Modified Rachford-Rice Equations Including Interfacial Contributions and their Application to the Nucleation Process

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The Rachford-Rice expressions [Rachford HH, Rice JD, Petroleum Trans AIME 1952;195:327-328] have been modified to include interfacial contributions in the calculation of the equilibrium coexistence between two macroscopic phases. It is shown that two-phase equilibrium states for first-order phase transitions from nucleation to the presence of evolved macroscopic phases can be characterized by using these generalized expressions. Thus, this new treatment allows the determination of the critical inclusion of nucleation of the so-called dispersed phase in a way similar to the determination of incipient new-phase formation points of a saturated phase on the binodal curve. © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 1907–1921, 2010
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Introduction

First-order phase transitions consist of the emergence and the growth of inclusions of a so-called dispersed phase inside a metastable phase until a stable equilibrium state with two evolved macroscopic phases is reached by the system.[1,2] A stable equilibrium coexistence between two evolved macroscopic phases is the final thermodynamic state for these phase transitions, whereas nucleation is the process by which the formation of the dispersed phase begins inside the metastable phase. In the final equilibrium state of these phase transitions, the resultant phases, the dispersed and continuous phases, have intensive properties different from the respective quantities of the original metastable phase. As first-order phase transitions are widely found in both industrial and natural processes (crystallization, condensation,

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evaporation, etc.), a significant number of experimental and theoretical works have been devoted to their study.[3–5] Concerning the equilibrium states of these phase transitions, however, the developments have commonly dealt with the nucleation process and the coexistence between macroscopic phases, separately. Thus, these independent works have arrived, on the one hand, to standard approaches for the nucleation process,[6,7] and on the other hand, to standard approaches for evolved macroscopic phases.[8–10] In all nucleation approaches, the dispersed phase inclusions are considered so small (clusters of few molecules) in comparison with the metastable phase that the intensive properties of the metastable phase are assumed constant during dispersed phase nucleation. However, this basic assumption is not satisfied by standard approaches for evolved macroscopic phases as described earlier, and hence they cannot be fit together with the standard nucleation approaches in a simple way. In addition, unlike classical nucleation approaches, the interfacial contributions to the free energy of the system are not usually touched by most standard approaches for evolved macroscopic phases. Among those approaches in the context of classical thermodynamics, the Rachford-Rice equations,[11] better known as the flash problem,[12–16] represent a widely used approach of dealing with necessary equilibrium conditions for systems where such contributions are negligible. The aim of this work is to describe the stable equilibrium state between two evolved macroscopic phases and the unstable equilibrium state of nucleation in an isothermal-isochoric-closed system by using the same classical thermodynamic framework. To achieve this aim, the Rachford-Rice equations are generalized to include interfacial contributions by using the concept of dividing surface introduced by Gibbs.[17] In this generalized approach, the thermodynamic states are altered not only by the presence or size of the dispersed phase inclusions,[18–20] but also by the mathematical corrections to the system as the result of introducing dividing surfaces. In this work, a detailed description of the peculiarities of closed systems is not intended, because several authors have already performed such developments.[21,22]

Thermodynamic Potential for Isothermal-Isochoric-Closed Systems

From the mathematical point of view, thermodynamic equilibrium states for either nucleation or evolved macroscopic phases come from the search for stationary points (necessary equilibrium conditions) of an appropriate thermodynamic potential describing first-order phase transitions. Thus, we have that the construction of such thermodynamic potential is the first issue that has to be performed by any approach, for which the description of the system under consideration is the first step. In this work, an isothermal-isochoric-closed system with E components, total volume V_t, total number of moles N_t, and temperature T is analyzed. At first, the system is formed by a single homogeneous metastable phase with pressure P_I. Once the nucleation process has taken place, the system is composed of two evolved macroscopic phases: the dispersed and continuous phases, whose intensive properties are different from the respective quantities of the original metastable phase. These two macroscopic phases are connected to each other by the so-called interfacial region, where the intensive properties of the system vary continuously from the bulk properties of the continuous phase to the bulk properties of the dispersed phase. In the case of classical thermodynamic approaches, the interfacial region represents a theoretical problem for the construction of the required thermodynamic potential, because homogeneous regions in internal equilibrium are required from the classical thermodynamic standpoint. To deal with this issue, Gibbs introduced the concept of dividing surface in his work about equilibrium of heterogeneous substances.[17] This dividing surface is an artificial boundary inserted into the interfacial region by an arbitrary but convenient mathematical condition, which allows the construction of homogenous regions in internal equilibrium. Better known as hypothetical phases,[23,24] these homogenous regions are considered as artificial phases. In the classical Gibbs' approach, the hypothetical phase enclosed by the dividing surface represents an inclusion of the dispersed phase inside the continuous phase. The basic difference between the actual system and the hypothetical system lies in the fact that a detailed description of the interfacial region is not necessary in the hypothetical system; the so-called surface excess quantities account for the interfacial contributions instead. These excess quantities are defined as the difference between the actual properties of the system and the corresponding properties of the hypothetical phases.

