

Droplet stability in a finite system: Consideration of the solid–vapor interface

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The thermodynamic stability of a single, one-component droplet in a finite system with adsorbing walls is investigated. The conditions under which a stable equilibrium state of the droplet is predicted to exist depend critically on the adsorption isotherm of the confining walls. If the amount absorbed remains finite when the pressure in the vapor is greater than the fluid's saturation pressure, then a stable equilibrium state is possible. When the model is extended to a system of multiple droplets, the stable equilibrium state is predicted to always correspond to a single droplet. © 2003 American Institute of Physics. [DOI: 10.1063/1.1554752]

I. INTRODUCTION AND BACKGROUND

A. Kelvin relation

The equilibrium conditions at an isothermal, spherical, one component liquid–vapor interface can be predicted by the Kelvin relation¹

$$P^V = P_\infty \exp\left[\frac{v_\infty^L(P^V - P_\infty + 2\gamma^{LV}/R)}{kT}\right], \quad (1)$$

where P is pressure, γ is surface tension, v is specific volume, R is the radius of curvature, k is the Boltzmann constant, and T is temperature. Superscripts L , V and LV refer to the liquid phase, vapor phase, and the liquid–vapor interface, and the subscript ∞ refers to saturation conditions. The derivation of the Kelvin relation assumes mechanical and thermal equilibrium at the interface, and equality of the chemical potentials of each phase. The saturation properties are evaluated at the system temperature. When the liquid is on the concave side of the interface, such as for a droplet, R is greater than zero. In this case, the Kelvin relation predicts that the pressure in the vapor will be always higher than the saturation pressure (i.e., at equilibrium, the vapor is supersaturated).

There have been many attempts to experimentally verify the Kelvin relation, but none have gotten agreement to within less than several percent.^{2,3} Some investigations have considered nonequilibrium processes, while the Kelvin relation applies only to an equilibrium state. One of the major difficulties is that the predicted difference between P^V and P_∞ is only significant for very small radii of curvature. For example, for water at 20 °C, a droplet radius smaller than 2.6 μm is necessary to get a difference between P^V and P_∞ of at least 1 Pa (for this and all subsequent calculations, thermophysical properties are taken from Ref. 4). For meaningful

droplet sizes ($R \geq 0.5$ nm), the pressure difference ($P^V - P_\infty$) on the right side of Eq. (1) is negligible compared to the pressure difference ($2\gamma^{LV}/R$), allowing the Kelvin relation to be recast as

$$P^V = P_\infty \exp\left(\frac{2\gamma^{LV}v_\infty^L}{RkT}\right), \quad (2)$$

a form that is often used. The assumption required to use this approximation has been noted.^{1,2}

B. Droplet stability

The stability of a single, one-component droplet was first investigated by Gibbs,⁵ who showed that such a droplet in an isothermal, unbounded expanse of its own vapor at a uniform pressure higher than the saturation pressure corresponding to the system temperature will have one equilibrium size, and that this state is unstable. The Kelvin relation can predict its value. The equilibrium state is unstable because mass transfer to or from the droplet has no effect on the pressure in the vapor. The unstable equilibrium state plays an important role in homogeneous nucleation,⁶ and has been observed in molecular simulations.^{7,8}

A second equilibrium state, which is stable, is predicted to exist in a one component system of finite size and mass.^{9,10} The equilibrium state is stable because mass transfer to or from the droplet has an effect on the system pressure. The pressure in the vapor when the droplet is in the stable equilibrium state is always above the saturation pressure, consistent with the Kelvin relation. In the work of Refs. 9 and 10, the effect of the solid–vapor interface was ignored. Rao and Berne⁹ support the prediction using molecular simulations, where the use of periodic boundary conditions eliminates the need to consider a solid–vapor interface. The work of Vogelsberger¹⁰ has been used to investigate droplet nucleation.^{11–13} There have been no experimental investigations of the predictions made in Refs. 9 and 10.

The addition of a second, nonvolatile component to the droplet can also bring about a stable equilibrium state.^{3,14,15} This is true for both the finite system and that investigated by

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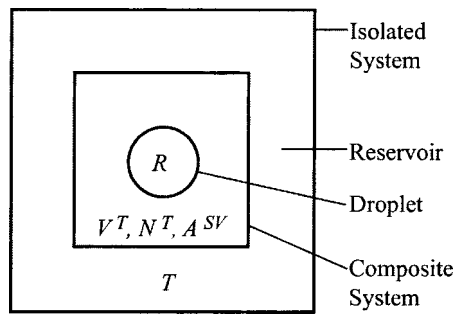


FIG. 1. System of interest. The isolated system is composed of a composite system surrounded by a reservoir. The composite system has fixed volume, mass and surface area and contains a spherical, one-component droplet in its own vapor.

