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Gas-liquid nucleation in two-dimensional fluids

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(Received 5 June 1995; accepted 26 October 1995)

A nonclassical theory of nucleation, based on the density-functional (DF) approach, is developed for the gas-liquid transitions of two-dimensional (2D) Lennard-Jones (LJ) fluids. The methods of Weeks-Chandler-Andersen perturbation theory are used to approximate the LJ potential with a temperature-dependent hard-disk diameter plus an attractive tail. The resulting free energy functional is then used to calculate the free energy barrier to nucleation. We find that the curvature of the 2D nucleus is not important to the rate of nucleation (in contrast to the 3D counterpart). The effect of curvature is readily inferred from the ratio of nucleation rate from classical Becker-Döring theory to that from DF theory. Our calculation suggests that classical nucleation theory actually works reasonably well for 2D LJ fluids in predicting the temperature-dependence of the nucleation rate (whereas for 3D LJ fluids it fails badly). © 1996 American Institute of Physics. [S0021-9606(96)50705-5]

I. INTRODUCTION

Our understanding of the nucleation of liquids from the vapor phase has long been dominated by the simple classical nucleation theory developed by Becker and Döring¹ (based on earlier work by Volmer and Farkas) and extended by Zeldovich.^{2,3} This theory invokes the capillarity approximation whereunder the free energy of a critical nucleus is calculated by treating it as a macroscopic droplet with bulk and surface free energies relative to the background vapor; the surface free energy is estimated from the surface tension of an equilibrium liquid-vapor interface. The classical theory was not seriously challenged until the eighties. However, recent experiments⁴⁻¹³ demonstrate that the classical theory fails badly in predicting the dependence of the nucleation rate on temperature. Deviations of several orders of magnitude are typical. A better theory of nucleation is called for.

Recently we have developed a nonclassical theory of nucleation,¹⁴ based upon the density-functional approach. In this theory the capillarity approximation is avoided. We showed how the density functional approach can be used to calculate the free energy of a droplet plus vapor. Effects such as the curvature dependence of the surface tension appear naturally in this theory, rather than being added as ad hoc assumptions. Molecular level detail can be incorporated if an accurate enough functional is employed. Moreover, this nonclassical theory goes over naturally to the classical theory in the limit of large droplets, that is, as the equilibrium vapor pressure curve is approached. When we applied the theory to a 3D Lennard-Jones gas-liquid transition, we found our results to be consistent with those from recent experiments.

In this work the focus will be the 2D gas-liquid transition. Not only are 2D fluids of theoretical importance, but they also have practical relevance. Although strict 2D fluids do not exist in the real world, many realistic systems exhibit 2D fluid characteristics. For example, physisorption of gases on solid surfaces,¹⁵ surfactants monolayers adsorbed on an air/water interface,¹⁶ and thinning by evaporation of com-

pletely wetted water films on clean mica surfaces.¹⁷

This paper is organized as follows. In Sec. II we outline both classical nucleation theory and our nonclassical approach. In Sec. III we show our calculated results and include comparison between the classical and nonclassical theories. The results are discussed and conclusions are given in Sec. IV.

II. NUCLEATION THEORY

The rate of homogeneous nucleation J is generally written as

$$J = J_0 e^{-\Delta\Omega^*/k_B T}, \quad (1)$$

where J_0 is the preexponential factor, T is the temperature, and $\Delta\Omega^*$ is the free energy of formation for the critical nucleus. The temperature dependence of the nucleation rate is mainly controlled by the exponential, while the preexponential factor is a slow function of temperature.¹⁸

A. The classical theory

In the Becker-Döring (classical) theory of gas-to-liquid nucleation,¹ the capillarity approximation is made such that $\Delta\Omega$ is taken as a sum of bulk and surface free energy contributions. In 2D the droplet is assumed to be circular and the interface between the gas and liquid is assumed to be a line. Thus, $\Delta\Omega$ can be expressed as

$$\Delta\Omega = -\pi r^2 \Delta p + 2\pi r \gamma, \quad (2)$$

where r and γ are the radius and line tension of a droplet, and $\Delta p = p_l - p_v$ is the pressure difference between the droplet and the vapor.

