Fusion of the Extended Modified Liquid Drop Model for Nucleation and Dynamical Nucleation Theory

D. Reguera and H. Reiss

Department of Chemistry and Biochemistry, UCLA, 607 Charles E. Young East Drive, Los Angeles, California 90095-1569, USA

(Received 28 April 2004; published 13 October 2004)

We present a new phenomenological approach to nucleation, based on the combination of the "extended modified liquid drop" model and dynamical nucleation theory. The new model proposes a new cluster definition, which properly includes the effect of fluctuations, and it is consistent both thermodynamically and kinetically. The model is able to predict successfully the free energy of formation of the critical nucleus, using only macroscopic thermodynamic properties. It also accounts for the spinodal and provides excellent agreement with the result of recent simulations.

DOI: 10.1103/PhysRevLett.93.165701 PACS numbers: 64.60.Qb, 82.20.Db, 82.60.Nh

During the last decade, there have been significant advances in the theory of nucleation. These have included the use of the i, v cluster [1], the Fisher droplet model [2,3], the application of density functional theory (DFT) [4], scaling relations [5], the introduction of dynamical nucleation theory (DNT) [6], and many impressive simulations [7,8]. Most of these developments require the use of an intermolecular potential, unfortunately not reliably available for most substances. For this reason, workers have continued to rely on the classical nucleation theory (CNT) which, despite its theoretical shortcomings, requires only macroscopic thermodynamic parameters.

Recently, we developed a model, the "extended modified liquid drop" (EMLD) model [9], that was able to reproduce with remarkable accuracy the properties of very small confined systems, without the use of an intermolecular potential. In this Letter, we present a new approach to nucleation with very useful properties, based on a combination of EMLD with DNT [6]. The new model does not require information concerning intermolecular potentials but, instead, using the same macroscopic parameters as CNT, is able to predict the spinodal. Moreover, it provides very good agreement with recent simulations of nucleation in Lennard-Jones systems [7] and fulfills scaling relations recently proposed in the literature [5].

EMLD focuses on the behavior of a very small "canonical" system of N molecules confined to a spherical volume V of radius R, at temperature T. Under appropriate conditions, a liquid drop can form inside V. The drop itself, modeled according to the "capillarity approximation," is assumed to contain n molecules and to be surrounded by an ideal gas, constituted by the remaining $N - n$ molecules. Under these assumptions, the free energy of formation $\Delta F(n)$ of the drop containing n molecules, at a fixed position within the container, can be evaluated by thermodynamic means alone, yielding [9]

$$\frac{\Delta F(n)}{k_B T} = -n \ln\frac{p_1}{p_{eq}} + \frac{\sigma A}{k_B T} + n\left(1 - \frac{v_l p_{eq}}{k_B T}\right) + N \ln\frac{p_1}{p_0}, \quad (1)$$

where $p_1 = (N-n)k_B T/(V - n v_l)$ is the pressure exerted by the ideal gas, p_{eq} is the vapor pressure of the bulk liquid, σ is the (planar) surface tension, A is the surface area of the spherical drop of radius r and n molecules, v_l is the volume per molecule in the liquid, and $p_0 = N k_B T/V$. The first three terms on the right-hand side of Eq. (1) represent the usual bulk term related to the saturation, the contribution of the surface, and the volume work, and the last term originates from the depletion of vapor molecules when a drop is formed. In the thermodynamic limit, $p_1 = p_0$ and the CNT expression for the free energy is recovered.

For systems containing just a few molecules, there are some additional contributions to the free energy of formation that become important. In the EMLD [9] two such contributions are incorporated. These are (i) the translation of the drop through the volume of the container [10] and (ii) the effect of fluctuations in n. (i) Since the drop does not have to appear precisely at the center of the container it can "collide" with the walls, thus contributing to the total pressure $p(n)$, which then consists of the sum of the gas pressure p_1 and the pressure p_{drop} exerted by the translating drop, regarded as a single ideal hard sphere molecule. Thus $p(n) = p_1(n) + k_B T \Theta(n)/V_c$, where $V_c = 4\pi(R - r)^3/3$ is the volume through which the center of the drop can translate, and $\Theta(n)$ is the unit step function. (ii) Although N, V, and T are held constant, the number n of molecules of the drop can fluctuate, so that the chance of having a drop of size n is given by

$$f(n) = \frac{e^{-\Delta F(n)/k_B T}}{\sum_{n=0}^{N} e^{-\Delta F(n)/k_B T}}. \quad (2)$$