Gibbs. In this case, the stability is a result of the lowering of the liquid chemical potential by the solute, generating equilibrium conditions at a pressure lower than the saturation value. The experimental results of La Mer and Gruen¹⁶ have been interpreted¹ as an example of this stable state and a verification of the Kelvin relation for a two-component system.

In recent reports, claims have been made to the effect that “the Kelvin equilibrium for a single component drop is always unstable.”³ We find that for a droplet in a finite system, a critical issue is the nature of the equilibrium adsorption isotherm that describes the adsorption on the confining walls. As the pressure in the vapor phase approaches a critical value, denoted as P_A^V , the amount of adsorption is predicted to asymptotically approach infinity. This pressure may be viewed as the pressure at which filmwise condensation occurs. The number and nature of the equilibrium states are predicted to depend on the value of P_A^V . The developed theory is extended to a system of multiple droplets.

II. THEORETICAL DEVELOPMENT

A. Description of system

The system of interest is shown in Fig. 1. It is composed of a composite system surrounded by a reservoir. The two parts make up an isolated system. The reservoir has a constant and uniform temperature T . The walls of the composite system are rigid, nonpermeable and diathermal. Thus, when the isolated system is at equilibrium, the composite system will have the same temperature as the reservoir. The composite system consists of a single, one-component spherical droplet in its own vapor. The droplet radius is R . The composite system has a volume V^T , a solid surface area A^{SV} , and contains N^T molecules. The superscript SV refers to the solid–vapor interface. Field effects are ignored. Based on the description of the composite system, it can be inferred that its independent variables are T , V^T , N^T , and A^{SV} . These are the independent variables of F , the Helmholtz potential.¹⁷ A minimum of F will correspond to a stable equilibrium state and a maximum will correspond to an unstable equilibrium state.

B. Determination of equilibrium conditions

For a bulk phase,

$$F = -PV + \mu N, \quad (3)$$

where μ is the chemical potential. For an interface,

$$F = \gamma A + \mu N. \quad (4)$$

For the system under consideration,

$$\begin{aligned} F &= F^V + F^L + F^{LV} + F^{SV} \\ &= -P^V V^V + \mu^V N^V - P^L V^L + \mu^L N^L + \gamma^{LV} A^{LV} \\ &\quad + \mu^{LV} N^{LV} + \gamma^{SV} A^{SV} + \mu^{SV} N^{SV}. \end{aligned} \quad (5)$$

The necessary condition for an equilibrium state is that the total differential of the Helmholtz potential is equal to zero.

For a system at constant and uniform temperature, the Gibbs–Duhem relation¹⁸ can be written for a bulk phase and an interface as

$$-VdP + Nd\mu = 0, \quad (6)$$

and

$$Ad\gamma + Nd\mu = 0, \quad (7)$$

respectively. The system constraints are

$$V^L + V^V = V^T, \quad N^V + N^L + N^{LV} + N^{SV} = N^T, \quad (8)$$

and a constant solid–vapor surface area. Setting dF to zero and applying the Gibbs–Duhem relation and the constraints gives the equilibrium conditions:

$$\mu^V = \mu^L = \mu^{LV} = \mu^{SV} \quad \text{and} \quad P^L - P^V = \frac{2\gamma^{LV}}{R}. \quad (9)$$

The first condition states that there is no net mass transfer between the four phases. The second condition is the Laplace equation. Thermal equilibrium has been assumed with the use of the Helmholtz potential. Solving the equilibrium conditions simultaneously will give an expression for the radius of an equilibrium droplet. This radius is called the critical radius, and is denoted by R_c .^{19–21} In Refs. 19–21, the critical radius is used to refer to the equilibrium size of a bubble in a liquid solution. Here, the same concept is applied to a droplet in its own vapor.

If the liquid phase is approximated as a slightly compressible liquid, and the vapor phase is approximated as an ideal gas, their chemical potentials can be expressed as¹⁸

$$\mu^L[T, P^L] = \mu^L[T, P_\infty(T)] + v_\infty^L(T)[P^L - P_\infty(T)], \quad (10)$$

and

$$\mu^V[T, P^V] = \mu^V[T, P_\infty(T)] + kT \ln \left[\frac{P^V}{P_\infty(T)} \right]. \quad (11)$$

With Eqs. (10) and (11), and noting that the chemical potentials of the liquid and vapor phases are equal at saturation conditions,¹⁸ the equivalence of the liquid and vapor phase chemical potentials in Eq. (9) can be simplified to give

$$R_c = \frac{2\gamma^{LV}}{\frac{kT}{v_\infty^L} \ln \left(\frac{P^V}{P_\infty} \right) + (P_\infty - P^V)}. \quad (12)$$

All fluid properties are assumed to be evaluated at T unless noted. Equation (12) can be rearranged to give the Kelvin relation, Eq. (1), with R equal to R_c .

