Scaling Properties of the Critical Nucleus in Classical and Molecular-Based Theories of Vapor-Liquid Nucleation

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Scaling relations are developed for the number g^* of molecules in the critical nucleus and the nucleation barrier height W^*. Density functional (DF) calculations for vapor-liquid nucleation confirm these relations and show systematic departure of the ratio $W^*/g^*\Delta\mu$ from its classical value of $1/2$ with increasing difference $\Delta\mu$ in the chemical potential between the supersaturated vapor and bulk condensed phase. Discrepancies between classical and DF nucleation theories and between the classical theory and experiment are interpreted using these results.

It has been recognized in recent years that homogeneous vapor-liquid nucleation plays a central role in many atmospheric processes. Accordingly, considerable attention has been paid to formulation of phenomenological theories, which try to predict nucleation rates quantitatively starting from macroscopic, measurable properties of fluids (for a review, see [1]). However, at present it is not clear that any of these theories is overall more successful than the classical nucleation theory [2]. On the other hand, more fundamental theoretical approaches that aim to describe the properties of nucleating clusters on a molecular level have been developed [3,4] in parallel with more sophisticated experimental techniques [1]. Below, we derive scaling properties for the critical nucleus which are in harmony with novel findings from both experimental and theoretical studies, and which it is hoped will guide the phenomenological efforts in a more productive direction.

Consider the nondimensional ratio $W^*/g^*\Delta\mu$, where W^* is the nucleation barrier height, g^* is the number of molecules in the critical nucleus, and $\Delta\mu$ is the free energy difference between the vapor, at a given saturation ratio S, and the bulk condensed phase driving the phase change. In classical nucleation theory (CNT) and related descriptions, for example, scaling correlations based on the capillary drop model [5], it is known that $W^*/g^*_{\mathrm{CNT}}\Delta\mu = 1/2$ (see also Viisanen *et al.* [6]). In this Letter we examine the critical nucleus both in CNT and density functional (DF) theory and show systematic departure in $W^*/g^*\Delta\mu$ from its classical value with increasing $\Delta\mu$. We first treat the general case of molecular clusters, and then specialize to a nonuniform spherical drop model of the critical nucleus for comparison with DF theory. Finally, the scaling relations are shown to provide a simple explanation for reported systematic discrepancies between CNT and DF theory, and between CNT and experiment [7].

The scaling relations are based on Eq. (1), which has been called the nucleation theorem [8],

$$\frac{d}{d\Delta\mu}W^* = -g^*. \tag{1}$$

Derivation of Eq. (1) for the classical nucleus was achieved by Kashchiev [9] who suggested its validity beyond the CNT. Viisanen *et al.* [6] follow a statistical mechanical approach, linking Eq. (1) with the properties of a constrained cluster distribution in the grand ensemble. Their results indicate that the nucleation theorem holds for arbitrary shaped clusters (the fluctuation does not have to be a drop), for multicomponent clusters, and even for clusters of noncritical size. Oxtoby and Kashchiev [8] follow a thermodynamic approach in their description of a multicomponent spherical drop nucleus using a dividing surface model for the interface. Later in this Letter we use the dividing surface approach to obtain a formally exact expression for $W^*/g^*\Delta\mu$ for a single-component nucleus in the nonuniform drop model.

Equation (1) greatly restricts the form that $W^*/g^*\Delta\mu$ can take as a function of $\Delta\mu$. To derive the scaling relations, consider the general expression

$$\frac{W^*}{g^*\Delta\mu} = \frac{1}{2} - f(g^*, \Delta\mu), \tag{2}$$

where $f(g^*, \Delta\mu)$ gives the departure from CNT. Differentiating Eq. (2) using the nucleation theorem gives

$$\Delta\mu \frac{d}{d\Delta\mu}g^* + 3g^* = 2\frac{d}{d\Delta\mu}(fg^*\Delta\mu). \tag{3}$$

To simplify the notation, the argument of f has been suppressed.

In the classical theory $f = 0$ and the solution of Eq. (3) for g^* is a homogeneous function of the form

$$g^*_{\mathrm{CNT}} = C(T)(\Delta\mu)^{-3} \tag{4a}$$

with $C(T)$ a function temperature alone. Equation (4a) has the form required by the capillary drop model of CNT, which yields an explicit formula for $C(T)$ through the Kelvin relation (2)

$$g^*_{\mathrm{CNT}} = \frac{32\pi\gamma_\infty^3}{3\rho_l^2}(\Delta\mu)^{-3}. \tag{4b}$$

ρ_l is the molecular number density in the condensed phase, which is assumed to be uniform in the capillarity approximation, and γ_∞ is the surface tension for a flat interface; curvature effects to the surface tension are not included in the CNT.

