Understanding Nucleation Phenomena at Large Metastability: From Gas-Liquid Transition to Metastable Solids and Polymers

M. Santra, R. S. Singh, S. Chakrabarty and B. Bagchi*
Solid State and Structural Chemistry Unit,
Indian Institute of Science, Bangalore – 560 012.
(http://www.liquid.sscu.iisc.ernet.in)
*Email: bbagchi@sscu.iisc.ernet.in

Abstract

We have revisited the apparently well-studied problem of nucleation and growth of a stable phase inside a parent metastable phase, particularly near the spinodal curve. We have undertaken extensive computer simulation studies to probe the molecular mechanism for the onset of instability in a wide range of systems (both for 2 and 3 dimensional Lennard-Jones fluid and nearest neighbour Ising model). We have constructed the multidimensional free energy surface of nucleation as a function of multiple reaction coordinates [1]. While the classical Becker-Döring (BD) picture of homogenous nucleation, that assumes the growth of a nucleus by single particle addition, holds good at low to moderate supersaturation, the formation of the new stable phase becomes more collective and spread over the whole system at large supersaturation. As the spinodal curve is approached from the coexistence line, the nucleation free energy barrier, as a function of the size of the *largest liquid-like cluster*, disappears at a supersaturation (well below the thermodynamic spinodal limit) that we term as kinetic spinodal [2]. Very close to the kinetic spinodal the free energy surface becomes quite flat and the critical nucleus grows by diffusion on a barrierless surface. We have developed an alternative formalism to treat nucleation at large supersaturation by introducing an extended set of order parameters in terms of the k^{th} largest liquid-like clusters, where k = 1 is the largest cluster in the system, k = 2 is the second largest cluster and so on [2]. We shall also discuss nucleation of metastable solids and collapsed state of polymers.

References:

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