It is desirable to have the expression for the critical radius in terms of the independent variables. By applying the system constraints, the assumption of an ideal vapor phase and by neglecting N^{LV} , the pressure in the vapor can be expressed as

$$P^V = \frac{\left(N^T - N^{SV} - \frac{4\pi R^3}{3u^L}\right)kT}{V^T - \frac{4\pi R^3}{3}}. \tag{13}$$

Equations (12) and (13) are two equations in four unknowns: R_c , R , N^{SV} , and P^V . It is important to distinguish between R_c and R . The critical radius, R_c , is a thermodynamic property of the system, and is only a function of its independent variables. It defines an equilibrium condition, and exists whether or not there is a droplet actually present in the system. The radius of an existing droplet, R , can take on any value as long as it satisfies the system constraints. At equilibrium, R_c must be equal to R , which reduces the problem to two equations in three unknowns. In order to close the two equations, a model of the solid–vapor interface is required.

The Brunauer-Emmett-Teller (BET) isotherm²² has historically been used to analyze a solid–vapor interface at equilibrium. It predicts the number of molecules, N^{SV} , that will adsorb on a smooth homogeneous solid surface at equilibrium as a function of the pressure in the vapor, P^V . By generalizing the derivation of the BET isotherm done by Hill,²³ the α isotherm is defined as²⁴

$$N^{SV} = \frac{MA^{SV}C\alpha \frac{P^V}{P_\infty}}{\left(1 - \alpha \frac{P^V}{P_\infty}\right)\left[1 + (C-1)\alpha \frac{P^V}{P_\infty}\right]}, \tag{14}$$

where M is the number of adsorption sites per unit area, and C and α are constants. The parameters M , C , and α are functions of temperature and must be determined experimentally. The model assumes that multilayer adsorption occurs, and that there is no interaction between stacks of adsorbed molecules. When $\alpha P^V/P_\infty$ is equal to unity, the number of adsorbed layers becomes infinite and filmwise condensation will occur. Thus, P_A^V is equal to P_∞/α . Keshavarz and Ward²⁴ have applied this isotherm to experimental results of water adsorbing on glass surfaces. The α isotherm is used in all the ensuing analysis. We note that the BET isotherm is recovered from Eq. (14) when α is equal to unity.

Equations (13) and (14) are two equations with the three unknowns N^{SV} , P^V , and R . They can be solved to give P^V and N^{SV} as functions of R . The critical radius can then be expressed as

$$R_c = R_c(T, V^T, N^T, A^{SV}, R).$$

With the requirement that R_c be equal to R in an equilibrium state, the equations have been closed. It is not possible to

solve the equations algebraically; a numerical solution is required. Before investigating the behavior of R_c , the Helmholtz potential will be formed.

C. Formation of the Helmholtz potential

The Helmholtz potential is given by Eq. (5). As it stands, there is no way of plotting F vs R . This problem can be resolved by introducing a reference condition F_0 , defined as the state where there is no droplet present in the system and the vapor is in equilibrium with the adsorbed phase. Thus,

$$F_0 = -P_0^V V^T + \mu^V[T, P_0^V]N_0^V + \gamma_0^{SV} A^{SV} + \mu^{SV}[T, \gamma_0^{SV}]N_0^{SV}, \tag{15}$$

where

$$P_0^V = \frac{(N^T - N_0^{SV})kT}{V^T}, \tag{16}$$

and N_0^{SV} and N_0^V are the number of molecules in the solid–vapor interface and the vapor phase in the reference state. N_0^{SV} can be found by solving Eqs. (13) and (14) with R set equal to zero. The solid–vapor surface tension in the reference state is γ_0^{SV} . By conservation of mass,

$$N_0^V + N_0^{SV} = N^T, \tag{17}$$

and as the two phases in the reference state are in equilibrium,

$$F_0 = -(N^T - N_0^{SV})kT + \mu^V[T, P_0^V]N^T + \gamma_0^{SV} A^{SV}. \tag{18}$$

As the vapor has been approximated as an ideal gas,

$$\mu^V[T, P_0^V] = \mu^V[T, P^V] + kT \ln\left(\frac{P_0^V}{P^V}\right). \tag{19}$$

By applying Eq. (8), subtracting F_0 from F gives

$$\begin{aligned} F - F_0 = & (\mu^L - \mu^V)N^L + (\mu^{LV} - \mu^V)N^{LV} \\ & + (\mu^{SV} - \mu^V)N^{SV} - (P^L - P^V)V^L + \gamma^{LV}A^{LV} \\ & + N^T kT \left[1 - \ln\left(\frac{P_0^V}{P^V}\right)\right] - P^V V^T \\ & + (\gamma^{SV} - \gamma_0^{SV})A^{SV}. \end{aligned} \tag{20}$$

At equilibrium, Eq. (9) can be applied, and Eq. (20) reduces to

$$\begin{aligned} F - F_0 = & 4\pi R^2 \gamma^{LV} - \frac{8\pi R^3 \gamma^{LV}}{3R_c} + N^T kT \left[1 - \ln\left(\frac{P_0^V}{P^V}\right)\right] \\ & - P^V V^T - N_0^{SV} kT + (\gamma^{SV} - \gamma_0^{SV})A^{SV}. \end{aligned} \tag{21}$$

Note that as F_0 is constant, $d(F - F_0)$ is equivalent to dF .