In general, f is nonzero, and without additional physics Eq. (3), which is simply an identity between its left- and right-hand sides through the nucleation theorem, cannot be solved. We assume here that each side of Eq. (3) vanishes as in the classical theory, yielding a unique class of homogeneous solutions, for g^* and for the product fg^*, as a generalization of the classical theory

$$g^* = C'(T)(\Delta\mu)^{-3} \tag{5a}$$

and

$$fg^* = D(T)(\Delta\mu)^{-1}, \tag{5b}$$

where the integration constants $C'(T)$ and $D(T)$ are functions only of T. (It is shown below that fg^* is related to the superficial density [8].) Although the homogeneity ansatz leading to Eqs. (5) is physically reasonable, we cannot prove it in general and base its justification on agreement with experiment and with calculations that follow. A reformulation of the ansatz in the nonuniform drop model is described following Eq. (13) below. Classical nucleation theory is recovered for $D(T) = 0$. Comparison of Eqs. (4a) and (5a) shows that in order to have $g^*/g^*_{\mathrm{CNT}} \to 1$ as $\Delta\mu \to 0$ we must have $C'(T) = C(T)$ or

$$g^* = \frac{32\pi\gamma_\infty^3}{3\rho_l^2}(\Delta\mu)^{-3} = C(T)(\Delta\mu)^{-3}, \tag{6}$$

suggesting that the Kelvin relation [Eq. (4b)] has validity beyond the capillary drop model of the classical theory.

Equations (2) and (5b) have the interesting consequence that the displacement between barrier heights in the classical and present theories is a function only of T,

$$W^* - W^*_{\mathrm{CNT}} = W^* - \frac{1}{2}g^*\Delta\mu = -D(T). \tag{7}$$

Combining Eqs. (6) and (7) gives

$$\frac{W^*}{g^*\Delta\mu} = \frac{1}{2} - \frac{D(T)}{C(T)}(\Delta\mu)^2, \tag{8}$$

showing recovery of CNT along the coexistence curve, $\Delta\mu = 0$, and quadratic dependence in the departure from CNT with increasing $\Delta\mu$. Note that while $C(T)$ is determined by Eq. (6), the function $D(T)$ must be obtained by a separate, model-dependent, calculation as now described.

In the DF theory of vapor-liquid nucleation [10] the nucleus is modeled as a nonuniform spherical drop. W^* is calculated from the grand potential, which can be expressed as an integral over the tangential component of the pressure tensor P_T. The latter is equal to minus the

free energy density [11], and can be written as [12]

$$P_T(r) = P_h(\rho_l(r)) + \frac{1}{2}\rho_l(r)\int \rho_l(r')w(|r - r'|)\,dr'. \tag{9}$$

Here $P_h(r)$ is the pressure of a uniform hard-sphere fluid at the equilibrium density, $\rho_l(r)$, and $w(|r - r'|)$ is the attractive part of the pairwise intermolecular potential. The equilibrium density is obtained from Eq. (9) using an iteration method as described by Zeng and Oxtoby [4]. The nucleation barrier height may then be obtained from $P_T(r)$ using [12]

$$W^*_{\mathrm{DF}} = -4\pi\int_0^\infty r^2[P_T(r) - P_0]\,dr, \tag{10}$$

where P_0 is the pressure of the vapor surrounding the drop. Finally, g^*_{DF} is obtained from the density profile,

$$g^*_{\mathrm{DF}} = 4\pi\int_0^\infty r^2[\rho_l(r) - \rho_0]\,dr. \tag{11}$$

Both g^* and g^*_{DF} represent the excess number of molecules present in the volume over the number present prior to cluster formation and are independent of the choice of dividing surface (see below). This definition differs from the capillary drop model, where the total number of molecules (g^*_{CNT}) present within the spherical boundary defined by the critical radius r^* is used [13].

The scaling relations, Eqs. (6)–(8), are demonstrated here through comparisons with results obtained from DF calculations for the Lennard-Jones fluid model of Ref. [4]. The abscissas of Figs. 1 and 2 contain the ratio of actual to equilibrium vapor fugacities, $f/f_0 = \exp(\Delta\mu/kT)$, where f/f_0 approaches S in the dilute vapor limit. Figure 1 shows the linear dependence between g^* and $\Delta\mu^{-3}$ predicted from Eq. (5a) at several different temperatures. Slopes obtained from the DF calculations (lines in Fig. 1) are in good agreement with the predicted values from Eq. (6). Table I compares the barrier heights in the classical and DF theories at fixed temperature. Note, in conformity with Eq. (7), that the displacements, given in column 5, vary by only a few percent while the barrier heights themselves vary over an order of magnitude. From the average displacement we obtain $D(T) = 19.8kT$ at this temperature. Substitution of $D(T)$, determined as in Table I from the average barrier height displacement at each temperature, and $C(T)$, from Eq. (6), into Eq. (8) gives the results shown in Fig. 2. There are no adjustable parameters in this comparison as the only unknown parameter contributing to the slope $D(T)$ is obtained from the DF calculations.