Several authors have already performed the construction of thermodynamic potentials by using the Gibbs' approach in the context of nucleation theories,[7,25,26] where the basic assumption of constant intensive properties of the metastable phase is used before proceeding with the search for stationary points. By this reason, the necessary equilibrium conditions derived in those works should not be used to describe the equilibrium coexistence between evolved macroscopic phases, where such assumption is not fulfilled, as mentioned before. However, recently, a thermodynamic potential that accounts for, in general, first-order phase transitions was proposed[27]:

$$\Delta F = \sum_{i=1}^{E} (\mu_{id} - \mu_{iI})N_{id} + \sum_{i=1}^{E} (\mu_{ic} - \mu_{iI})N_{ic} + \sum_{i=1}^{E} (\mu_{is} - \mu_{iI})N_{is} + V_d(P_I - P_d) + V_c(P_I - P_c) + \sigma A. \quad (1)$$

Here, F is the Helmholtz free energy, μ the chemical potential, N the number of moles, V the total volume, P the pressure, σ the specific surface energy, and A the surface area inclusion. The subscripts c, d, and I indicate the continuous, dispersed, and metastable phases, respectively. Similarly, the subscript i denotes the component i and the subscript s the surface excess quantities. Equation 1 represents the free-energy change between an arbitrary nonhomogeneous state and the metastable phase from nucleation to evolved macroscopic phases inside an isothermal-isochoric-closed system, where the volume constraint

$$V_t = V_d + V_c \quad (2)$$

and the mass constraints

$$N_{it} - (N_{id} + N_{ic}) = N_{is}; i = 1, \ldots, E \quad (3)$$

for the total number of moles of the component i in the system N_{it} are satisfied. The former constraint establishes a finite total volume, and even though the latter constraint is usually conceived as a conventional mass balance, it actually defines the surface excess number of moles N_{is}; this point will be discussed in detail later on.

Starting with Eq. 1, one can proceed to search for stationary points of the free-energy change by taking the respective partial derivatives with respect to the independent variables of the system. This procedure implies that such independent variables are known in advance via theoretical or experimental arguments. Alternatively, the total differential of the free-energy change can be directly calculated from Eq. 1, with which the necessary partial derivatives and the independent variables of the system can be explicitly identified. In the case of Eq. 1, we have that such total differential is given by[27]

$$d(\Delta F) = \sum_{i=1}^{E} (\mu_{id} - \mu_{is}) dN_{id} + \sum_{i=1}^{E} (\mu_{ic} - \mu_{is}) dN_{ic} + \left(P_c - P_d + \frac{2\sigma}{r} + \frac{\chi}{A}\right) dV_d, \quad (4)$$

where a fixed spherical geometry was assumed in its derivation, and hence r corresponds to both the position of the dividing surface and the inclusion radius. In Eq. 4, χ accounts for the strain energy associated with changes of the curvature, besides being conceived as a degree of freedom to place the dividing surface. In an isothermal-isochoric-closed system, Eq. 4 represents the total differential of the Helmholtz free-energy change in terms of the properties of the hypothetical phases and the surface excess quantities, with N_{id}, N_{ic}, and V_d as independent variables. Finally, it is worth pointing out that, by definition, the properties of both hypothetical phases and the excess quantities in Eqs. 1 and 4 are dependent on the choice of the position of the dividing surface, but the free-energy change of the system is independent of it.