To determine an expression for the last term in Eq. (21) in terms of the independent variables, a method developed by Keshavarz and Ward²⁴ is used. For a solid–vapor interface under isothermal conditions the Gibbs–Duhem relation, Eq. (7), may be written as

$$\left(\frac{\partial \gamma^{SV}}{\partial \mu^{SV}}\right)_T = -\frac{N^{SV}}{A^{SV}}. \tag{22}$$

As the chemical potential in the solid–vapor interface is equal to that of the vapor, and the vapor has been assumed to behave ideally,

$$\gamma^{SV} - \gamma_0^{SV} = -kT \int_{P_0^V}^{P^V} \frac{N^{SV}}{A^{SV} P^V} dP^V. \quad (23)$$

With N^{SV} from Eq. (14), the right side of Eq. (23) can be integrated to give

$$\gamma^{SV} - \gamma_0^{SV} = kTM \ln \left[\frac{\left(1 - \alpha \frac{P^V}{P_\infty}\right) \left(1 + (C-1) \alpha \frac{P_0^V}{P_\infty}\right)}{\left(1 - \alpha \frac{P_0^V}{P_\infty}\right) \left(1 + (C-1) \alpha \frac{P^V}{P_\infty}\right)} \right], \quad (24)$$

so that the Helmholtz potential can be expressed as

$$F - F_0 = F - F_0(T, V^T, N^T, A^{SV}, R).$$

Thus, given the values of the independent variables T , V^T , N^T , and A^{SV} , and α -isotherm parameters M , C , and α , the Helmholtz potential can be plotted as a function of the droplet radius R and the stability of the system can be analyzed.

III. THEORETICAL INVESTIGATION

The function $\alpha(T)$ in the α isotherm determines the pressure P_A^V at which film-wise condensation will occur. Recent experiments²⁴ have suggested that for water adsorbing on glass, α is slightly greater than unity ($\alpha - 1$ on the order of 10^{-7}), so that the asymptote is found to occur at a pressure less than the saturation value. We start by considering the stability of the droplet using the α -isotherm for the case of α equal to or greater than unity.

A. α equal to or greater than unity

In Fig. 2(a), a plot of R_c vs R for α equal to unity is shown. The values of T , V^T , N^T , and A^{SV} are chosen as 20 °C, 0.0041 m³, 3.1×10^{20} , and 0.038 m², respectively, and the fluid is water. These values are typical of an apparatus recently used to investigate water droplet evaporation.²⁵ At this temperature, the saturation pressure is 2339 Pa, and with α equal to unity, P_A^V is equal to 2339 Pa. The α -isotherm parameters C and M are taken as 425.3 and 9.2×10^{16} m⁻², values found for water adsorbing on glass at 20 °C in Ref. 24. While these values are only indicated to be valid for pressures very close to the asymptote, we use them over the entire pressure range to keep the analysis reasonable. As will be seen, it is the location of the asymptote that is the most important feature of the isotherm.

The critical radius is always less than zero, and it will never intersect with the line R_c equal to R [also shown in Fig. 2(a)]. Therefore, there are no equilibrium states with a droplet present. The only equilibrium state is when there is no droplet present. This is the reference state F_0 . Other values of the independent variables were considered, and this result was always found. In Fig. 2(b), a plot of $F - F_0$ as a function of R is shown. The Helmholtz potential is a monotonically increasing function of R with a global minimum at R equal to zero.

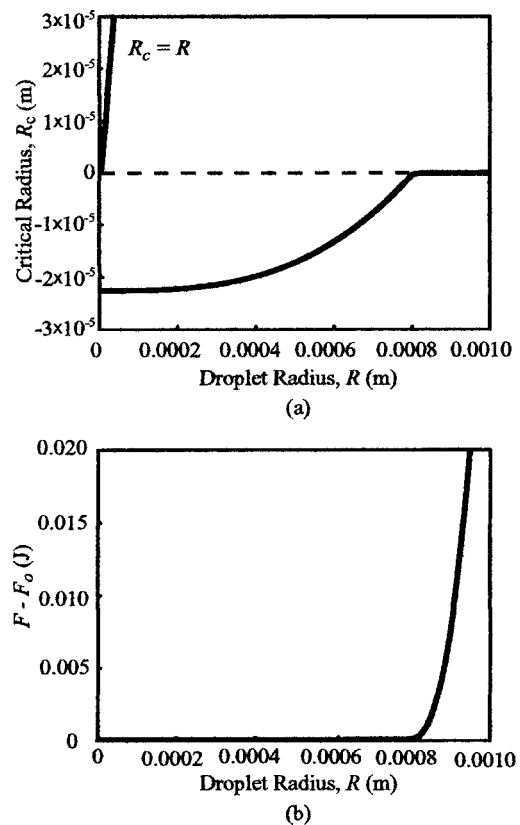


FIG. 2. (a) Critical radius and (b) Helmholtz potential plotted as a function of the droplet radius for α equal to unity. As the curve for the critical radius does not intersect with the line R_c equal to R , there are no equilibrium states with a droplet present.

