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THERMODYNAMICS AND PHENOMENOLOGICAL NUCLEATION THEORIES

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Abstract

Phenomenological nucleation theories are considered from the viewpoint of Gibbs' surface thermodynamics. We point out in defining the critical nucleus that it is important to make a distinction between the number of molecules enclosed by the surface of tension and the excess number of molecules over the uniform vapor phase. We show that the Kelvin equation should be employed in determining the size of the critical nucleus even if the nucleus free energy contains a size-dependent surface energy term. Furthermore, we derive a new equation for the size-dependent surface tension that differs from the Tolman relation. Density functional calculations support the new formula.

Keywords Nucleation, Surface tension, Clusters, Density functional theory

Introduction

Phenomenological nucleation theories have become increasingly popular in the recent years. Models incorporating size dependent surface tensions and/or parameters that are determined using critical properties of the fluids in question sometimes succeed in predicting the nucleation behavior more accurately than the classical nucleation theory (CNT) does. However, in spite of the original enthusiasm inspired by the Dillmann-Meier (DM) theory [1], it has become evident that overall the phenomenological theories do not perform much better than the CNT [2], and when they do, the success is more or less accidental [3]. Our aim is to take a critical look at the phenomenological theories starting from fundamental thermodynamical principles. We will show that certain assumptions that are often made in these theories are thermodynamically inconsistent. We will also make use of the fact that the classical form of Kelvin equation (containing the surface tension of a flat interface) predicts the equimolar radius of the critical nucleus well down to nuclei of about 40 molecules [4], and derive a new equation for the size-dependence of surface tension.

Gibbs' thermodynamics

We consider a spherical cluster with a volume V and excess number of molecules g over the uniform vapor phase. At this point we do not fix the volume in any way, *i.e.* V and g are independent variables. We can then write $g = n_l - n_v + n_s$, where $n_l = V\rho_l$ and $n_v = V\rho_v$ with ρ_l and ρ_v densities of the uniform liquid and vapor phases, respectively, and n_s is the surface excess number of molecules that corrects for the difference between the step profile and the actual interfacial density profile.

The free-energy change to create the cluster can now be expressed as [5]

$$\Delta G = (P_v - P_l)V + (\mu_l - \mu_v)n_l + (\mu_s - \mu_v)n_s + \Phi(g, V). \tag{1}$$

Here the P's are the pressures and the μ's the chemical potentials of the uniform liquid and vapor phases, and Φ is an excess energy term dependent on both V and g that includes the surface free energy and all other possible energetical contributions. The critical nucleus, denoted by an

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asterisk, is in unstable equilibrium with the environment. Thus we can set the partial derivatives of ΔG with respect to V, n_l, and n_s zero and obtain the following conditions:

$$\mu_l^* = \mu_s^* = \mu_v \tag{2}$$

$$\Delta P^* = P_l^* - P_v = \frac{\partial \Phi^*}{\partial V^*} \tag{3}$$

The work of nucleus formation is then

$$W^* = \Delta G^* = -\Delta P^* V^* + \Phi^* \tag{4}$$

The above development is completely general. We now proceed to a somewhat more specialized direction by assuming that the excess free energy can be divided into two parts:

$$\Phi^*(g^*, V^*) = A^* \sigma^*(g^*, V^*) + F(g^*), \tag{5}$$

where A^* is the surface area, $\sigma^*(g^*, V^*)$ is the surface tension, and F is an arbitrary function that is assumed to depend on g^* only and not on the location of the dividing surface (as an example, we refer to the $\tau \ln(g^*)$-term of the Fisher droplet model [6] present in several phenomenological nucleation theories.) We fix the dividing surface to be the surface of tension ($\partial\sigma^*(g^*, V^*)/\partial V^* = 0$), and denote the corresponding volume, surface area, and radius with a subscript s. The surface tension is now a function of g^* only, and Eqs. 3 and 4 become

$$\Delta P^* = \frac{2\sigma^*(g^*)}{R_s^*} \tag{6}$$

$$W^* = -\Delta P^* V^* + F(g^*) + A_s^* \sigma(g^*). \tag{7}$$

Equation (6) is the Laplace relation and R_s^* denotes the nucleus radius at the surface of tension. Assuming incompressibility of the liquid phase ($\Delta P^* V^* = n_l^* \Delta\mu^* = n_l^*(\mu_v(P_v) - \mu_l(P_v)) \simeq n_l^*(\mu_v(P_v) - \mu_{coex})$) these become

$$\Delta\mu^* = \frac{2\sigma^*(g^*)v}{R_s^*} \tag{8}$$

$$W^* = -\Delta\mu^* n_l^* + F(g^*) + A_s^* \sigma(g^*). \tag{9}$$

Here the first equality is the Kelvin relation and v denotes the liquid phase molecular volume. The classical nucleation theory is obtained by assuming that $F = 0$, and that the surface of tension is located at the equimolar surface, whence g^* becomes equal to n_l^*, and the surface tension becomes equal to the bulk surface tension ($\sigma = \gamma_\infty$) [7].