As mentioned before, one of the most important characteristics of the Gibbs' approach is the introduction of excess quantities (the surface excess quantities, the specific surface energy, the strain energy, and the surface area), which obey the following fundamental relations:[6,27]

$$dU_s = TdS_s + \sum_{i=1}^{E} \mu_{is} dN_{is} + \sigma dA + \chi dr \quad (5)$$

and the well-known Gibbs adsorption isotherm

$$\sum_{i=1}^{E} N_{is} d\mu_{is} + A d\sigma = \chi dr. \quad (6)$$

Here, μ_{is} are the surface excess chemical potentials. The aforementioned equations are general equations that have to be satisfied by the surface excess quantities during first-order phase transitions. The surface excess quantities are commonly treated as state functions of an "interfacial phase", the well-known interface. In this work, however, the surface excess quantities are considered as mathematical corrections to the properties of hypothetical phases with respect to the actual properties of the system as the result of introducing the Gibbs' dividing surface. In addition, as mentioned before, the interface is the connecting region between two phases; hence, unlike any other phase, the interface cannot be thermodynamically defined by itself. By this reason, it is necessary to suggest relations between the surface excess quantities and the hypothetical phases, as will be shown later on. Because of the aforementioned statements, the word interface will only be used for simplicity hereafter.

Necessary Equilibrium Conditions

A minimum of the free-energy change given by Eq. 1 provides the necessary conditions for the equilibrium coexistence between evolved macroscopic phases, whereas a saddle point accounts for the critical inclusion of formation of a dispersed phase, that is, the necessary equilibrium conditions of nucleation.[28,29] Thus, the former stationary point is a stable equilibrium state and the latter stationary point is an unstable equilibrium state. The coefficients of the independent variables N_{id}, N_{ic}, and V_d in Eq. 4 give directly the partial derivatives of the free-energy change needed for determining such necessary equilibrium conditions; therefore, the general necessary equilibrium conditions for first-order phase transitions are given by

$$\left[\frac{\partial(\Delta F)}{\partial N_{id}}\right]_{N_{ic}, V_d, N_{jd},\, j \neq i} = \mu_{id} - \mu_{is} = 0, \quad (7)$$

$$\left[\frac{\partial(\Delta F)}{\partial N_{ic}}\right]_{N_{id}, V_d, N_{jc},\, j \neq i} = \mu_{ic} - \mu_{is} = 0, \quad (8)$$

and

$$\left[\frac{\partial(\Delta F)}{\partial V_d}\right]_{N_{id}, N_{ic}} = P_c - P_d + \frac{2\sigma}{r} + \frac{\chi}{A} = 0. \quad (9)$$

Equations 7 and 8 are the well-known equalities of chemical potentials, and Eq. 9 is the generalized Laplace's equation. The first two equations can be combined to yield

$$\mu_{is} = \mu_{id} = \mu_{ic}. \quad (10)$$

This equation gives the necessary equilibrium conditions and the connection between the surface excess chemical potentials and the hypothetical phases, that is, this equation states constant chemical potential throughout the system and allows setting the surface excess chemical potentials equal to the respective values of either the dispersed phase or the continuous phase at equilibrium conditions. One of the most outstanding attributes of the above necessary equilibrium conditions lies in the fact that they are not tied to assumptions about the connection between the excess quantities and the state variables of the hypothetical phases, particularly in the case of the specific surface energy.[27]

Application to the nucleation process

Considering that Eqs. 9 and 10 provide the necessary equilibrium conditions during first-order phase transitions, their application to the nucleation process requires only the basic assumption of all nucleation theories, which conceives the dispersed phase inclusions as such small entities that the initial state of the continuous phase, the homogeneous metastable phase, is not altered by their emergence. In terms of the continuous phase, this statement means that the intensive properties of the continuous phase are held invariant and set equal to the respective quantities of the original metastable phase during dispersed phase nucleation, that is, the following conditions are assumed:

$$\mu_{ic} = \mu_{i\mathrm{I}};\ i = 1, \ldots, E \tag{11}$$

and

$$P_{\mathrm{c}} = P_{\mathrm{I}}. \tag{12}$$

From these assumptions, together with Eqs. 9 and 10, we have that the necessary equilibrium conditions of nucleation take the form of

$$P_{\mathrm{I}} - P_{\mathrm{d}} + \frac{2\sigma}{r_{\mathrm{C}}} + \frac{\chi}{A} = 0 \tag{13}$$

and

$$\mu_{is} = \mu_{i\mathrm{d}} = \mu_{i\mathrm{I}}; i = 1, \ldots, E. \tag{14}$$

These $E + 1$ equations give the intensive properties of the so-called critical inclusion of the dispersed phase. The critical inclusion size, the critical radius r_{C}, establishes the inclusion size from which a dispersed phase inclusion grows spontaneously inside the metastable phase to give rise to an evolved macroscopic inclusion. The aforementioned system of equations can be transformed into a more practical system of equations that determines the intensive properties of the critical inclusion:[27]

