Thermodynamics, gas-liquid nucleation, and size-dependent surface tension

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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 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, and derive a new equation for the size-dependent surface tension that differs from the Tolman relation. Density functional calculations support the new formula.

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 [1]-[3] 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 [4]. 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.

A recent development in nucleation studies is the proof of the so-called nucleation theorem [5]-[7] that allows for the measurement of the molecular content of critical nuclei. Making use of the nucleation theorem, it has been shown experimentally [6], [8] that the classical Kelvin equation predicts the number of molecules in critical nuclei, g^*, surprisingly accurately for clusters that are larger than about 40 molecules. The Kelvin equation works well also when compared with results produced using the density functional (DF) theory of nucleation [4]. Below, we will show that, together with a thermodynamically consistent formulation of nucleation phenomenology, this discovery leads to a new form for size-dependent surface tension. We will also show that the new form describes surface tensions calculated using the DF theory better than the expression derived originally by Tolman [9].
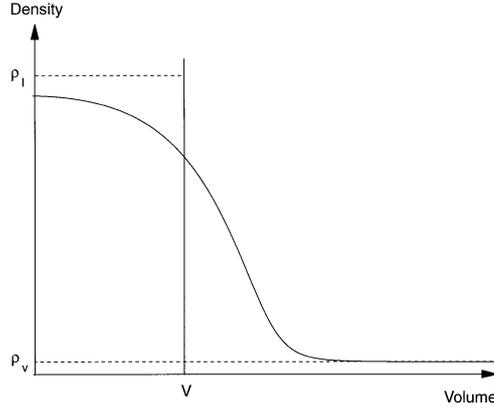
Fig. 1. – A schematic figure of the density profile at the gas-liquid interface illustrating the calculation of the various molecular numbers mentioned in the text. The area between the density profile and the uniform vapor density corresponds to g. Note that the actual density of the nucleus does not have to reach bulk liquid density even at the center.

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 (see fig. 1).

The free-energy change to create the cluster can now be expressed as [7]

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

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 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: $\mu_l^* = \mu_s^* = \mu_v$; and $\Delta P^* = P_l^* - P_v = \partial \Phi^* / \partial V^*$. The work of nucleus formation is then $W^* = \Delta G^* = -\Delta P^* V^* + \Phi^*$.

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: $\Phi^*(g^*, V^*) = A^* \sigma^*(g^*, V^*) + F(g^*)$, 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 [10] present in several phenomenological nucleation theories [1]-[3]). 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 we have for ΔP^* and W^*

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

$$W^* = -\Delta P^* V^* + F(g^*) + A_s^* \sigma^*(g^*). \tag{3}$$

Equation (2) is the Laplace relation and R_s^* denotes the nucleus radius at the surface of tension. Assuming incompressibility of the liquid phase $(\Delta P^* V^* = n_l^* \Delta \mu^* = n_l^*(\mu_v(P_v) - \mu_l(P_v)) \simeq$

$n_1^*(\mu_v(P_v) - \mu_{coex}))$, these become

$$\Delta\mu^* = 2\sigma^*(g^*)v/R_s^*, \tag{4}$$

$$W^* = -\Delta\mu^* n_1^* + F(g^*) + A_s^*\sigma^*(g^*). \tag{5}$$

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_1^*, and the surface tension becomes equal to the bulk surface tension ($\sigma = \gamma_\infty$) [11].

Two points are worth noting. First, the number of molecules n_1^* appearing in eqs. (4) and (5) 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 [1], [3] results from confused treatment of V^*, g^*, and n_1^*, and it is not thermodynamically correct.

Next, we note that eqs. (4) and (5) can be combined to give

$$W^* = \Delta\mu^* n_1^*/2 + F^*. \tag{6}$$

On the other hand, following Rowlinson and Widom [11], we have

$$W^* = 2\pi \int_0^\infty R^2 \left[P_N(R) - P_v\right] dR = 2\pi \int_0^{R_s} R^2 \left[P_l - P_v\right] dR = n_1^*\Delta\mu^*/2, \tag{7}$$

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 [12], these do not alter the Gibbs' thermodynamics. DF expressions for the pressure tensor components [13], on the other hand, appear to be sufficiently well averaged that path ambiguities associated with the molecular definitions do not arise. Comparison of eqs. (6) and (7) 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.

