LETTERS TO THE EDITOR

The Letters to the Editor section is divided into four categories entitled Communications, Notes, Comments, and Errata. Communications are limited to three and one half journal pages, and Notes, Comments, and Errata are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 1997 issue.

COMMUNICATIONS

Interfacial curvature free energy, the Kelvin relation, and vapor–liquid nucleation rate

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The interfacial curvature free energy is shown to cause a significant barrier height correction to the classical nucleation rate. This correction is found to be temperature dependent, but independent of nucleus size. Density functional (DF) calculations are presented for a nonuniform spherical droplet model of the nucleus. Calculations for the surface tension, as a function of nucleus size, and for the interfacial curvature free energy support theoretical predictions and provide an explanation for systematic discrepancies between classical and DF nucleation theories and between the classical theory and experiment. © *1997 American Institute of Physics.* [S0021-9606(97)51912-X]

Measurements of vapor-liquid nucleation rate have shown systematic departure from predictions of classical nucleation theory (CNT). In particular, it has been observed that although the CNT accurately describes the slope when the logarithm of the nucleation rate is plotted vs supersaturation (S) at fixed temperature, a temperature dependent correction to the classical rate is needed to bring theory in line with experiment.[1] Recent theoretical results yield a molecular-based approach to interpretation of the slope measurements in terms of the number of molecules in the critical nucleus.[2] Thus the departure from CNT shows up largely as a shift in nucleation rate and less as a deviation in nucleus size. Although this partial success has been considered quite remarkable given the crude approximations of CNT, the reasons for it have remained a mystery.

The molecular-based approach has been used to obtain general free-energy scaling properties of a critical nucleus under the assumption that the critical nucleus size is given by the Kelvin relation, as in the classical theory.[3] It was found that the nucleation barrier height can differ from the CNT prediction by a temperature-dependent amount $D(T)$ that is independent of nucleus size. These results are supported by density functional (DF) calculations and are consistent with the systematic discrepancies observed between CNT and experiment mentioned above.[1,3] However, the molecular basis for persistence of the Kelvin relation beyond the capillary drop model of CNT has not been determined, nor has any physical basis been given for the barrier height displacement $D(T)$.

In the present communication we address these issues using a nonuniform spherical droplet model of the nucleus. Motivated by a recent study of liquid-vapor states of inhomogeneous fluids by Romero-Rochin and Percus,[4] we identify the barrier height displacement with the interfacial curvature free energy and use density functional calculations to confirm the predicted results. These authors obtained the following result for the surface free energy Ω_s of a spherical drop:[4]

$$Q_s \simeq 4\pi R^2 \left[\gamma_\infty + \frac{k_s}{R^2} \right] + O(\xi_b/R), \tag{1}$$

where γ_∞ is the bulk surface tension for a flat interface and k_s is the rigidity coefficient ($4\pi k_s$ is the interfacial curvature free energy). The last term contains corrections on the order of the width ξ_b of the interfacial profile divided by the radius R of the drop. We will show that Eq. (1) itself follows from the Kelvin relation and that the latter provides a nonpertubative model for the higher order terms. Thus the independent foundation for Eq. (1) described in Ref. 4 is shown here to be consistent with the Kelvin relation and indicative of the validity of its extension to nucleation theory beyond the classical capillary drop model.

Consider, as two models of the critical nucleus, a classical capillary drop and a diffuse drop held in unstable equilibrium with a supersaturated vapor at temperature T. In the capillary model of CNT the nucleus is represented as a spherical drop having properties of a bulk sample of the nucleated phase, including a curvature-independent surface tension γ_∞ and uniform density ρ_l.[5] For the diffuse nucleus we allow the more general case of a nonuniform spherical drop whose density profile is shown schematically in Fig. 1. Analytic results for the diffuse nucleus will be obtained using Gibbs dividing surface methods.[5,6] The dividing surface is a mathematical construct that can be placed at any radius R and does not affect the physical properties of the drop. Thus the pressure difference given by the generalized Laplace relation,[5]

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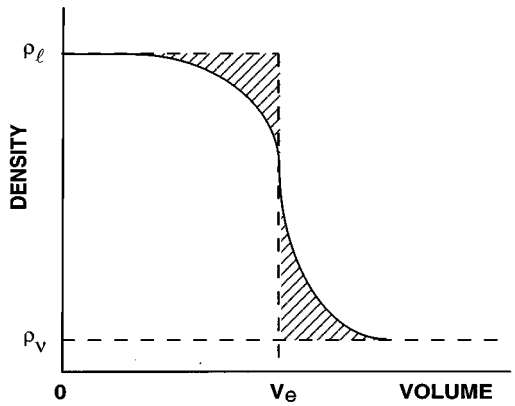

