

NANOSCIENCE COLLOQUIUM

Beyond Classical Nucleation Theory: What Operando Analysis of Solution Structure during the Crystallisation of Organic Solutes Tells Us about Homogeneous Nucleation Kinetics

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ABSTRACT: For almost 100 years, classical nucleation theory (CNT) has been used to model and analyse the kinetics of nucleation from solution, with applications across all branches of science involving crystallisation. Its limitations have been discussed widely [1], especially with a view to the assumptions about microscopic events taking place during nucleation. The critical information required for developing improved and/or alternative nucleation theories is a detailed understanding of the molecular structure evolution in supersaturated, metastable solutions. We apply multiple advanced X-ray characterisation techniques to obtain information about the changes in local structure around solutes in the metastable zone. These include time-resolved X-ray pair distribution function (XPDF) measurements, real-time X-ray phase contrast imaging (XPCI) imaging of nucleating solutions and X-ray core level spectroscopies such as near-edge X-ray absorption fine structure (NEXAFS), X-ray Raman scattering (XRS) [2] and X-ray photoelectron spectroscopy (XPS). In combination with neutron scattering [3] and other techniques these studies provide increasing evidence that the critical step in homogeneous nucleation of organic species from solution is the formation of clusters of solvated solute molecules, which desolvation events coming after clustering. In effect, this view represents a two-step nucleation process that can be modelled by equilibrium thermodynamics and transition state theory. I will show how such an analysis results in conceptually less constrained models than CNT, based on an empirical rate parameter that is accessible experimentally.