To conclude the treatment of the spherical drop nucleus, we derive a formally exact expression for $W^*/g^*\Delta\mu$ using dividing surface arguments [14]. These methods yield, as the first equality in Eq. (12) below, an equation similar to Eq. (10) but in terms of the normal component of the pressure tensor P_N. [Adding the two expressions
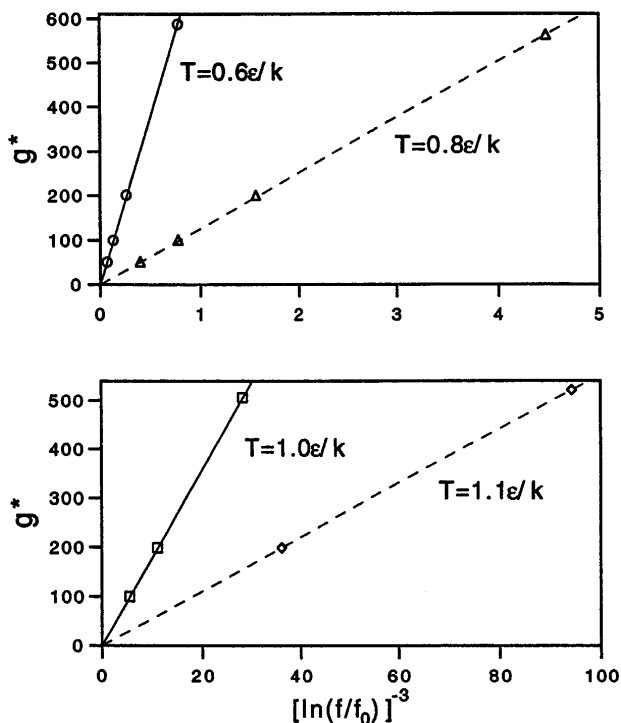
FIG. 1.   Density functional results for g^* (markers) and comparison with scaling (lines) from Eq. (5a). Temperatures are given in reduced units kT/ε, where ε is the characteristic energy for the Lennard-Jones system of Ref. [4].

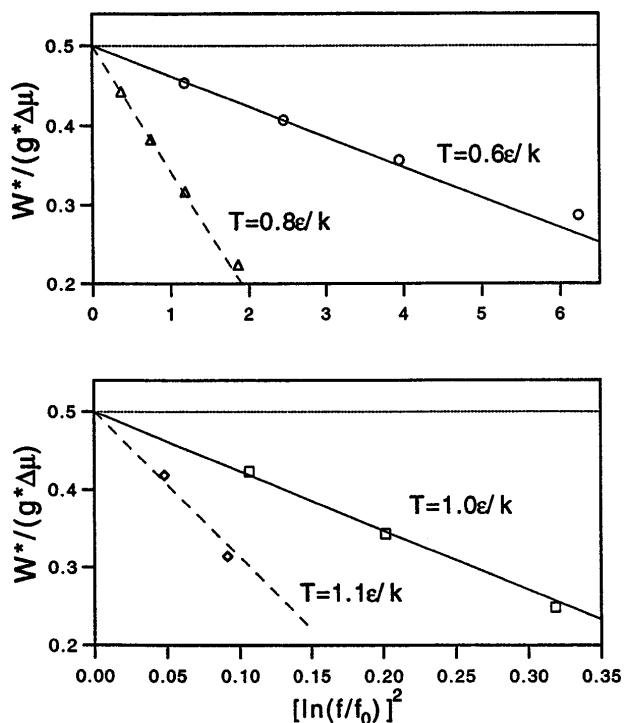FIG. 2.   Density functional results for $W^*/g^*\Delta\mu$ (markers) and comparison with scaling (lines) from Eq. (8). Temperatures are as reported in Fig. 1. DF results at each temperature are for the same conditions as in Fig. 1. Horizontal lines are the prediction of classical nucleation theory.

yields a generalization of the Gibbs relation for $3W^*$ as a volume integral over $P_N(r) - P_T(r)$.] For the choice that the dividing surface is placed at the radius $R = R_s$, where R_s defines the surface of tension [2,14], the methods described in Ref. [14] furnish the second equality in Eq. (12),

$$2W^* = 4\pi \int_0^\infty r^2 [P_N(r) - P_0]\, dr$$
$$= 4\pi \int_0^{R_s} r^2 (P^\alpha - P_0)\, dr = \frac{4\pi R_s^3}{3}\rho_l \Delta\mu$$
$$= n_L^* \Delta\mu , \qquad (12)$$