Two points are worth noting. First, the number of molecules n_l^* appearing in Eqs. (8) and (9) is not the same (unless the surface of tension happens to coincide with the equimolar surface) as the number given by the nucleation theorem, g^*, which is accessible to measurement. Thus, experimental determinations of g^* should not without reservation be compared with estimates of the molecular content of the critical nucleus derived from phenomenological nucleation theories that assume size-dependent surface tension. Secondly, the correct theoretical equation to determine the radius of the critical nucleus is the Kelvin relation even if the theory contains a nonzero $F(g^*)$ and a size-dependent σ. The cubic equation for determining the critical nucleus size that appears in some phenomenological theories (*e.g.* [1]) results from confused treatment of V^*, g^*, and n_l^*, and it is not thermodynamically correct.

Next, we note that Eqs. (8) and (9) can be combined to give

$$W^* = \frac{1}{2}\Delta\mu^* n_l^* + F^*. \tag{10}$$

On the other hand, following Rowlinson and Widom [7], we have

$$W^* = 2\pi \int_0^\infty R^2 \left[P_N(R) - P_v\right] dR = 2\pi \int_0^{R_s} R^2 \left[P_l - P_V\right] dR = \frac{1}{2} n_l^* \Delta\mu^*, \tag{11}$$

where $P_N(R)$ is the normal component of the pressure tensor. Note that while "path" ambiguities associated with certain molecular definitions of the pressure tensor have been reported [8], these do not alter the Gibbs' thermodynamics. DF expressions for the pressure tensor components [9], on the other hand, appear to be sufficiently well average that path ambiguities associated with the molecular definitions do not arise. Comparison of Eqs. (10) and (11) suggest that $F(g^*) = 0$ in general. Thus we obtain the important result that no corrections in the form of $F(g^*)$ are required if the surface free energy is evaluated at the surface of tension.

Surface tension

The phenomenological theory developed above (Eqs. 8 and 11) is not complete without a form for the size dependence of the surface tension. The usual procedure is to apply an expansion based on Tolman's famous formula [10]

$$\sigma(R_s) = \gamma_\infty \frac{R_s}{R_s + 2\delta}. \tag{12}$$

Equation (12) derives from an integration over R assuming a constant value for the Tolman length $\delta = R_e - R_s$. However, it has been shown in DF calculations [3] that in the size range of critical nuclei δ is a strong function of radius, which makes the use of the Tolman equation in nucleation studies questionable (even though it is accurate at the planar limit). We note that an alternative expression can be derived using the classical form of Kelvin equation:

$$\Delta\mu = \frac{2\gamma_\infty v}{R_e(CNT)}. \tag{13}$$

This equation has been shown both experimentally [4] and in DF calculations [3] to produce a surprisingly accurate estimate of R_e down to very small nucleus sizes. Eqs. (8) and (13) together yield a simple result which should hold as long as the latter equation produces a correct R_e and the liquid phase can be considered incompressible:

$$\frac{\sigma(g^*)}{\gamma_\infty} = \frac{R_s}{R_e} = \frac{R_s}{R_s + \delta} \tag{14}$$

We have tested Eqs. (12) and (14) with density functional calculations of the nucleation properties of an Argon-like Lennard-Jones fluid. The DF code computes density profiles of critical nuclei at given supersaturations and temperatures, as well as coexistence densities, chemical potentials, and surface tensions. The size dependent surface tension $\sigma^*(g^*)$ and the radius to the surface of tension R_s^* were extracted from the DF data using the methods described by Talanquer and Oxtoby [3]. Figure 1 shows the result of the calculation at $T = 0.8\epsilon/k$ where ϵ is the LJ energy parameter. Note that we have corrected both the current theory and the Tolman formula for the finite compressibility and for the nonzero vapor density of the LJ fluid [11]. The surface tension size dependence is clearly better represented with the new theory than with the Tolman formula. We believe that this will be the case also with incompressible molecules.

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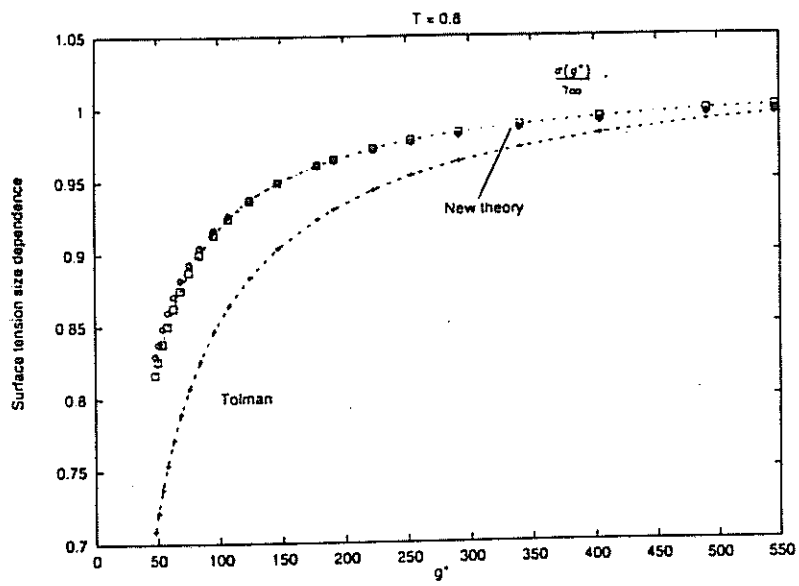

Figure 1 Comparison of surface tension size dependences calculated from density functional results using Eqs. (6) and (7) with $F = 0$ (squares), from the Tolman formula (crosses); and from the new theory (diamonds).