591a Statistical Mechanics of Nucleation: Replacement Partition Function

Isamu Kusaka

Despite a considerable progress in both our understanding of statistical mechanics of nucleation and computational techniques in recent years, the usefulness of truly molecular level approaches is still limited in many practical applications, and a phenomenological theory must take its place. Such a theory inevitably utilizes some parameters whose values must be determined by a macroscopic measurement. Here, it becomes crucial that the connection be examined carefully between the macroscopic parameters of the phenomenology and molecular level concepts.

Currently, classical theory remains to be the dominant theory used in practice in correlating outcome of nucleation experiments. In this theory, the connection just indicated has been at the heart of the debate concerning the so-called replacement partition function. Given the large discrepancy between the theoretical and experimental nucleation rate that confronts classical theory, it appears worthwhile to re-examine this concept.

In particular, we derive a formula for the replacement partition function in terms of the classical phase integral, and present a new methodology to evaluate it by means of bulk liquid simulation. In the case of vapor to liquid phase nucleation of truncated and shifted Lennard-Jones fluids, the resulting Lothe-Pound factor was found to decreases significantly with increasing temperature and decreasing cluster size. For the ranges of the temperature and the cluster size we studied, the Lothe-Pound factor is found to be several orders of magnitude smaller than the original estimate by Lothe and Pound. The talk will focus on application of the theory to the case of crystal nucleation from a solution.