FIG. 1. Schematic density profile in the diffuse droplet model. The dashed vertical line marks the equimolecular dividing surface defined such that $(\rho_l-\rho_v)V_e=4\pi(R_e)^3(\rho_l-\rho_v)/3$ is equal to the integrated excess density.

$$P_l-P_v=\frac{2\gamma(R)}{R}+\left[\frac{\partial\gamma}{\partial R}\right], \tag{2}$$

where P_l and P_v are the pressures at the center and exterior to the drop, respectively, is independent of R. $\gamma(R)$ is the surface tension for the dividing surface located at the radius R [see also Eq. (7) below], and the square-bracketed term gives the derivative of γ with respect to a mathematical displacement of the dividing surface. The bracketed term vanishes for placement of the dividing surface at the surface of tension ($R=R_s$) where $\gamma(R)$ assumes its minimum value, γ_s. In addition to the surface of tension we will require properties at the equimolecular dividing surface ($R=R_e$) defined by the equal areas construction of Fig. 1 and characterized by the property that the formal derivative in Eq. (1) equals $\partial\gamma_e/\partial R_e$, the partial derivative for the actual radius dependence at constant temperature.[5]

The generalized Kelvin relation for an incompressible nucleus follows from Eq. (2) upon equating the chemical potentials of the vapor and the bulk liquid at the center of the drop:[5]

$$P_l-P_v=\rho_l\Delta\mu-(P_v-P_\infty), \tag{3}$$

where P_∞ is the equilibrium vapor pressure of the condensed phase for a planar surface and $\Delta\mu=\mu_v-\mu_\infty$ is the difference between the chemical potential of the supersaturated vapor and the bulk condensed phase driving the phase change. The P_v-P_∞ term corrects for nonequilibrium vapor density. Returning to the two drop models, we see from Eq. (3) that if the values of ρ_l, μ_v, and P_v are specified, the value of P_l is determined. We will assume that the core region of the diffuse drop remains characterized by the bulk phase density ρ_l. Then for fixed vapor pressure, P_l must not only be independent of the choice of dividing surface used in Eq. (2), but independent as well of which model (classical capillary or diffuse interface) is used to represent the drop. Thus we obtain the important equalities:

$$P_l-P_v=\frac{2\gamma_\infty}{R^*}=\frac{2}{R_e}\left(\gamma_e+\frac{R_e}{2}\frac{\partial\gamma_e}{\partial R_e}\right)=\frac{2\gamma_s}{R_s}, \tag{4}$$

where R^* is the radius of the critical nucleus in the capillary drop model of CNT, $\gamma_e\equiv\gamma(R_e)$, and both R_e and R_s refer to the diffuse nucleus of critical size. The first equality of Eqs. (4) is the classical Laplace relation. The second and third equalities result on setting $R=R_e$ and $R=R_s$ in Eq. (2). Equation (4) is based solely on the assumption that the nucleus has an incompressible core of density equal to that of the bulk phase. The Kelvin relation for R^* follows from Eq. (3) and the classical Laplace relation:

$$R^*=2\gamma_\infty/[\rho_l\Delta\mu-(P_v-P_\infty)]. \tag{5}$$

We now investigate the assumption [Eq. (6a)] that Eq. (5) can be used to predict the critical radius R_e of the diffuse droplet model. The following equalities are equivalent through Eqs. (4):

$$R_e=R^*, \tag{6a}$$

$$\gamma_e+\frac{R_e}{2}\frac{\partial\gamma_e}{\partial R_e}=\gamma_\infty, \tag{6b}$$

$$\frac{\gamma_\infty}{R_e}=\frac{\gamma_s}{R_s}. \tag{6c}$$

We emphasize that Eqs. (6a)–(6c) satisfy, but are not consequences of Eq. (4). However, if any member from the set, Eqs. (6a)–(6c), holds, the others hold likewise by virtue of their equivalence through Eq. (4). For example, Eq. (6a) is a restatement of the homogeneity ansatz of Ref. 3. Equations (6b) and (6c) are, therefore, equivalent expressions of the homogeneity ansatz through Eq. (4), as are Eqs. (6d) and (6e). Integration of Eq. (6b) at constant temperature gives

$$R_e^2\gamma_e=R_e^2\gamma_\infty+k_s(T).$$

[Here k_s is simply a constant of integration; it is shown below that k_s is the rigidity coefficient of Eq. (1).] Thus we obtain an explicit form for the curvature dependence of γ_e, which is also equivalent to Eq. (6a):

$$\gamma_e=\gamma_\infty+\frac{k_s}{R_e^2}. \tag{6d}$$

The pair of conditions $\gamma_e=\gamma_\infty$ and $\partial\gamma_e/\partial R_e=0$ assumed in CNT[5] is seen to be a special case of Eqs. (6) for which $k_s=0$. Before discussing k_s, we show that Eqs. (6) imply a difference in the nucleation barrier heights predicted using the classical and diffuse droplet models that is independent of R_e.

