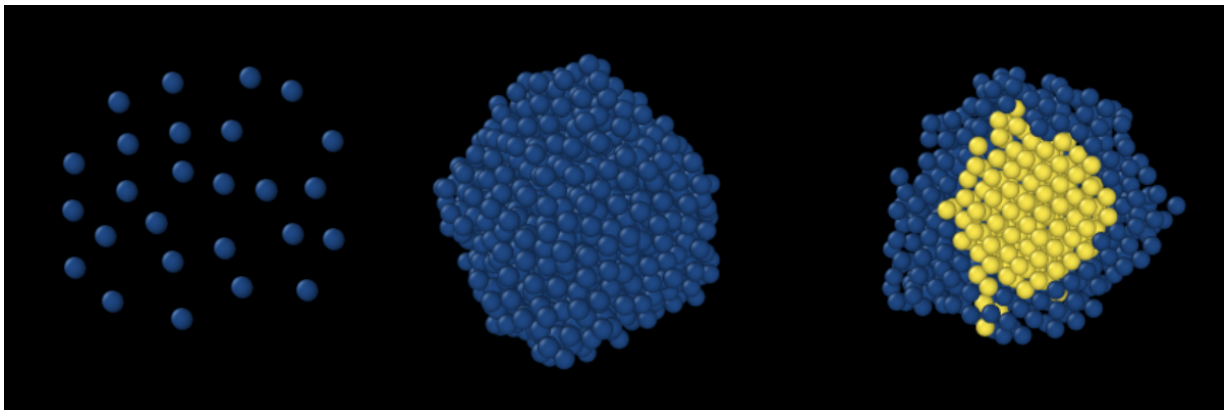
A Molecular Theory of Crystal Nucleation from Dilute Phases

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In a typical molecular simulation, the occurrence of nucleation is a rare event. Hence, simulating a nucleation event requires sophisticated enhanced sampling techniques such as umbrella sampling, transition path sampling, metadynamics, etc. While there has been a tremendous progress in the development of techniques to simulate crystal nucleation from melts, technical challenges persist in our ability to simulate crystal nucleation of solutes from solutions. These difficulties are rooted in the need to maintain constant chemical potential of the solute in the solution during the formation of the nucleus. Towards addressing these issues, we present a molecular theory of crystal nucleation from dilute phases such as vapors or dilute solutions. Using statistical mechanics, we derive an exact expression for free energy of formation of the nucleus. The molecular theory of nucleation is then developed from this expression, which is applicable when the concentration of the nucleating species is very dilute. The theory can model the nonclassical two-step crystal nucleation seen in many systems. We have applied the theory to study and analyze the crystal nucleation pathways from Lennard-Jones vapor and NaCl solution. We find that prior explanations of the two-step mechanism based on lower barrier height for liquid nuclei is incomplete. The analysis from the molecular theory reveal that a complete explanation would also require consideration of anisotropy in the diffusion constants for growth of liquid droplets vis-à-vis the crystal nuclei.

Keywords: Crystal Nucleation, Lennard-Jones, NaCl solution, Fokker-Planck



Snapshots of crystal nucleus formed via two-step nucleation from a subcooled vapor