Toward a phenomenological theory of nucleation [378a]

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Background

Nucleation plays an important role in various contexts ranging from formation of atmospheric aerosols to material processing. A quantitative description of these processes often requires an accurate estimate on the rate of nucleation as an input. Classical nucleation theory has been used extensively in practice to predict this quantity. The essential content of classical theory is as follows.[1] The steady state nucleation rate J is given by

$$J_{ss} = J_0 e^{-W/k_B T}, \tag{1}$$

where W, k_B, and T denote, respectively, the reversible work of critical nucleus formation, the Boltzmann factor, and the absolute temperature. J_0 is a constant determined by kinetic considerations. Since W appears in the exponent, an accurate evaluation of W is expected to be more important than that of J_0. Classical theory draws from the following formally exact expression for W due to Gibbs:[2]

$$W = \frac{16\pi\gamma^3}{3(\Delta P)^2}, \tag{2}$$

where γ is the surface tension between the metastable parent phase and the nucleating phase. ΔP denotes the difference between two pressures, one pertaining to the nucleating phase if it existed in bulk at the same temperature and chemical potential as the metastable phase, and the other to the metastable phase. We note that γ pertains to the critical nucleus and hence in general differs from the surface tension of macroscopic interface γ_∞. The difficulty in applying Eq. (2) lies in the fact that this size dependent γ usually is inaccessible to experiments. Thus, classical nucleation theory introduces an approximation of replacing γ by γ_∞, which is experimentally accessible, thereby leading to the expression

$$W^{cl} = \frac{16\pi\gamma_\infty^3}{3(\Delta P)^2}. \tag{3}$$

Unless the degree of supersaturation is sufficiently small, however, the approximation $\gamma \approx \gamma_\infty$ introduces a significant error in the estimated free energy barrier of nucleation. In fact, a thermodynamic consideration demands that γ and hence W vanish at the mean-field spinodal, while W^{cl} does not. This holds equally true for both vapor phase condensation and bubble nucleation. Since J_{ss} depends exponentially on W, it is not surprising that the classical prediction of J_{ss} can be off by many orders of magnitude when compared against experimentally determined J_{ss}.

To overcome the shortcoming of classical theory, a considerable effort has been expended to elucidate the molecular level details of nucleation by means of statistical mechanical machinery such as the density functional theory (DFT) and computer simulation. However, their ability to make quantitative predictions is still somewhat limited due to both computational difficulties involved in the current approaches and the lack of model potentials that can accurately represent actual systems of interest. The latter difficulty is amplified by the fact that nucleation behavior is very sensitive to the details of the model potentials.

For this reason, it is important to pursue phenomenological approaches to nucleation as well. Recently, an important step in this direction was taken by McGraw and Laaksonen,[3] who put forward a scaling proposition regarding the free energy barrier of nucleation for the vapor phase nucleation in a single component system. The content of the scaling proposition is that the difference between the actual nucleation barrier W and the barrier calculated using classical theory W^{cl} is a function only of temperature and in particular is independent of supersaturation:

$$W - W^{cl} = f(T). \tag{4}$$

Koga and Zeng[4] motivated this scaling proposition by means of a series expansion of the free energy barrier near the phase coexistence boundary. In addition, recent simulation studies provide empirical validation of the scaling proposition in vapor phase condensation of single component Lennard-Jones fluids,[5] ethane, and n-butane.[6]

Subsequently, Talanquer[7] determined the form of the scaling function $f(T)$ to ensure thermodynamic consistency, i.e., the vanishing of the free energy barrier at the mean-field spinodal. The resulting scaling relation reads

$$W/W^{cl} = 1 - \xi^2, \tag{5}$$

where $\xi = \Delta\mu/\Delta\mu_s$ with $\Delta\mu$ denoting the difference in chemical potential between the parent phase at a supersaturated state and that at saturation. $\Delta\mu_s$ is the value of $\Delta\mu$ evaluated at the mean-field spinodal. In short, ξ is the degree of supersaturation scaled to vary from zero to unity as the parent phase density changes from that at the phase coexistence to the mean-field spinodal. Talanquer's approach was later extended to the case of bubble nucleation by Shen and Debenedetti.[8] Still more recently, Kashchiev put forward another scaling relation:[9]

$$W/W^{cl} = (1-\xi)(1+\xi/2)^2, \tag{6}$$

in which the scaled degree of supersaturation is defined as $\xi = \Delta P/\Delta P_s$, where ΔP has the same meaning as in Eq. (2) and ΔP_s is the value of ΔP evaluated at the mean-field spinodal.

Interestingly, the scaling functions put forward by these workers exhibit a certain universality in that the ratio W/W_{cl}, given as a function of a properly normalized degree of supersaturation, is independent of (1) the system temperature, (2) whether one is concerned with the vapor phase condensation or the bubble formation, and (3) the material under consideration. In particular, the material specific part of W is contained entirely within W_{cl}, which in turn depends only on the bulk thermodynamic quantities that are readily accessible experimentally. Thus, such a universal scaling function, if it exists in reality, will be particularly useful in making a quantitative predictions of W.