The dependence of $\gamma(R)$ on dividing surface location is given by Ono and Kondo:[6]

$$\gamma(R)=\frac{R_s^2\gamma_s}{3R^2}+\frac{2\gamma_s R}{3R_s}. \tag{7}$$

Evaluating Eq. (7) at $R=R_e$ and using Eq. (6c) to eliminate γ_s gives:

$$\gamma_\infty=\frac{3\gamma_e R_e^3}{R_s^3+2R_e^3}. \tag{8}$$

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The nucleation barrier height in the diffuse droplet model is most simply expressed in terms of conditions at the surface of tension:[5]

$$W^* = \frac{4\pi R_s^2 \gamma_s}{3} = 4\pi R_e^2 \gamma_e \left(\frac{R_s^3}{R_s^3 + 2R_e^3} \right), \tag{9}$$

which we have rewritten [second equality in Eq. (9)] using Eqs. (6c) and (8). Similarly for the barrier height in the classical theory we obtain

$$W^*_{\mathrm{CNT}} = \frac{4\pi R_e^2 \gamma_\infty}{3} = 4\pi R_e^2 \gamma_e \left(\frac{R_e^3}{R_s^3 + 2R_e^3} \right) . \tag{10}$$

The first equality is the Gibbs expression for the classical barrier height, after substituting R_e for R^* using Eq. (6a), and the second equality uses Eq. (8). Subtracting Eq. (9) from Eq. (10) and using Eq. (8) we obtain:

$$W^*_{\mathrm{CNT}} - W^* = 4\pi R_e^2 (\gamma_\infty - \gamma_e). \tag{11}$$

From Eqs. (11) and (6d) we obtain, as an important corollary of assuming $R_e = R^*$, that the difference between the classical and diffuse droplet model nucleation barrier heights is independent of R_e:

$$W^*_{\mathrm{CNT}} - W^* = -4\pi k_s \equiv D(T). \tag{6e}$$

Note that the converse also applies: Since Eq. (6d), and therefore Eq. (6a), follows from Eqs. (11) and (6e), a constant barrier height shift implies $R_e = R^*$.

Density functional calculations both for a flat interface ($\Delta\mu = 0$) and for finite size drops were carried out using the Lennard-Jones argon model of Zeng and Oxtoby[7] as previously described.[3] The results shown in Fig. 2 confirm Eq. (6d) and yield the temperature dependent values for k_s given in the caption. Figure 2 was constructed for R_e equal to R^* from Eq. (5), and γ_e values from Eq. (11) with calculated values for W^* from the DF model.

The rate of nucleation is generally expressed in exponent-prefactor form as $J = K\exp(-W^*/kT)$. Thus Eq. (6e) yields a change in nucleation rate of the form $J/J_{\mathrm{CNT}} = (K/K_{\mathrm{CNT}})\exp[(W^*_{\mathrm{CNT}} - W^*)/kT] = (K/K_{\mathrm{CNT}}) \times \exp(-4\pi k_s/kT)$. To illustrate the size of the effect that we are considering, assume for the moment that the prefactor is unchanged from its classical value K_{CNT}. Then for $k_s = -kT$ the rate correction is $J/J_{\mathrm{CNT}} \simeq \exp(4\pi) \approx 3 \times 10^5$ (see Fig. 2 for the range of values of k_s computed in the DF model). Temperature dependent corrections measured by Adams *et al.*,[1] albeit for a different material (nonane), are in the range $10^2 \leq J/J_{\mathrm{CNT}} \leq 10^9$. Our results suggest that nucleation rate measurements can provide experimental determination of the interfacial curvature free energy, $4\pi k_s = -D(T)$. Accurate determination of this quantity, through comparison between experimental rate measurements and the capillary drop model of classical theory, will require a consistent treatment of the prefactor correction, K/K_{CNT}. Recent estimates of K/K_{CNT}, including the $1/S$ factor[8] and a revised estimate for the replacement free energy factor (approximately 10^4),[9] when combined suggest values for K/K_{CNT} of order 10^3.