Although such fluctuations are important only in very small systems, consistent thermodynamic properties should be obtained as averages using $f(n)$ as a weighting function. In particular, the pressure should be obtained by averaging $p(n)$ above to yield

$$P = \langle p(n) \rangle = \sum_{n=0}^{N} f(n) \left[p_1(n) + \frac{k_B T}{V_c} \Theta(n) \right]. \qquad (3)$$

The exception to this rule is the total Helmholtz free energy, which should be calculated using the standard relation

$$\Delta F = -k_B T \ln \sum_{n=0}^{N} e^{-\Delta F(n)/k_B T}. \qquad (4)$$

Pressure-volume isotherms predicted by the EMLD, using Eq. (3), for systems containing Lennard-Jones (LJ) argon with different molecular contents N, at $T = 85$ K, are plotted in Fig. 1. For large N, the isotherms, have a van der Waals looplike shape, whose origin can be qualitatively understood. At very small volumes, almost all molecules are condensed into a drop, leaving just a few vapor molecules tightly squeezed between the drop and the boundary of V. As V increases, the pressure decreases (due to a decrease of vapor density) until a minimum pressure is reached. At this point the evaporation of the drop is the dominant effect and results in an increase in pressure. If V continues to be increased, a point is reached where the pressure of the vapor can no longer equal the equilibrium pressure of the diminishing evaporating drop so that it evaporates completely, leaving only ideal gas and its corresponding pressure in the container. However, below a certain N, in this case in the neighborhood of $N = 15$, the loop disappears due to the effect of fluctuations, and the P-V isotherm simply exhibits a monotone decrease. Later, we see that this phenomenon is related to the occurrence of a spinodal.

The isotherms predicted by the EMLD in Fig. 1 display a remarkable agreement with those that have been generated by means of Monte Carlo (MC) simulations, regarded as experimental measurements [9,11].

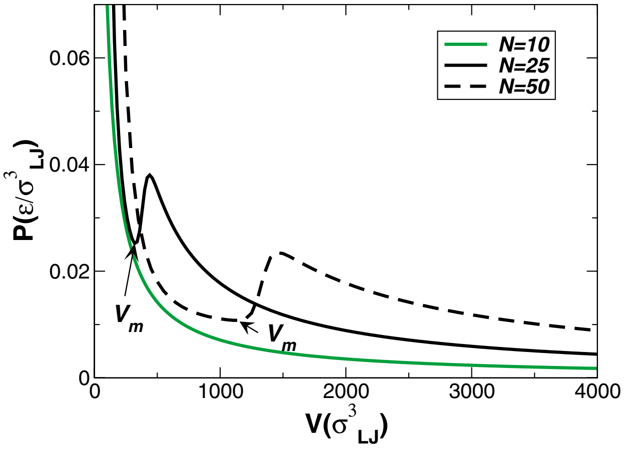

FIG. 1 (color online). P-V isotherms for LJ argon at $T = 85$ K and different values of N. The values of the surface tension, liquid density, and equilibrium vapor pressure are the same as in Ref. [9].

The excellent accuracy achieved by EMLD in the description of a canonical system then becomes the basis of the formulation of a new model of nucleation with surprising properties. This model is based on the assumption that the N, V, T system described by the EMLD, becomes, *as a whole,* the physical drop for nucleation. We demonstrate that this "drop" is not only thermodynamically consistent, but also the proper definition from the dynamical point of view.

Notice that this N, V, T system, as a whole, constitutes a kind of a "diffuse" cluster that includes some vapor and differs from the compact capillarity cluster of CNT by the presence of the volume V as a defining variable. The necessity of including the volume as a relevant variable in the description of a physical cluster was already noted by molecular theories, such as in the formulation of the (i, v) cluster [1]. However, the main problem was the absence of a nonarbitrary physical criterion for selecting the volume, aggravated by the relative insensitivity of the free energy to volume in some ranges [12]. However, there are strong arguments, both from thermodynamics and from kinetics, that support the notion that the volume V_m corresponding to the minimum of the P-V isotherm of Fig. 1, for each value of N, is appropriate for the physical cluster.

Talanquer and Oxtoby provided some excellent physical insight concerning the choice of V in their work [13] on DFT in the canonical ensemble. They noticed that sets of N, V clusters could be found with identical liquidlike cores but surrounded by different amounts of "vapor." For a given N, the cluster in this set with the least vapor was chosen to be the *stable N* cluster. The requirement of a minimum amount of vapor corresponds to the lowest vapor pressure and thus to the volume V_m that denotes the minimum of the P-V isotherm for each N.