A nucleus (e.g., liquid droplet) can grow only if there is a large enough fluctuation of $\Delta\Omega$ to overcome the free energy barrier $\Delta\Omega^*$. The latter can be determined from the extremal condition,

$$\left. \frac{\partial \Delta \Omega}{\partial r} \right|_{T,p} = 0, \quad (3)$$

from which one can derive the radius of the critical nucleus

$$r^* = \frac{\gamma}{\Delta p}. \quad (4)$$

Moreover, if the liquid is assumed to be incompressible and the gas to be ideal, the pressure difference Δp can be written in terms of $\Delta \mu = \mu - \mu_{\text{sat}}$ or of the supersaturation $S = p_v/p_{\text{sat}}$, where μ_{sat} and p_{sat} are the chemical potential and pressure at gas-liquid equilibrium,

$$\Delta p = \rho_l \Delta \mu = \rho_l k_B T \ln S. \quad (5)$$

Combining Eqs. (2), (4), and (5) results in the free energy formation for a critical nucleus,

$$\Delta \Omega_{\text{CL}}^* = \frac{\pi \gamma^2}{\rho_l \Delta \mu} = \frac{\pi \gamma^2}{\rho_l k_B T \ln S}. \quad (6)$$

The classical rate of nucleation per unit volume is then given by

$$J_{\text{CL}} = J_0 e^{-\Delta \Omega_{\text{CL}}^*/k_B T}. \quad (7)$$

The pre-exponential factor J_0 in Eq. (7) can be calculated via (see Appendix)

$$J_0 = \frac{n(1)^2}{S} \sqrt{\frac{\Delta \mu a_1}{2 \pi m}}, \quad (8)$$

where m is the atomic mass, $n(1)$ is the number density of monomer nuclei, and a_1 is the area per particle in the bulk liquid. Without losing generality we use elemental Ar as a typical LJ system¹⁹ in the present study.

B. The density-functional approach

In density-functional theory a knowledge of the interatomic potential for the systems is required.²⁰ Here, we deal with fluids with a pair-additive interatomic potential $\phi(r)$ and assume $\phi(r)$ that can be divided into a large repulsive part $\phi^{(1)}(r)$ and a small (perturbative) attractive part $\phi^{(2)}(r)$,

$$\phi(r) = \phi^{(1)}(r) + \phi^{(2)}(r). \quad (9)$$

In this case, the intrinsic Helmholtz free energy is a functional of the system density $\rho(\mathbf{r})$ and can be expressed exactly²⁰ as

$$F[\rho] = F_1[\rho] + \frac{1}{2} \int_0^1 d\xi \int \int d\mathbf{r} d\mathbf{r}' \phi^{(2)}(|\mathbf{r} - \mathbf{r}'|) \times \rho^{(2)}(\mathbf{r}, \mathbf{r}'; \phi_\xi^{(2)}). \quad (10)$$

Here F_1 is the Helmholtz free energy of the reference system [particles that interact via potential $\phi^{(1)}(r)$], ξ is the charging parameter ($0 \leq \xi \leq 1$), and $\rho^{(2)}$ is the pair distribution function, which is related to the radial distribution function $g^{(2)}$ through

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}) \rho(\mathbf{r}') g^{(2)}(\mathbf{r}, \mathbf{r}'). \quad (11)$$

Since the pair distribution function $\rho^{(2)}$ is generally unknown for inhomogeneous systems, we have made a random phase approximation (RPA) (Ref. 20) to $\rho^{(2)}$, that is,

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}'; \phi_\xi^{(2)}) \approx \rho(\mathbf{r}) \rho(\mathbf{r}'). \quad (12)$$

This is based on the fact that the RPA generally works quite well for weakly inhomogeneous fluids, e.g., for gas-liquid interfaces.^{20,21}

The reference system here has been taken to be hard disks. The free energy of hard disks is determined via

$$F_1[\rho] \approx \int d\mathbf{r} f_h[\rho(\mathbf{r})], \quad (13)$$

where f_h denotes the Helmholtz free energy density of a hard-disk fluid at density ρ . Note that in Eq. (13) a local density approximation (LDA) is used based on the fact that the LDA has been well examined for weakly inhomogeneous fluids.^{20,21}