The phenomenological nucleation theory developed above (eqs. (4) and (7)) 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 [9]

$$\sigma(R_s) = \gamma_\infty R_s/(R_s + 2\delta). \tag{8}$$

Equation (8) 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 [4], [14] 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). On the other hand, it has been shown both experimentally [6], [8] and in DF calculations [4] that the classical Kelvin equation $\Delta\mu = 2\gamma_\infty v/R_e$(CNT) can be used to accurately estimate the equimolar radius $R_e = (3g^*/4\pi)^{1/3}$ even for very small nuclei. The classical Kelvin equation together with eq. (4) then yields a simple result which should hold as long as the former equation produces a correct R_e and the liquid phase can be considered incompressible:

$$\sigma(g^*) = \gamma_\infty R_s/R_e = \gamma_\infty R_s/(R_s + \delta). \tag{9}$$
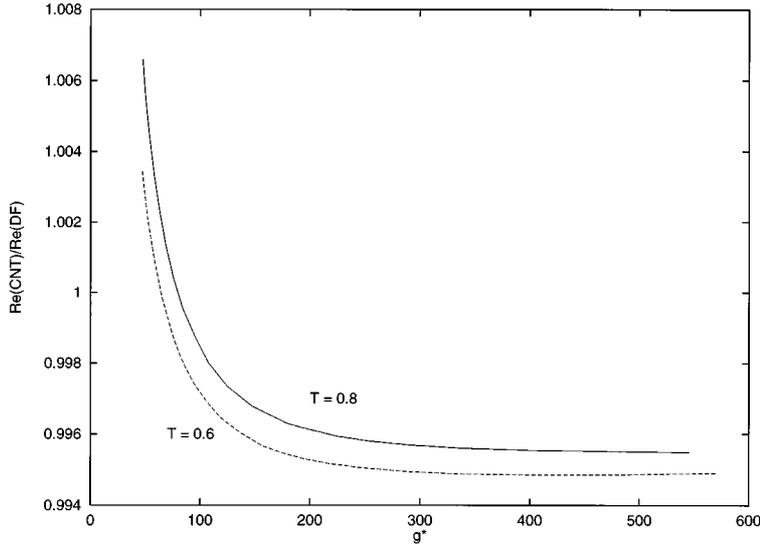
Fig. 2. – Comparison of equimolar radii produced by the classical nucleation theory and the density functional theory. The reduced temperatures are in units of the Lennard-Jones energy parameter $\epsilon/k = 119.8$ K.

We have tested eqs. (8) and (9) with density functional calculations of the nucleation properties of an argon-like Lennard-Jones fluid [15]. 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 vapor densities of the model LJ fluid are elevated compared to real molecular fluids, especially at high supersaturations and temperatures. The radius R_e in the classical Kelvin equation is the equimolar radius which in the density functional theory is calculated taking account of the background vapor density (see ref. [4]). To be consistent with the DF calculations, we account for the nonzero vapor density also in the classical Kelvin equation [16]:

$$\Delta\mu = v\left(2\gamma_\infty/R_e(\text{CNT}) + \Delta P_v\right), \tag{10}$$

where ΔP_v is the difference between the pressures of the supersaturated and coexistence vapors. We emphasize that the chemical-potential difference here is that between the supersaturated and the coexistence vapors, and that the molecular volume refers to the coexistence value.

Figure 2 compares classical and DF equimolar radii at two different temperatures. The classical predictions are very good at both temperatures even though the LJ liquid is quite compressible, which is in conflict with the assumptions made in deriving the Kelvin equation. We believe that the compressibility of the liquid is causing the $R_e(\text{CNT})/R_e(\text{DF})$ ratios to rise above unity at small nucleus sizes. It is possible that the compressibility is affecting both the surface tension and the liquid density in such a way that the effects are canceling in the Kelvin equation above about $g^* = 100$. At larger nucleus sizes the ratios remain slightly below 1, which may be caused by numerical error in the DF calculations.