To understand why no equilibrium states exist, consider the derived equilibrium conditions. The Laplace equation and the equivalence of the liquid and vapor chemical potentials were combined to give the Kelvin relation. It predicts that the pressure in the vapor at equilibrium must be higher than the saturation pressure. By choosing α equal to unity, the pressure in the vapor cannot be greater than the saturation pressure, or filmwise condensation will occur. These two equilibrium conditions are mutually exclusive, and it is therefore impossible for there to be any equilibrium states with a droplet present, stable or unstable. Using the same reasoning, there will be no equilibrium states if α is greater than unity (i.e., when the location of the pressure asymptote is below the saturation pressure).

Based on these results, a stable droplet is not predicted to exist under any conditions. This result has arisen from the inclusion of the adsorbed phase. However, while the experimental results of Keshavarz and Ward²⁴ suggest that α is greater than unity for a water–glass system, nothing in the derivation of the α isotherm requires this to be true. We next consider the case of α less than unity, where the pressure asymptote is at a location above than the saturation pressure.

B. α less than unity

For the same independent variables used in the previous section, the curves of R_c and $F - F_0$ as functions of R are plotted in Fig. 3 for α equal to 0.9999, which corresponds to

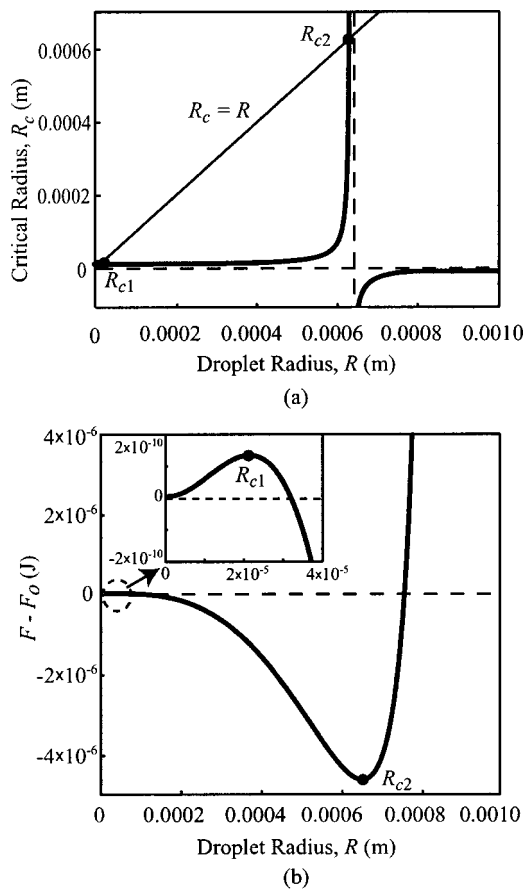


FIG. 3. (a) Critical radius and (b) Helmholtz potential plotted as a function of the droplet radius for α equal to 0.9999. There are two equilibrium states with a droplet present.

a P_A^V value of 2339.23 Pa. The results are significantly different compared to those shown in Fig. 2. The critical radius is now positive over a certain range of R , and there are two intersections with the line R_c equal to R . There are thus two equilibrium radii. This is not unexpected, as both the Kelvin relation and the α -isotherm equation can be satisfied as the pressure in the system can be above the saturation value without the possibility of filmwise condensation. The equilibrium radii are 2.05×10^{-5} m and 6.46×10^{-4} m and will be denoted by R_{c1} and R_{c2} , respectively. From Fig. 3(b), the first equilibrium state is unstable (a maximum of $F - F_0$), while the second is stable (a minimum). The pressure in the vapor in the unstable equilibrium state is 2339.123 Pa and in the stable equilibrium size is 2339.004 Pa. Both of these pressures are above the saturation pressure, consistent with the Kelvin relation, and below P_A^V .

C. Number of equilibrium states

Experimentally, the equilibrium pressure in the vapor could not be distinguished from the saturation pressure for the values of α considered. With this in mind, it is possible to predict how the equilibrium state will change if one of the independent variables is changed.