The grand potential of the system is related to the Helmholtz free energy through

$$\Omega[\rho] = F[\rho] - \mu \int d\mathbf{r} \rho(\mathbf{r}), \quad (14)$$

where μ is the chemical potential. At equilibrium the density profile of a liquid-vapor surface can be determined from the variational condition

$$\delta \Omega / \delta \rho(\mathbf{r}) = 0. \quad (15)$$

Substituting Eqs. (10)–(14) into Eq. (15) results in

$$\mu = \mu_h[\rho(\mathbf{r})] + \int d\mathbf{r}' \phi^{(2)}(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}'), \quad (16)$$

where μ_h is the local chemical potential of the hard-disk fluid.

In the homogeneous limit ($\rho = \text{constant}$), Eqs. (10), (12), and (13) leads to the Helmholtz free energy density

$$f(\rho) = f_h(\rho) - \frac{1}{2} \alpha \rho^2, \quad (17)$$

where $\alpha = -\int d\mathbf{r}' \phi^{(2)}(r')$. From Eq. (17) one can obtain bulk properties of the fluid such as the liquid-gas coexistence densities and the critical point.

III. RESULTS FOR A 2D LENNARD-JONES FLUID

The Lennard-Jones (12-6) potential has the form

$$\phi_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (18)$$

where ϵ and σ are characteristic energy and size parameters (for Ar, $\epsilon_{\text{Ar}}/k_B = 119.8$ K, $\sigma_{\text{Ar}} = 3.40$ Å). In the past two decades extensive work has been done toward understanding properties of 2D LJ fluids, for example, the equation of state,^{22–28} liquid-vapor coexistence densities,^{29–32} phase diagram,²³ critical phenomena,^{32,33} and liquid-vapor interface.^{32,34,35} Some simulation results for 2D LJ fluids are listed in the caption of Fig. 1.

FIG. 1. Liquid-gas coexistence phase diagram. The long-dashed curve is obtained from the present theory while the diamond dots are from the Gibbs Monte Carlo simulation (Ref. 31). The scaled critical and triple point temperatures [from molecular dynamics simulation (Ref. 23)] are 0.533 and 0.415, respectively.

We have used the Weeks, Chandler, and Anderson (WCA) perturbation scheme to divide the LJ potential into a repulsive part,³⁶

$$\phi_1^{\text{WCA}}(r) = \begin{cases} \phi_{\text{LJ}}(r) + \epsilon & r < r_{\min} \\ 0 & r \geq r_{\min} \end{cases}$$

and a weak attractive part

$$\phi_2^{\text{WCA}}(r) = \begin{cases} -\epsilon & r < r_{\min} \\ \phi_{\text{LJ}}(r) & r \geq r_{\min} \end{cases}.$$

Here $r_{\min} = 2^{1/6}\sigma$ is the distance at which $\phi_{\text{LJ}}(r)$ exhibits its minimum. We then describe the repulsive reference system [with interatomic potential $\phi_1^{\text{WCA}}(r)$] by using a fluid of hard disks with a temperature-dependent diameter $d(T)$. For simplicity of calculation, we have followed Lu, Evans, and Telo da Gama²¹ to calculate $d(T)$ via

$$d(T) = \frac{a_1 T + 1}{a_2 T + a_3} \sigma, \quad (19)$$

where $a_1 = 0.56165 k_B/\epsilon$, $a_2 = 0.60899 k_B/\epsilon$, and $a_3 = 0.92868$ are obtained by fitting $d(T)$ to the hard disk diameter,

$$d^{\text{BH}}(T) = \int_0^\infty [1 - e^{-\phi_1^{\text{WCA}}(r)/k_B T}] dr, \quad (20)$$

of Barker-Henderson.³⁷

A. Bulk properties and line tensions

As mentioned in Sec. II, one can calculate the bulk properties of a 2D LJ fluid by using Eq. (17); for example, one can derive the pressure and chemical potential of a fluid,