Density functional results

To test the validity of the above mentioned predictions of the existing scaling propositions, we calculated W/W_{cl} for square-well fluids and truncated and shifted Lennard-Jones fluids within the framework of DFT. Representative results of this calculation are shown in Fig. 1. From the figure, W/W_{cl} is indeed seen to be nearly independent of the model potentials. We note that the scaling function is also nearly independent of the well-width or the cut-off radius characterizing the model potentials as well as the temperature. [Not shown.] However, as already pointed out by Shen and Debenedetti,[8] the scaling function obtained by the DFT calculation differentiate bubble nucleation from the vapor phase condensation, behavior in odds with the existing scaling propositions. [Compare Figs. 1 (a) and (b).] The scaling function for bubble nucleation in the simple fluids also differs from that in the polymer-gas mixture.[10]

To summarize our findings, the scaling function does exist but its scope is much more limited than was envisaged in the phenomenological scaling propositions of Talanquer or Kashchiev. By examining the scaling functions obtained by DFT, we speculate that the failure of the existing scaling propositions lies in the fact that they fail to capture the non-zero slope of W/W_{cl}, given as a function of the normalized supersaturation, at the low supersaturation limit.

Phenomenological theory of nucleation

A useful phenomenological theory of nucleation may be obtained if we could somehow predict the functional form of the scaling function W/W^{cl}. Following Koga and Zeng,[4] we express W/W^{cl} as a series expansion:

$$W/W^{cl} = 1 + a_1\xi + a_2\xi^2 + a_3\xi^3 + \cdots \tag{7}$$

Truncating the series at the second order term and demanding that $W/W^{cl} = 0$ at $\xi = 1$, we obtain

$$W/W^{cl} = 1 + a_1\xi - (1 + a_1)\xi^2 \tag{8}$$

where a_1 is the slope of W/W_{cl} at the low supersaturation limit. We calculate this slope by applying the diffuse interface theory (DIT)[11] at the low supersaturation limit, where DIT is expected to be most accurate. We note that this approach requires only bulk thermodynamic quantities of homogeneous fluids, i.e., pressure and molar entropy of the phases involved, as the input. The resulting scaling function is compared against the DFT results in Fig. 1 and seen to be fairly successful in reproducing free energy barrier calculated by DFT for both vapor phase condensation and bubble nucleation, though the agreement is worse for the latter case. A formal extension of this phenomenological approach to multicomponent system is straightforward. We are currently examining quantitative accuracy of such approach.

Acknowledgments

This work was supported by the seed grant provided through the Ohio State University.

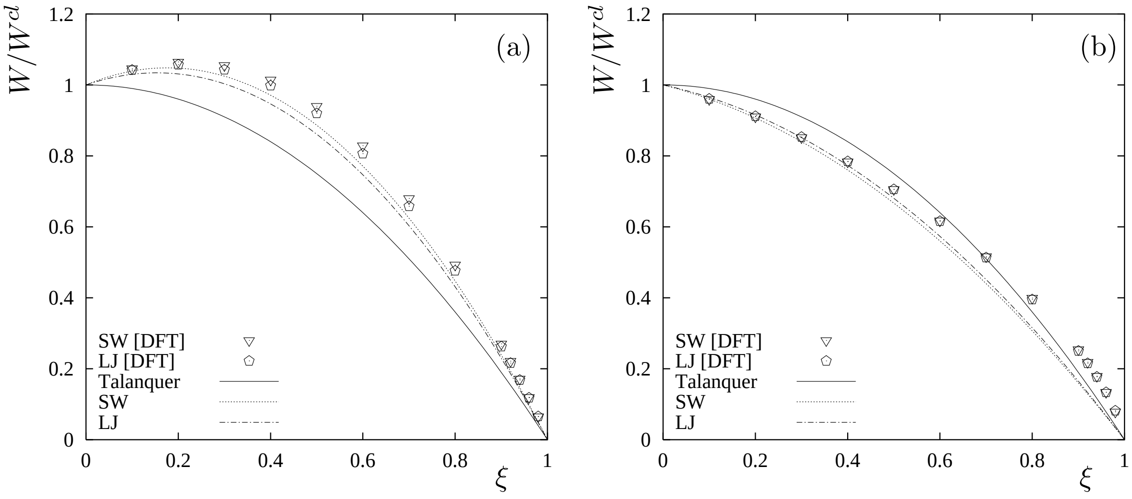

Figure 1: The scaled free energy barrier W/W^{cl} as a function of a scaled degree of supersaturation ξ (a) for vapor phase condensation and (b) for bubble nucleation. SW stands for the square-well potential with its well-width 4 times the hard core diameter. LJ stands for the Lennard-Jones potential truncated and shifted at 4 times the Lennard-Jones diameter so that the potential vanishes beyond this distance. The solid line is Talanquer's scaling function, while dashed lines represent the predictions of a phenomenological theory.

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