Suppose that the temperature of the system discussed in Sec. III B is raised to 21 °C while V^T , N^T , and A^{SV} are held constant. The adsorption isotherm parameters are assumed to

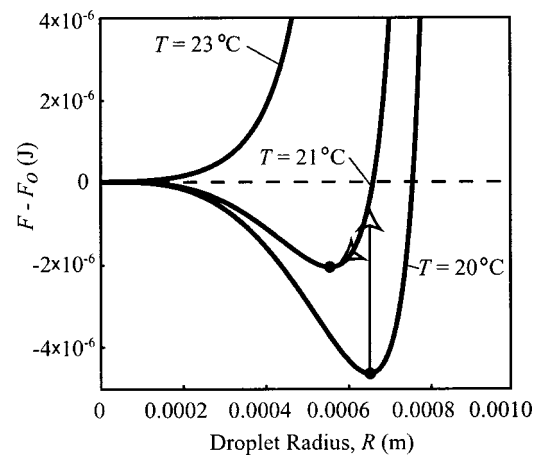


FIG. 4. Helmholtz potential plotted as a function of the droplet radius at three different temperatures. As the temperature increases, the size of the stable equilibrium size decreases until there are no equilibrium states with a droplet present.

be valid over a small range of temperatures without significant error. The value of α is held constant. As the saturation pressure for a pure substance is a monotonically increasing function of temperature, the saturation pressure used in the calculations will increase. For equilibrium to be restored, the pressure in the vapor will need to rise to a value slightly above the new saturation pressure. The only source of mass is the droplet, and it will evaporate until the new equilibrium pressure is reached. The stable equilibrium size should decrease, and this is what is found. The mass in the adsorbed phase does not change significantly. A plot showing $F - F_0$ vs R at temperatures of 20 and 21 °C is shown in Fig. 4. Also indicated is the path that the droplet would follow as it moved between equilibrium states. The system responds so as to minimize $F - F_0$, and this is accomplished by the droplet getting smaller. A similar thought process can be used to predict the effect of changing the other independent variables.

Now consider the case of changing the temperature of the example system to 23 °C. The droplet will evaporate, raising the pressure in the vapor. However, in this case, it completely evaporates, and the resulting equilibrium state is a homogeneous superheated vapor in equilibrium with the adsorbed phase. There is not enough mass in the droplet to raise the pressure to above the new saturation value. A plot of $F - F_0$ at 23 °C is also shown in Fig. 4. Note that there is a global minimum when the radius is equal to zero. It is a stable equilibrium state.

As the system temperature increases, the system goes from having two droplet equilibrium states to having none. There will be a transition point where there is one equilibrium state. This will correspond to an inflection point on the $F - F_0$ curve, and is therefore an unstable equilibrium state. Thus, even when α is less than unity, for there to be a stable equilibrium state at a temperature T , there are further restrictions on the values of the independent variables V^T , N^T , and A^{SV} . For the case of no adsorption, this issue has been addressed.²⁶

IV. COMPARISON TO PREVIOUS WORK

The results of Sec. III are now compared to the predictions of Refs. 5, 9, and 10. If no adsorption occurs, Eq. (12) can still be applied for the critical radius, but the expressions for the Helmholtz potential, Eq. (21), and the relevant pressure terms, Eqs. (13) and (16), simplify to

$$F - F_0 = 4\pi R^2 \gamma^{LV} - \frac{8\pi R^3 \gamma^{LV}}{3R_c} + N^T kT \left[1 - \ln \left(\frac{P_0^V}{P^V} \right) \right] - P^V V^T, \quad (25)$$

$$P^V = \frac{\left(N^T - \frac{4\pi R^3}{3v^L} \right) kT}{4\pi R^3 - V^T}, \quad (26)$$

and

$$P_0^V = \frac{N^T kT}{V^T}. \quad (27)$$

In this case, the reference state corresponds to all the mass being in the vapor. This is the result obtained in Refs. 9 and 10.

In the limit of

$$N^T \gg \frac{4\pi R^3}{3v^L} \quad \text{and} \quad V^T \gg \frac{4\pi R^3}{3}, \quad (28)$$

Eqs. (25)–(27) simplify to

$$F - F_0 = 4\pi R^2 \gamma^{LV} - \frac{8\pi R^3 \gamma^{LV}}{3R_c}, \quad (29)$$

and

$$P_0^V = P^V = \frac{N^T kT}{V^T}. \quad (30)$$

This is the system that was investigated by Gibbs,⁵ and corresponds to a case where the droplet is in an unbounded reservoir with uniform pressure. Note that the expression for the critical radius is now explicit in terms of the system parameters. The independent variables are P^V and T and the reference condition corresponds to a homogeneous vapor phase with pressure P^V .

These two systems can be investigated in the same manner as done in the Sec. III. The same values of the independent variables are used. A comparison of the equilibrium states for the systems considered is given in Table I.

For the case of a droplet in a unbounded reservoir with uniform pressure, the critical radius is only greater than zero when pressure in the vapor is larger than the saturation pressure. When R is equal to R_c in Eq. (29), an extremum exists that is a maximum and thus corresponds to an unstable equilibrium state. This state can be considered as a barrier to nucleation.⁶

For the system with no adsorption on the solid surface, the behavior is similar to the case with adsorption and α less than unity. This is because there is no upper limit to the allowed value of P^V . There are two equilibrium states: one

TABLE I. Comparison of the three models. Where applicable, the independent variables are $T=293.15$ K, $N^T=3.1 \times 10^{20}$, $V^T=0.00041$ m³, and $A^{SV}=0.0378$ m². The saturation pressure is 2339 Pa.