$$p = p_h - \frac{1}{2} \alpha \rho^2, \quad (21)$$

$$\mu = \mu_h - \alpha \rho. \quad (22)$$

The hard-disk pressure p_h is determined from the scaled-particle equation of state³⁸

$$p_h = \frac{\rho k_B T}{(1 - \eta)^2}, \quad (23)$$

where $\eta = (\pi/4)\rho d^2$ is the packing fraction of hard disks, whereas the hard-disk chemical potential μ_h is determined via

$$\frac{\partial p_h}{\partial \rho} = \rho \frac{\partial \mu_h}{\partial \rho}. \quad (24)$$

At a given temperature T , the coexisting gas-liquid densities of a 2D LJ fluid are obtained by solving equations

$$\mu_l(\rho_l, T) = \mu_v(\rho_v, T), \quad (25)$$

$$p_l(\rho_l, T) = p_v(\rho_v, T). \quad (26)$$

The calculated coexisting density curve is shown in Fig. 1, together with the coexisting densities from the Gibbs Monte Carlo simulation for 2D LJ fluids.³¹ The scaled critical temperature is 0.533, which is determined by molecular dynamics simulation.²³ The agreement between the present density-functional theory and simulations is only fair. This is caused in part by the use of simple $d^{\text{BH}}(T)$ [see Eq. (20)] instead of the more complex $d^{\text{WCA}}(T)$,³⁶ and in part by the mean-field assumption underlying the present theory. In this work, however, we do not attempt to exactly reproduce the simulation results, but only to explore the curvature effect of nuclei on the nucleation rate in 2D. This curvature effect can be inferred by comparing the rates from the classical theory with those of the density-functional theory. In order to have a meaningful comparison the surface tensions needed in the classical theory are calculated from the present theory; thus this analysis of the curvature effect on nucleation is self-consistent. In fact a similar analysis was done for 3D nucleation¹⁴ and results were later confirmed by computer simulation.⁴⁴

The density profile of the gas-liquid interface at equilibrium $\rho(\mathbf{r}) = \rho(y)$ can be calculated by solving the integral equation

$$\mu_h(\rho(y)) = \mu - \int d\mathbf{r} \phi_2^{\text{WCA}}(|\mathbf{r} - \mathbf{r}'|) \rho(y') \quad (27)$$

by iteration.¹⁴ Solution of Eq. (27) is substituted into Eq. (14) to compute the gas-liquid line tension γ through the relation $\gamma = (\Omega + pA)/L$, where A is the area and L the length of the interface. The results of density profiles and line tensions at temperatures between the scaled triple and critical points are displayed in Figs. 2(a) and 2(b). To our knowledge there have been no computer simulations of the line tensions for the *full* LJ fluids. We are aware of only one molecular dynamics simulation of line tension³⁴ ($\gamma^* \gamma \sigma / \epsilon = 0.05$ at $T^* = k_B T \epsilon = 0.427$) for a *truncated* LJ fluid. This line tension is

FIG. 2. (a) The density profiles of the equilibrium gas-liquid interface at the scaled temperatures $T^*=0.42$ (solid curve), 0.44 (long dashed curve), 0.46 (dashed curve), 0.48 (dotted curve), and 0.5 (dotted-dashed curve). (b) The equilibrium gas-liquid line tensions vs temperature.

much smaller than those from this calculation. This is expected since potential truncation always leads to a smaller interfacial tension.

B. Gas-liquid nucleation

In density-functional theory, the density profile $\rho(r)$ of a nucleus is no longer taken as a sharp step profile (which is assumed in the classical theory) but is determined from the integral equation

$$\mu(\rho(r)) = \mu - \int d\mathbf{r}' \rho(r') \phi_2^{\text{WCA}}(|\mathbf{r} - \mathbf{r}'|). \quad (28)$$