which converts the integrand to a step function equal to $P^\alpha - P_0$ for $r < R_s$, where P^α is the interior pressure at the center of the drop, and equal to zero for $r > R_s$. The third equality, which assumes incompressibility and low vapor density, relates the change in chemical potential, the bulk interior phase density, $\rho_l = \rho_l(0)$, and the difference in pressure at the center and outside of the drop. From the first and last terms in Eq. (12) we obtain the solution

$$\frac{W^*}{g^*\Delta\mu} = \frac{1}{2}\frac{n_L^*}{g^*} = \frac{1}{2}\left[1 - \frac{n_S^*}{g^*}\right], \qquad (13)$$

where n_L^* is defined as the number of molecules contained within the volume bounded by the surface of tension for uniform interior density equal to ρ_l. The second equality of Eq. (13) follows from $g^* = n_L^* + n_S^* - n_V^*$,

where n_S^* divided by $4\pi R_s^2$ is the superficial density and $n_V^* = 4\pi R_s^3/3$ times the vapor density [8]. [In conformity with the third equality in Eq. (12), we have not included the displaced vapor component n_v^*.] Thus we obtain $W^* = n_L^*\Delta\mu/2$, highlighting the importance of R_s, while the equimolecular dividing surface R_e provides a very good approximation for the classical radius r^* [15]. The equality $D(T) = n_S^*\Delta\mu/2$ from Eqs. (7) and (13) provides a physical interpretation for the departure from CNT in terms of the superficial density.

The homogeneity ansatz can be simply reformulated in terms of the equimolecular dividing surface as follows: Consider for simplicity an incompressible nucleus in the limit of low vapor density. The condition $g^* = g^*_{CNT}$ from Eq. (6) implies that $R_e = r^*$ because n_S^* vanishes at

TABLE I.   Critical nucleus properties at $T = 0.8\varepsilon/k$, where ε is the characteristic energy for the Lennard-Jones system of Ref. [4] and k is the Boltzmann constant. Energies $\Delta\mu$ and W^* are in units of kT.

$\Delta\mu$	g^*	W^*_{CNT}	W^*_{DF}	$W^*_{CNT}-W^*_{DF}$
0.607	562.6	170.7	151.0	19.7
0.863	200.0	86.3	66.0	20.3
1.089	100.4	54.7	34.6	20.1
1.362	50.9	34.7	15.6	19.1

the equimolecular surface, and we assume that the vapor displaced by the nucleus is negligible. For the center pressure P^{α} to have the same value in the capillary and nonuniform drop models [Eq. (12)], this equality of radii and the generalized Laplace relation [14] require $\gamma_{\infty} = \gamma_e + (R_e/2)d\gamma_e/dR_e$, where γ_e is the surface tension at the equimolecular dividing surface. This condition is equivalent to homogeneity because the converse, leading to equality of g^* and g^*_{CNT} as required by Eq. (6), also applies. The pair of conditions, $\gamma_e = \gamma_{\infty}$ and $d\gamma_e/dR_e = 0$, used in constructing the working formulas of CNT [2] is seen to be a special case of the present theory. This reformulation provides context for the homogeneity ansatz used to separate Eq. (3) and can be used as an alternate basis on which to develop the present theory.

In addition to providing an excellent description of the DF results, the scaling theorems [Eqs. (6)–(8)] are supported by experiment. Each of the factors in $W^*/g^*\Delta\mu$ is subject to measurement [6]. Rate plots of $\ln(J)$ vs $\ln(S)$ at constant T, where J is the nucleation rate, have been used to compare CNT and DF theories, and CNT and experiment [6,7]. It has been observed that CNT provides accurate estimates for the number of molecules in the critical nucleus as derived experimentally from the slope, $d\ln(J)/d\ln(S)$, using the nucleation theorem [6,7]. Another observation is that the curves for $\ln(J)$ tend to be uniformly displaced vertically with respect to each other in such comparisons. Specifically, the ratios $J_{\text{CNT}}/J_{\text{exp}}$ and $J_{\text{CNT}}/J_{\text{DF}}$, while dependent on the temperature, are only weakly dependent on $\Delta\mu$ [7]. The scaling theorems provide a simple explanation for these observations. In the first case, the equality $g^* = g^*_{\text{CNT}}$ from Eq. (6) justifies the observation that CNT is an excellent predictor of the number of molecules in the critical nucleus. In the second case, the constant displacement in W^* from its classical value [Eq. (7)] implies a constant displacement in $\ln(J) = \ln(K) - W^*/kT$. (Differences in the logarithm of the rate prefactor K are usually negligible in such comparisons.) These results suggest that the systematic discrepancies observed between CNT and experiment can be effectively parametrized by the single scaling parameter $D(T)$ in the present theory.

The scaling theorems constrain the departure from CNT and therefore can guide the construction of phenomenological nucleation theories. Like the nucleation theorem itself, extensions of the present approach will likely apply to multicomponent systems. Finally, the statistical foundation for homogeneity and its limits of validity remain to be explored.

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