	Ref. 5: Unbounded reservoir with uniform pressure	Refs. 9 and 10: Finite system with no adsorption	Current Work: Solid–vapor interface considered in a finite system, $\alpha=0.9999$
R_{c1} (m)	4.00×10^{-9}	4.00×10^{-9}	2.05×10^{-5}
R_{c2} (m)	N/A	8.05×10^{-4}	6.46×10^{-4}
$F - F_0(R_{c1})$ (J)	4.89×10^{-18}	4.89×10^{-18}	1.28×10^{-10}
$F - F_0(R_{c2})$ (J)	N/A	-0.0415	-4.66×10^{-6}
$P^V(R_{c1})$ (Pa)	3060.100	3060.100	2339.123
$P^V(R_{c2})$ (Pa)	N/A	2339.773	2339.004

unstable and one stable. The unstable size is analogous to the unstable size found for the droplet in a pressure reservoir. This can be seen by considering Eq. (25) in the limits of Eq. (28). In this case, the expressions for the critical radius and the thermodynamic potential become equivalent to those of Gibbs for the same temperature and a pressure of P_0^V . For this case, P_0^V is equal to 3060.1 Pa. This is the value used for the reservoir pressure in the evaluation of Eq. (29). The values of the radius and the potential at the unstable equilibrium are thus the same in both cases. Due to the very small equilibrium droplet size, the finite nature of the system has no effect and the vapor phase acts like an unbounded reservoir.

In the finite system, the stable equilibrium exists because mass transfer to or from the droplet will have an effect on the system pressure. If a droplet is in the stable equilibrium state and some liquid evaporates, the pressure in the vapor will increase. To return to equilibrium, the pressure must decrease, and this is accomplished by having some of the vapor condense on the droplet, bringing it back to its original size. A similar argument can be made for the case of vapor condensing on the liquid surface.

While the behavior exhibited in both finite systems (with and without adsorption) is qualitatively similar, the conditions at both the unstable and stable equilibrium states are different. The unstable radius for the system where there is adsorption is four orders of magnitude larger than that when the adsorbed phase is not considered. The value of the Helmholtz potential is also much greater. This occurs because the pressure in the system is being restricted by the adsorbed phase. The unstable equilibrium must occur at a pressure just above the saturation value. This state can still be considered as a barrier to nucleation, which in this case will be much higher than for either of the other systems considered. The stable size when the adsorbed phase is considered is smaller, and this is because of the mass in the solid–vapor interface. The value of the potential is accordingly smaller.

V. SYSTEM WITH MULTIPLE DROPLETS

The theory developed can be extended to a system of n droplets. Neglecting the adsorption, one finds

$$\begin{aligned}
 F - F_0 = & 4\pi\gamma^{LV} \sum_{i=1}^n R_i^2 - \frac{8\pi\gamma^{LV}}{3R_c} \sum_{i=1}^n R_i^3 - \left(\frac{N^T - \frac{4\pi}{3v^L} \sum_{i=1}^n R_i^3}{V^T - \frac{4\pi}{3} \sum_{i=1}^n R_i^3} \right) V^T kT \\
 & + N^T kT \left[1 - \ln \left(\frac{N^T}{N^T - \frac{4\pi}{3v^L} \sum_{i=1}^n R_i^3} \frac{V^T - \frac{4\pi}{3} \sum_{i=1}^n R_i^3}{V^T} \right) \right], \tag{31}
 \end{aligned}$$

where

$$R_c = \frac{2\gamma^{LV}}{\frac{kT}{v_\infty^L} \ln \left[\frac{\left(N^T - \frac{4\pi}{3v^L} \sum_{i=1}^n R_i^3 \right) kT}{\left(V^T - \frac{4\pi}{3} \sum_{i=1}^n R_i^3 \right) P_\infty} \right] + P_\infty - \frac{\left(N^T - \frac{4\pi}{3v^L} \sum_{i=1}^n R_i^3 \right) kT}{V^T - \frac{4\pi}{3} \sum_{i=1}^n R_i^3}}. \tag{32}$$

Thus,

$$F - F_0 = F - F_0(T, V^T, N^T, R_1, \dots, R_n).$$

As shown in Sec. IV, not considering the adsorption generates the same qualitative behavior as choosing α to be less than unity.