To test eqs. (8) and (9), we have to extract R_s and $\sigma(g^*)$ from the DF data. To do this, we follow Talanquer and Oxtoby [4] and use eqs. (2) and (3) (with $F(g^*) = 0$). Now, however, the calculated value of $\sigma(g^*)$ *implicitly includes* the compressibility effect, and we have to rederive eq. (9) to include compressibility corrections to other variables appearing in eq. (4). The chemical-potential difference between the supersaturated vapor and liquid at the
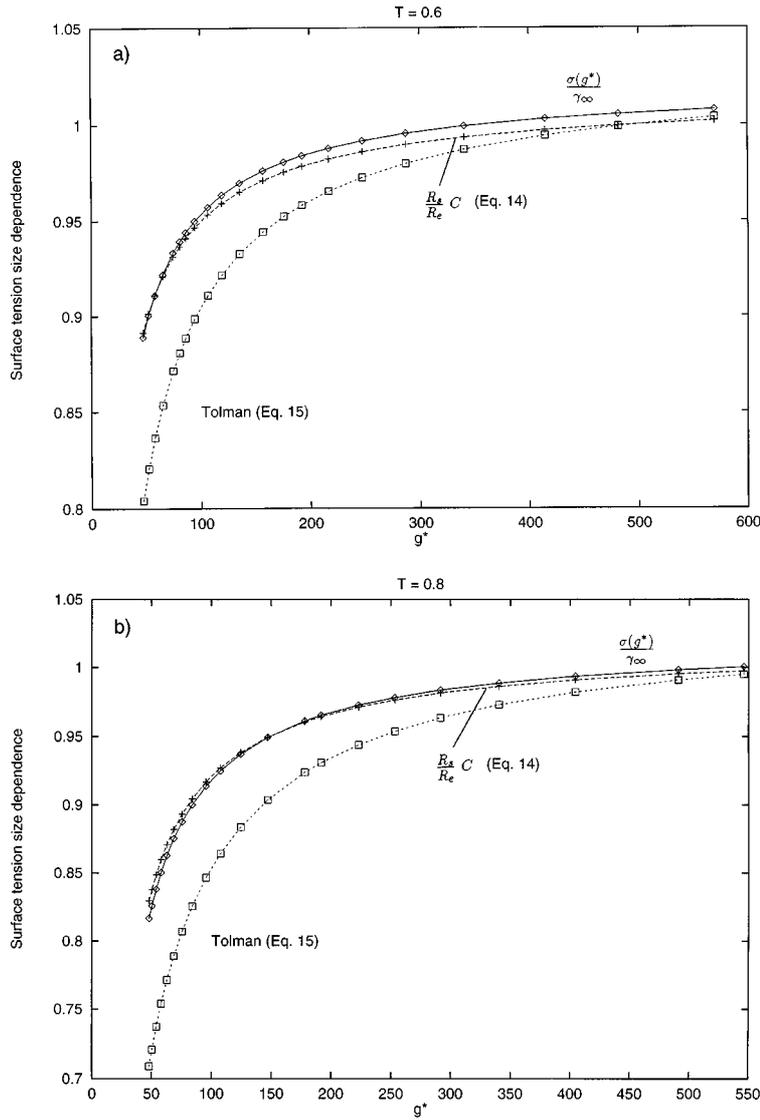
Fig. 3. – Comparison of surface tension size dependences calculated from density functional results using eqs. (2) and (3) with $F = 0$ (diamonds), from eq. (14) (crosses), and from eq. (15) (squares).

corresponding pressure P_v is given by

$$\mu_v(P_v) - \mu_l(P_v) = \Delta\mu + \Delta\mu_l = \int_{P_v}^{P_l} \rho_l^{-1} dP \,, \tag{11}$$

where $\Delta\mu_l = \mu_{\text{coex}} - \mu_l(P_v)$. Taking the liquid density ρ_l to be a linear function of pressure, we have

$$\Delta\mu + \Delta\mu_l = \Delta P \frac{\ln\left[\rho_l(P_l)/\rho_l(P_v)\right]}{\rho_l(P_l) - \rho_l(P_v)} \equiv \Delta P \bar{v} \,, \tag{12}$$

and we obtain using eq. (2)

$$\Delta\mu + \Delta\mu_l = 2\sigma(g^*)\bar{v}/R_s . \tag{13}$$

Assuming that $R_e(\text{CNT}) = R_e$, eqs. (10) and (13) then yield the compressible counterpart of eq. (9):

$$\frac{\sigma(g^*)}{\gamma_\infty} = \frac{R_s}{R_e} \frac{v(\Delta\mu + \Delta\mu_l)}{\bar{v}(\Delta\mu - v\Delta P_v)} \equiv \frac{R_s}{R_e} C . \tag{14}$$

Similarly we can correct for the Tolman relation, eq. (8) to have

$$\frac{\sigma(g^*)}{\gamma_\infty} = \left(2\frac{R_e}{R_s}C^{-1} - 1\right)^{-1} . \tag{15}$$

All the quantities in eqs. (14) and (15) can be obtained from DF calculations. Figures 3a) and b) compare the two equalities at two different temperatures. In both cases the surface tension size dependence is clearly better represented with the compressibility-corrected fraction $C(R_s/R_e)$ than with the corresponding Tolman form. Below about 300 molecules the difference between the two forms is notable. The slight inaccuracy of $C(R_s/R_e)$ in predicting $\sigma(g^*)/\gamma_\infty$, on the other hand, reflects exactly the difference between the classical and DF radii seen in fig. 2. This leads us to believe that also with incompressible molecules eq. (9) holds just as accurately as the classical Kelvin relation does.

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