As was discussed in Ref. 14, the solution of Eq. (28) is unstable because the critical nucleus is physically unstable. In the earlier work¹⁴ we developed a special method to determine the density profile of a critical nucleus. The same method is used in this work. In essence one starts by guessing a density profile (usually a step profile with a jump at R_i) and then solves Eq. (28) by iteration. At each iteration $\Delta\Omega$ is determined. For a large R_i , the nucleus is growing with increasing number of iterations, while for a small R_i , the nucleus is shrinking until it becomes a monomer. In both cases $\Delta\Omega$ always decreases with increasing number of iterations. If a particular guess R_i^* is taken, the $\Delta\Omega$ would remain to be a constant over many iterations (typically hundreds). This constant is the free energy of formation $\Delta\Omega_{\text{DF}}^*$ for a critical nucleus. With $\Delta\Omega_{\text{DF}}^*$, one can compute the rate of nucleation via

$$J_{\text{DF}} = J_0 e^{-\Delta\Omega_{\text{DF}}^*/k_B T}. \quad (29)$$

Since J_0 is a slow function of temperature one can use the same pre-exponential factor J_0 as in the classical nucleation theory. The latter approximation has been shown to be quite good, at least for LJ fluids.¹⁸

We have calculated the gas-to-liquid rates of nucleation at several temperatures between the scaled triple point ($T^*=0.42$) and critical point ($T^*=0.5$). For each temperature, the chemical potential change $\Delta\mu$ is determined by fixing $J_{\text{CL}} = 1 \text{ cm}^{-2} \text{ s}^{-1}$. With the same $\Delta\mu$ and temperature T , we evaluate J_{DF} from Eq. (29) and monitored the temperature dependence of the ratio $J_{\text{CL}}/J_{\text{DF}}$. Results are shown in Fig. 3, where J_{CL} is fixed to be $1 \text{ cm}^{-2} \text{ s}^{-1}$. We find the classical theory overestimates the rate by a factor of 2 at $T^*=0.42$ and 10 at $T^*=0.5$, respectively. Comparing this result with the earlier one for 3D LJ fluids,¹⁴ the curve in Fig. 3 is, in fact, quite “flat.” For 3D LJ fluids, we found at temperatures near the triple point the classical theory under-

FIG. 3. Ratios of the gas-to-liquid nucleation rate of the classical theory to the density-functional theory vs temperature.

FIG. 4. The same as in Fig. 3, but for the liquid-to-gas nucleation.

estimates the rate by five orders of magnitude, while at a temperatures not far from the critical point it could overestimate the rate by several orders of magnitude. This indicates a much stronger curvature effect in 3D.

We have also calculated the liquid-to-gas rates of nucleation (cavitation) for the same temperatures. Here the chemical potential change $\Delta\mu$ is negative. The density profile is inverted with a gaslike density at the center of the nucleus (for a bubble) and a liquidlike density outside. Results for the temperature dependence of J_{CL}/J_{DF} are shown in Fig. 4. Again we find the rate ratio changes only by a factor of 5 from near the triple point to near the critical point whereas in the case of 3D (Ref. 14) a typical rate ratio is ten orders of magnitude. This indicates that the curvature effect is quite small for 2D cavitation.

IV. DISCUSSION AND CONCLUSION

In this work we have developed a nonclassical theory of nucleation (based on the density-functional approach) for 2D LJ gas-liquid transitions. We use methods of hard-disk perturbation theory to approximate the LJ potential with a temperature-dependent hard-disk diameter plus an attractive tail. We then use density-functional theory to calculate the free energy barrier to nucleation, retaining the classical pre-exponential factor. Comparison between the rates from the classical and nonclassical theory has been made in a self-contained and self-consistent fashion.

Interestingly, we find the Becker-Döring classical theory of nucleation is quite successful for both gas-to-liquid and liquid-to-gas transitions at 2D, which is in sharp contrast to the 3D LJ gas-liquid transitions for which the classical theory fails badly in the prediction of the temperature-dependence of nucleation rates. This large difference between 2D and 3D is attributed to the effect of the curvature of the nuclei on the rates of nucleation. For temperatures ranging from the triple point to the critical point we find that

typical critical nuclei have more atoms in 2D than in 3D even though the atoms are confined to a plane in 2D. If we imagine that a 3D critical nucleus is compressed into a 2D one, the latter would have a much larger radius and thus much smaller curvature. Therefore, the curvature effect at 2D on nucleation rate is much smaller and the capillarity approximation works better.