$$\frac{z_{i\mathrm{t}}\phi_{i\mathrm{I}}(z_{1\mathrm{t}}, \ldots, z_{\mathrm{Et}}, P_{\mathrm{I}})}{x_{i\mathrm{d}}\phi_{i\mathrm{d}}(x_{1\mathrm{d}}, \ldots, x_{\mathrm{Ed}}, P_{\mathrm{d}})} - \frac{z_{j\mathrm{t}}\phi_{j\mathrm{I}}(z_{1\mathrm{t}}, \ldots, z_{\mathrm{Et}}, P_{\mathrm{I}})}{x_{j\mathrm{d}}\phi_{j\mathrm{d}}(x_{1\mathrm{d}}, \ldots, x_{\mathrm{Ed}}, P_{\mathrm{d}})} = 0;\ i = 1, \ldots, E-1; i \neq j \tag{15}$$

and

$$\frac{P_{\mathrm{d}}}{P_{\mathrm{I}}} - \frac{z_{j\mathrm{t}}\phi_{j\mathrm{I}}(z_{1\mathrm{t}}, \ldots, z_{\mathrm{Et}}, P_I}{x_{j\mathrm{d}}\phi_{j\mathrm{d}}(x_{1\mathrm{d}}, \ldots, x_{\mathrm{Ed}}, P_{\mathrm{d}})} = 0. \tag{16}$$

Here, ϕ_{ij} denotes the fugacity coefficient of the component i in the phase j with x_{ij} as the corresponding mole fraction, and $z_{i\mathrm{t}}$ denotes the total mole fraction of the component i in the metastable phase, which corresponds to the total mole fraction of the system as well. The dividing surface in the above system of equations is the well-known surface of tension ($\chi = 0$).[30] The mole fraction of the component E in the dispersed phase is calculated from

$$\sum_{i=1}^{E} x_{i\mathrm{d}} = 1. \tag{17}$$

The system of equations given by Eqs. 15 and 16 is of general application, and hence it determines the intensive properties of the critical inclusion for drops, bubbles, crystals, etc., as long as fugacities can be used to characterize the dispersed and metastable phases. It is important to stress that the aforementioned system of equations is independent of any excess quantity, which implies that the corresponding interfacial region does not play any role in determining the thermodynamic state of the critical inclusion; it is determined by the thermodynamic state of the homogeneous metastable phase only. This statement seems to be in direct contradiction to the basic idea where the excess quantities are regarded essential to describe tiny inclusions such as the critical inclusion. This apparently contradictory statement will be undertaken in detail later on.

Once the intensive properties of the critical inclusion are calculated, the ratio of the specific surface energy to the critical radius is given by the expression[27]

$$\frac{2\sigma}{r_{\mathrm{C}}} = P_{\mathrm{I}}\left(\sum_{i=1}^{E}\frac{z_{i\mathrm{t}}}{K_{i\mathrm{I}}} - 1\right), \tag{18}$$

where $K_{i\mathrm{I}} = \phi_{i\mathrm{d}}/\phi_{i\mathrm{I}}$ is the well-known equilibrium ratio of the component i in terms of fugacity coefficients. Bearing in mind that, according to Eqs. 15 and 16, the intensive properties of the critical inclusion are independent of the excess quantities, we have that the ratio $2\sigma/r_{\mathrm{C}}$ on the left-hand side of Eq. 18 is also independent of the excess quantities. In addition, it can be shown that the ratio $2\sigma/r_{\mathrm{C}}$ has a single value for a given thermodynamic state of the metastable phase, irrespective of the used method to determine the specific surface energy.[27] Equation 18 is notable for the expression inside the parenthesis, which is the well-known expression for determining the incipient new-phase formation points on the binodal curve.[8–10] Although Eq. 18 was derived from the necessary equilibrium conditions for nucleation, the expression inside the parenthesis can also be obtained from the Rachford-Rice equations when the so-called molar phase fraction goes to zero.[31] Hence, Eq. 18 can be seen, on the one hand, as the first application of the Rachford-Rice equations to the nucleation process and, on the other hand, as the first connection between the Rachford-Rice equations and excess quantities.