Vogelsberger²⁷ assumes that all the droplets have the same size. Under this assumption, the

$$\sum_{i=1}^n R_i^2 \quad \text{and} \quad \sum_{i=1}^n R_i^3$$

terms in Eqs. (31) and (32) are replaced by

$$nR^2 \quad \text{and} \quad nR^3,$$

respectively. Vogelsberger's model assumes that the number of droplets is an independent variable, i.e.,

$$F - F_0 = F - F_0(T, V^T, N^T, R, n).$$

This model can be used to predict that the total volume of liquid at equilibrium will be independent of n . Thus, the stable equilibrium droplet size for a system with n droplets, R_c^n , can be predicted if the stable equilibrium size for single droplet, R_c^1 is known:

$$R_c^n = n^{-1/3} R_c^1. \tag{33}$$

From a thermodynamic standpoint, this is not correct. The physical radius of each droplet can take on different values, and must be considered independently in the formulation of R_c and $F - F_0$.

For the case of two droplets (n equal to 2), a plot of $F - F_0$ [from Eq. (31)] vs R_1 and R_2 is shown in Fig. 5. The independent variables are the same as those used in the single droplet analysis, and for simplicity, the adsorption is neglected.

The surface has four extrema. There is a local maximum at A, a saddle point at B and minima at C and D. Of interest are the minima, which correspond to stable equilibrium

states. The stable equilibrium states at both C and D correspond to only one droplet being present in the system.

The surface is symmetric about the line R_1 equal to R_2 . Perpendicular to this line, $F - F_0$ always decreases. If the two droplets start with the same size, thermodynamics is unable to predict the final configuration of the system, other than that it will contain only one droplet of the equilibrium size. Which droplet takes on this size is not known. Fluctuations on the molecular level will determine which droplet will remain. Once one droplet gets bigger than the other, by the net transfer of one molecule from the vapor, the rest of the path is defined. The above analysis can be extended to systems with more than two droplets, and the same behavior is observed. The stable equilibrium state always contains one droplet. The radius in this state is the same critical radius found previously, 8.05×10^{-4} m (see Table I). There is no stable state where both droplets can exist simultaneously. This is contrary to the predictions of Eq. (33), which would

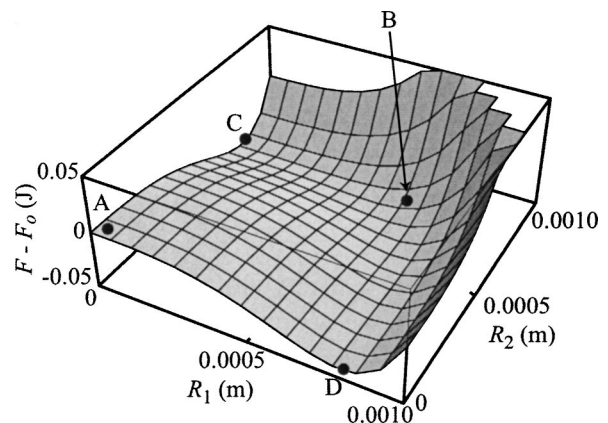


FIG. 5. Helmholtz potential plotted as a function of the droplet radii for a system with two droplets. The system walls are nonadsorbing. There are two equivalent stable equilibrium states (points C and D), each of which corresponds to the presence of one droplet.

have two droplets present in the stable equilibrium state, each with a radius of 6.39×10^{-4} m.

The most important thing to take from this analysis is that the critical radius is a thermodynamic property of the system, and only a function of the independent variables T , V^T , N^T , and A^{SV} . It is not dependent on the initial state of the system (i.e., the initial number of droplets is not an independent variable).

VI. DISCUSSION AND CONCLUSION

To make a firm statement about the stability of a single, one-component droplet in a finite system, the value of α in the α isotherm, Eq. (14), is required. As the theoretical development does not give an indication of whether α should be greater than or less than unity, experimental results may be required to elucidate the answer. The precision of the measurements required (pressures to within less than 1 Pa) are difficult to obtain in any case, let alone near saturation conditions.

The recent experiments of Keshavarz and Ward²⁴ suggest that for water adsorbing on glass, α is greater than unity, and the pressure asymptote of the isotherm is at a value lower than the saturation pressure. This result, combined with the theory developed in Sec. II, predict that no stable droplet equilibrium size will exist, in agreement with the discussion of Reiss and Koper.³ The key point here is that the nature of the stability is directly a result of the adsorption isotherm used to model the solid–vapor interface.

However, there is nothing in the development of the α isotherm that requires the pressure asymptote to be below the saturation pressure. If α is chosen to be less than unity, the asymptote will be above the saturation pressure, and a stable droplet is predicted to exist at a given temperature provided the system volume, mass and solid surface area satisfy further constraints. If a solid surface exists for which α is less than unity, such a stable droplet could be used as an ideal initial condition for a droplet evaporation experiment, which are typically entirely transient.²⁵ In fact, this technique has been used in molecular simulations of droplet evaporation.^{28,29}

When the analysis is extended to a system that initially contains more than one droplet, the stable equilibrium state is always found to correspond to a single droplet. This is contrary to previous investigations that assumed that all the

droplets will take on the same size. In nonequilibrium systems, such as droplet nucleation, such equilibrium relations must be used with caution.

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