In the future we will examine the above conclusion by computer simulations. The difficulty with the latter approach, however, is in identifying what atoms are actually in a droplet at any given time, and in studying by equilibrium techniques a state that is inherently unstable; a true critical droplet tends either to grow or to disappear with time. A few empirical criterions have been proposed for identifying droplets in a simulation.³⁹⁻⁴² Recently, Reiss and co-workers^{43,44} took an important step in showing how a constraint on the droplet volume can explicitly be put into the simulation. This allows accurate determination of droplet free energies.

To date there are no experimental results on line tensions for two-dimensional fluids. Since the rates of nucleation are easier to measure,¹⁷ one can use the Becker-Döring theory or other improved classical theory⁴⁵ to infer the line tensions of 2D fluids. Line tensions measured in this way should be reasonably reliable, provided that, as shown for LJ fluids in this work, the classical theory works well in 2D.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation and by the Research Council of the University of Nebraska-Lincoln. Acknowledgment is also made to the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this work, under Grant No. 29062-AC9.

APPENDIX: DERIVATION OF EQS. (6)–(8) FOR 2D GAS-LIQUID TRANSITIONS

We start with the general equation for the steady-state rate of nucleation⁴⁶

$$J = \frac{n(1)}{\sum_{i=1}^{\infty} \frac{1}{\beta(i)f(i)}}, \quad (30)$$

where $\beta(i)$ is the forward rate at which a nucleus of size i gains particles and $f(i)$ is defined by

$$f(i) = \prod_{j=1}^{i-1} \frac{\beta(j)}{\gamma(j+1)}, \quad (31)$$

and where $\gamma(i+1)$ is the backward rate at which a nucleus of size $i+1$ loses particles.

Considering gas-to-liquid transitions, Oxtoby has shown that $f(i)$ can be further written as⁴⁶

$$f(i) = S^{i-1} \prod_{j=1}^{i-1} \frac{\beta_e(j)}{\gamma_e(j+1)} = S^{i-1} e^{-\Delta G_i/k_B T}, \quad (32)$$

where the subscript e denotes quantity at equilibrium states, S is the supersaturation, and ΔG_i is the Gibbs free energy change for the formation of a nucleus of size i .

Under the capillarity approximation the free energy change can be written as

$$\Delta G_i = \gamma L(i), \quad (33)$$

where γ is the line tension and $L(i)$ is the interfacial line length of a nucleus of size i . If the nucleus is taken to be circular and to have the same area per particle a_1 as the bulk liquid, then

$$L(i) = 2(\pi i a_1)^{1/2}. \quad (34)$$

Combining Eqs. (30)–(34) one can obtain

$$J = \frac{n(1)}{\sum_{i=1}^{\infty} \beta_e(i) S^i e^{-\theta i^{1/2}}}, \quad (35)$$

where the dimensionless line tension θ is defined by

$$\theta = 2(\pi a_1)^{1/2} \gamma / k_B T. \quad (36)$$

By assuming (1) that the critical nucleus i^* is large enough so that the sum in Eq. (35) can be replaced by an integral, and (2) that β_e varies slowly with i so that $\beta_e(i) \approx \beta_e(i^*)$, one can use the usual steepest descent method to evaluate the sum in Eq. (35). The result is

$$J = n(1) \beta_e(i^*) (\theta / 8\pi)^{1/2} (i^*)^{-3/4} e^{-\theta^{2/4} \ln S}, \quad (37)$$

where

$$i^* = \left(\frac{\theta}{2 \ln S} \right)^2. \quad (38)$$

If the kinetic rate of a 2D ideal gas is used to estimate the forward rate $\beta_e(i)$, that is,

$$\beta_e(i) = (k_B T / 2\pi m)^{1/2} [n(1)/S] L(i), \quad (39)$$

where m is the mass of particles, then inserting Eqs. (38) and (39) into Eq. (37) will give rise to Eqs. (6)–(8).

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