It is in kinetic considerations that DNT [6] enters the picture. Since nucleation is a nonequilibrium kinetic process, it is reasonable to search in the theory of rate processes for a physical criterion for establishing the value of V. From this point of view, the proper definition of a cluster should be connected to the kinetics of the addition and loss of cluster molecules. Defining a cluster as a collection of N molecules confined to an arbitrary volume V, the pioneering development [6] by Schenter *et al.* of DNT shows (using variational transition state theory [14]) that the proper kinetic definition of the volume of a cluster is the one that minimizes its evaporation rate. It can be demonstrated that this requirement is realized by selecting the V which minimizes the change of free energy with respect to volume, i.e., the V that minimizes the pressure. But this is just the value of V at the minimum of a P-V isotherm like those in Fig. 1, and it is exactly the choice suggested by Talanquer and Oxtoby. Thus, the thermodynamic and the kinetic criteria are identical. The volume at the isotherm minimum, $V_m(N)$, is then the volume used in defining the EMLD-DNT cluster.

Now, $V_m(N)$ can be obtained numerically as the minimum, $\partial P/\partial V|_{V_m} = 0$, of Eq. (3), but we have also verified that a very good approximation to V_m can be obtained following a simpler route. The minimum of the P-V isotherm marks the physical onset of evaporation, and this onset corresponds to the volume at which the *stable* drop in the canonical ensemble becomes *metastable*. Therefore, a good approximation to V_m can be obtained from the simultaneous solution of $\partial \Delta F(n, N, V)/\partial n|_{V_m, n_d} = 0$ and $\Delta F(n_d, N, V_m) = 0$, equations which define the stable drop and the onset of metastability, respectively.

Once V has been specified, the next step involves the use of the accurate value of the free energy of the whole N, V, T system offered by Eq. (4). This value can be used to construct the work of formation of the new physical EMLD-DNT cluster in the μ, V, T open system. The latter is the ensemble relevant to nucleation. It is easy to prove, either from thermodynamics [15] or from statistical mechanics, that at a chemical potential μ and pressure p, the Gibbs free energy or the grand potential are related to the Helmholtz free energy of cluster formation as follows:

$$\Delta G = \Delta\Omega = \Delta F(N, V_m) - V_m \Delta p + N \Delta\mu_0, \qquad (5)$$

where $\Delta p = p_0 - p$ and $\Delta\mu_0 = \mu_0 - \mu$. Although N is the natural size variable for the model, it is worth stressing that it is not the physical molecular *excess* of the cluster, which is determined by the nucleation theorem [16].

Equation (5) provides the Gibbs free energy of formation of an EMLD-DNT cluster of N molecules for an arbitrary value of chemical potential μ or saturation ratio. However, for nucleation the most important quantity is the nucleation barrier, i.e., the free energy of formation of the *nucleus*. Imposing $\partial\Delta G/\partial N|_{V_m,T} = 0$ on Eq. (5), it is easy to show that by choosing $\Delta\mu_0$ and p in Eq. (5), equal to the chemical potential difference $\Delta\mu_0^*$ and the pressure P of the N, V_m, T system, each value of N then becomes the size N^* of a critical nucleus (corresponding to different values of supersaturation), and Eq. (5) gives the height of the nucleation barrier in both the constant pressure and constant μ systems, namely,

$$\Delta G^* = \Delta\Omega^* = \Delta F(N^*, V_m) - V_m(p_0 - P) + N^* \Delta\mu_0^*, \qquad (6)$$

where $\Delta F(N^*, V_m)$ is given by Eq. (4), P is given by Eq. (3), and, for an ideal vapor, $\Delta\mu_0^* = k_B T ln p_0/P$. Equation (6) gives the work of formation of the nucleus, rendered physically significant through the use of the physically nonarbitrary cluster volume. The results for LJ argon at $T = 85$ K are plotted in Fig. 2 and compared with $\Delta G^*_{\mathrm{CNT}} = 16\pi v_l^2 \sigma^3 / 3(k_B T \ln S)^2$, the prediction of CNT under the same conditions (where $S = P/p_{eq}$ is the saturation ratio).