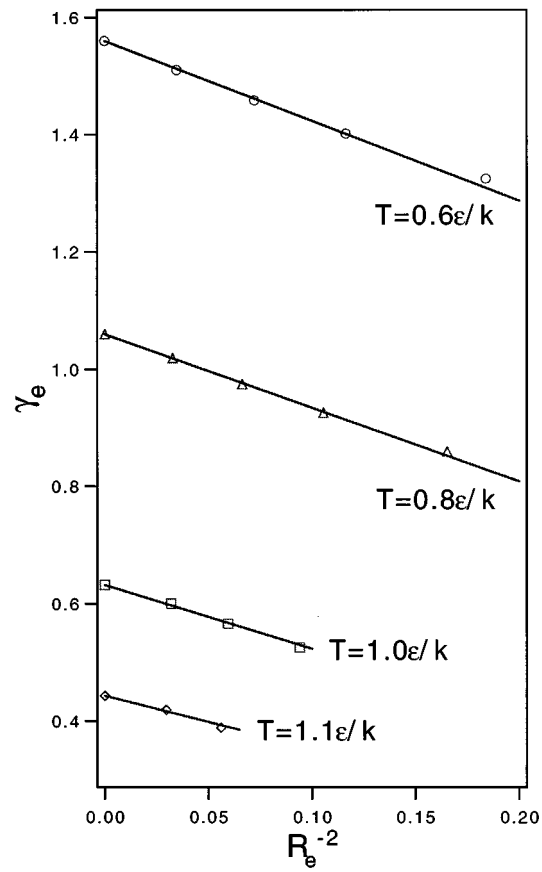

FIG. 2. Density functional results for γ_e (markers) and comparison with Eq. (6d) (lines). Temperatures are given in units of ϵ/k where ϵ is the characteristic energy for the Lennard-Jones system of Ref. 7 and k is the Boltzmann constant. R_e is in units of σ, which is the characteristic Lennard-Jones distance, and γ_e is in units of ϵ/σ^2. From the linear fits we obtain $k_s = -1.366\ \epsilon = -2.276\ kT$ at $T = 0.6$, $k_s = -1.261\ \epsilon = -1.576\ kT$ at $T = 0.8$, $k_s = -1.085\ \epsilon = -1.085\ kT$ at $T = 1.0$, and $k_s = -0.901\ \epsilon = -0.819\ kT$ at $T = 1.1$.

Finally, we derive the surface free-energy Ω_s from the Kelvin radius assumption [Eq. (6a) and its equivalents] and identify k_s with the rigidity coefficient. We obtain:

$$\Omega_s = 3W^* = 4\pi R_s^2 \gamma_s = 4\pi (R_e^2 + 2k_s)$$
$$= 4\pi R_e^2 \left(\gamma_\infty + \frac{k_s}{R_e^2} \right) + 8\pi k_s . \tag{12}$$

The first two equalities are from Ref. 5, the third equality follows Eqs. (6e), (9), and (10), and the last equality uses Eq. (6d). From the third equality of Eq. (12) and setting $\xi_b \equiv R_e - R_s$, which is the Tolman length,[5] we obtain a cubic equation in ξ_b:

$$\Omega_s = 4\pi R_e^2 \left(\gamma_\infty + \frac{k_s}{R_e^2} \right)$$
$$- 8\pi R_e^2 \gamma_\infty \left[\left(\frac{\xi_b}{R_e} \right) - \left(\frac{\xi_b}{R_e} \right)^2 + \frac{1}{3} \left(\frac{\xi_b}{R_e} \right)^3 \right] \tag{13}$$

as an explicit, nonpertubative, result for Ω_s including correction for the finite thickness of the interface. Equation (13)

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has the same structure as Eq. (1) with the identifications $R=R_e$ (as in Ref. 10) and $k_s(T)$ equal to the rigidity coefficient.

The unit-area elastic curvature free-energy (k_s/R^2), which is neglected in classical nucleation theory, has been interpreted as arising from the square Laplacian term in a local density expansion for the free energy of the nonuniform drop[4,11] just as the surface tension originates from the square gradient term.[11,12] Accordingly, the present theory, based on Eqs. (4) and (6a), seems to incorporate extension of square-gradient formulations of classical nucleation theory[12] to include the square Laplacian terms. The latter, from the preceding analysis, are predicted to shift the nucleation barrier height without affecting the size of the critical nucleus itself. Further analysis of the present model for diffuse droplets requires evaluation of higher-order terms in Eq. (1) for comparison with the predictions of Eq. (13). Nonetheless, the present model [represented by Eq. (6d)] is supported by the results of DF calculations (Fig. 2) even though the interfacial profiles for the cases studied, particularly at the smaller values of R_e, were found to be quite broad (e.g., values of ξ_b/R_e approaching 0.2 at $T=0.8$). The breakdown, suggested in Fig. 2 at the smallest nucleus size, appears to be more related to compressibility of the Lennard-Jones argon nucleus[13] and to the fact that the center density of the nucleus starts to deviate considerably from the bulk liquid density for the smallest clusters [in violation of assumptions used in Eq. (4)].

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