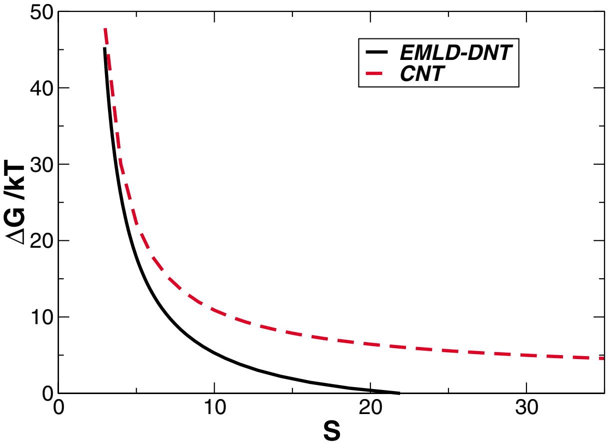

FIG. 2 (color online). Free energy of formation of the critical cluster as a function of the saturation ratio for argon at $T = 85$ K using the EMLD-DNT model Eq. (6) (solid line) and CNT (dashed line).

The most impressive feature in Fig. 2, and therefore of the new model, is the appearance of the signature of the spinodal, i.e., of the vanishing of the nucleation barrier at a sufficiently high saturation ratio. In contrast, CNT predicts a finite value of the nucleation barrier for all values of supersaturation. The vanishing of the barrier coincides with the fact mentioned earlier that, for very small values of N, the P-V isotherm has no minimum (see Fig. 1). This new feature originates in the inclusion of both translation and fluctuation in the theory. Without both ingredients, Eqs. (5) and (6) would reproduce the standard CNT result.

Figure 3 shows the results of a recent MC simulation, by ten Wolde and Frenkel [7], of the nucleation barrier in a LJ system. These authors worked in the N, P, T ensemble and simulated a truncated and shifted LJ fluid ($R_c = 2.5\sigma_{LJ}$) at reduced temperature, $T = 0.741$. Under

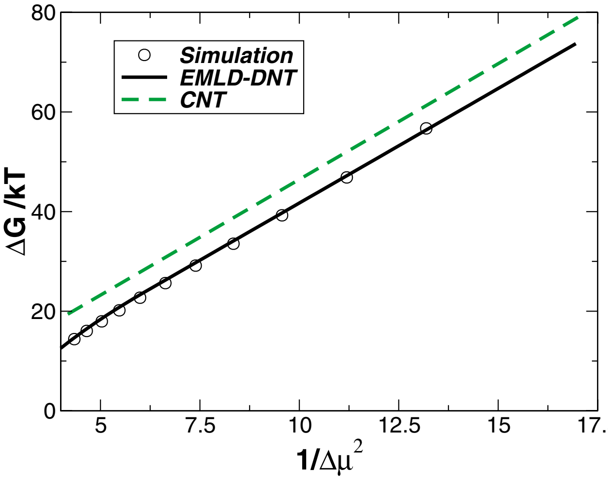

FIG. 3 (color online). Free energy of formation of the critical cluster as a function of $1/\Delta\mu^2$ for a truncated and shifted LJ fluid ($R_c = 2.5$) at reduced temperature $T = 0.741$ using the EMLD-DNT model Eq. (6) (with the LJ equation of state) (solid line) and CNT (dashed line). The circles are the data from the simulation of Ref. [7].

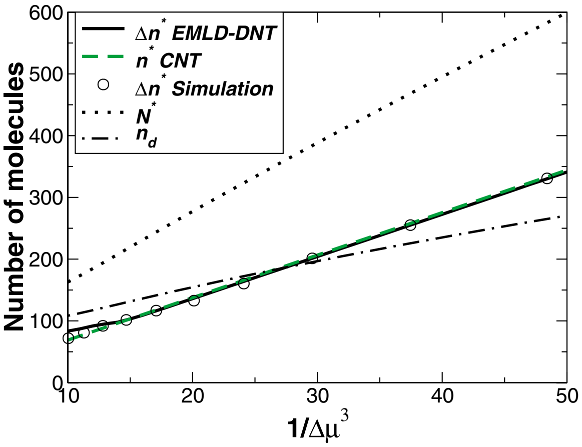

FIG. 4 (color online). Number of molecules in the critical cluster Δn^* as a function of $1/\Delta\mu^3$, for a LJ fluid at $T = 0.741$, as predicted by the EMLD-DNT (solid line) and the CNT (dashed line), compared to the simulation results of Ref. [7] (open circles). The total number of molecules N^* confined in the volume V_m in the EMLD-DNT cluster and n_d (see the text) are also plotted.

these conditions, the pressure of the supersaturated LJ vapor differs significantly from the behavior of an ideal gas. To account for this, we used in our model, instead of ideal gas values, the values of pressure and chemical potential obtained from the LJ equation of state [17], properly accounting for the truncation and shift of the potential at $R_c = 2.5\sigma_{\text{LJ}}$, in the manner of reference [18]. The agreement between the new model and the simulation is remarkable, especially for nucleation where severe discrepancies between theory and experiment/simulation are common.

Recently, McGraw and Laaksonen [5] proposed a set of scaling relations for nucleation that seem to be obeyed by most simulations and experimental data. These relations predict a constant offset between the actual nucleation barrier and that of the CNT. Figure 3 plots the value of the barrier as a function of $1/\Delta\mu^2$ for the new model, the simulations of Ref. [7] and CNT. The slopes are the same, and the values differ only by a constant offset, showing that the new model also satisfies these scaling relations.

Finally, the molecular excess Δn associated with a cluster is rigorously defined, in terms of the nucleation theorem [16], by $\partial\Delta G/\partial\Delta\mu|_{V,T} = -\Delta n$. Figure 4 plots the molecular excess Δn^* for the critical nucleus obtained from the simulations of Ref. [7], and that predicted by the EMLD-DNT model, and by CNT as a function of $1/\Delta\mu^3$, for a LJ fluid at $T = 0.741$. The agreement among the three approaches is excellent, confirming the accuracy of the EMLD-DNT model and supporting the scaling relations [5]. Also, the value of N^* of the corresponding (N^*, V_m, T) cluster is plotted in Fig. 4 for comparison. From this figure it is clear that the number of molecules in the container is in general not the molecular excess of the cluster. This shows that the EMLD-DNT cluster involved in nucleation is a diffuse physical entity still containing a significant number of vaporlike molecules.

In summary, we have presented a new phenomenological model for nucleation (EMLD-DNT) that shares the ingredients and simplicity of CNT, but which, by properly including translation and fluctuations and employing a nonarbitrary cluster volume defined by kinetics (DNT), is able to reproduce the spinodal. We have shown that the new cluster model is both thermodynamically and kinetically consistent and that, for LJ fluids, its predictions agree remarkably well with both simulations and scaling relations. The simplicity and consistency of the new model offer the promise of providing simple yet accurate predictions of nucleation rates for more complicated substances. The revised predictions for nucleation rates, provided by the model, may have important impacts in a broad diversity of fields, especially in the material and atmospheric sciences.

This work has been supported by the National Science Foundation under NSF Grant No. CHE-03013563. We thank P. R. ten Wolde for sending us his simulation data.

[1] C. L. Weakliem and H. Reiss, J. Chem. Phys. **99**, 5374 (1993).
[2] M. E. Fisher, Rep. Prog. Phys. **30**, 615 (1967).
[3] A. Dillmann and G. E. A. Meier, J. Chem. Phys. **94**, 3872 (1991); V. I. Kalikmanov and M. E. H van Dongen, Phys. Rev. E **47**, 3532 (1993).
[4] D.W. Oxtoby and R. Evans, J. Chem. Phys. **89**, 7521 (1988).
[5] R. McGraw and A. Laaksonen, Phys. Rev. Lett. **76**, 2754 (1996).
[6] G. K. Schenter, S. M. Kathmann, and B. C. Garrett, Phys. Rev. Lett. **82**, 3484 (1999).
[7] P. R. ten Wolde and D. Frenkel, J. Chem. Phys. **109**, 9901 (1998).
[8] S. Auer and D. Frenkel, Nature (London) **409**, 1020 (2001).
[9] D. Reguera *et al.*, J. Chem. Phys. **118**, 340 (2003).
[10] Translational entropy of mixing is not included.
[11] H. Reiss and D. Reguera, J. Phys. Chem. B **108**, 6555 (2004).
[12] J. K. Lee, J. A. Barker, and F. F. Abraham, J. Chem. Phys. **58**, 3166 (1973); **60**, 246 (1974).
[13] V. Talanquer and D.W. Oxtoby, J. Chem. Phys. **100**, 5190 (1994).
[14] G. K. Schenter, S. M. Kathmann, and B. C. Garret, J. Chem. Phys. **110**, 7951 (1999).
[15] D. J. Lee, M. M. Telo da Gama, and K. E. Gubbins, J. Chem. Phys. **85**, 490 (1986).
[16] R. K. Bowles *et al.*, J. Chem. Phys. **115**, 1853 (2001).
[17] J. K. Johnson, J. A. Zollweg, and K. E. Gubbins, Mol. Phys. **78**, 591 (1993).
[18] B. Smit, J. Chem. Phys. **96**, 8639 (1992).