Application to evolved macroscopic phases

Once the dispersed phase nucleation has taken place, the respective inclusions grow spontaneously by changing the properties of the original metastable phase until a stable thermodynamic state with two macroscopic phases is reached by the system. In this stable state, the basic assumption of nucleation given by Eqs. 11 and 12 is no longer satisfied; consequently, we have that the necessary equilibrium conditions are now Eqs. 9 and 10 directly. Although these equations are derived for one inclusion of the dispersed phase, in fact several inclusions develop inside the continuous phase during first-order phase transitions. In the specific case of nucleation, this condition can be disregarded because of the same basic assumption of constant intensive properties of the metastable-continuous phase. This assumption implies that the thermodynamic state of the metastable phase remains unvarying, irrespective of the number of inclusions inside the system. This is not the case for the final stable state of first-order phase transitions and hence more than one inclusion should be taken into account in this specific case. If several inclusions are regarded in the analysis, it can be shown that all intensive properties of the different inclusions have the same values, if an equilibrium state is present.[20] Then, considering that the equilibrium coexistence between two evolved phases is the main concern here, Eqs. 9 and 10 remain valid for every macroscopic inclusion of the dispersed phase in the system. However, the constraints of an isothermal-isochoric-closed system given by Eqs. 2 and 3 have to be modified to take into account the effect of several inclusions in the size of the dispersed phase, and consequently in the properties of the continuous phase. These constraints are modified as follows:

$$V_{\mathrm{t}} = V_{\mathrm{c}} + \lambda V_{\mathrm{d}} \tag{19}$$

and

$$N_{i\mathrm{t}} - (N_{i\mathrm{c}} + \lambda N_{i\mathrm{d}}) = \lambda N_{i\mathrm{s}};\ i = 1, \ldots, E. \tag{20}$$

Here, λ is the number of identical inclusions with volume V_{d} and number of moles $N_{i\mathrm{d}}$ of the component i. In what follows, it is assumed that the dispersed phase inclusions are uniformly distributed over the continuous phase and therefore they interact amongst themselves through the continuous phase only.

Equations 9 and 10, together with Eqs. 19 and 20, constitute the needed system of equations to determine equilibrium states of an isothermal-isochoric-closed system. Usually, numerical solutions to this system of equations deal with the excess quantities as functions of state of a surface phase (the interface),[32] meaning that a three-phase equilibrium problem has to be solved where macroscopically there are two phases actually. On the other hand, if the excess quantities are treated as mathematical corrections as discussed before, then we keep a two-phase equilibrium problem, where the two phases correspond to the hypothetical phases defined by the Gibbs' approach. It is worth pointing out that even though several authors have undertaken the equilibrium coexistence between macroscopic phases considering interfacial contributions,[18–22] the surface excess number of moles has not apparently been included before the present study. Thus, bearing these ideas in mind, we define the hypothetical number of moles $N_{i\mathrm{h}}$ of the component i as follows:

$$N_{i\mathrm{h}} \equiv N_{i\mathrm{c}} + \lambda N_{i\mathrm{d}} = N_{i\mathrm{t}} - \lambda N_{i\mathrm{s}}; i = 1, \ldots, E. \tag{21}$$

From this expression, we also have that the total number of moles of both the continuous and the dispersed phase, and the total surface excess number of moles N_{s} must satisfy:

$$N_{\mathrm{h}} = N_{\mathrm{c}} + \lambda N_{\mathrm{d}} = N_{\mathrm{t}} - \lambda N_{\mathrm{s}}. \tag{22}$$

The last expressions on the right-hand side of Eqs. 21 and 22 are directly obtained from Eq. 20. These equations show the hypothetical number of moles as the result of subtracting the surface excess number of moles from the total number of moles in the system; thus, the hypothetical number of moles coincides with the total number of moles, if there is no surface excess number of moles. In the case of classical nucleation theories, Eqs. 21 and 22 make an important distinction from the usual treatment given to the surface excess number of moles by these theories.[7,28,33] There, the surface excess number of moles is conceived as a quantity that corrects only the number of moles of the dispersed phase $N_{i\mathrm{d}}$, because the actual number of moles in the inclusion is the aim in classical nucleation theories. In this work, however, such actual number of moles is not intended for being calculated by itself, because the stable equilibrium states between evolved macroscopic phases, the dispersed and continuous phases, will be described as a whole. Therefore, the corrections have to be applied to the entire system.

Taking Eqs. 21 and 22 as starting point, we can set aside the excess quantities from the necessary equilibrium conditions for the time being, and then we can be concentrated on the properties of the hypothetical phases only. Thus, in a way similar to that used for obtaining Eqs. 15 and 16, we can use fugacity coefficients to express Eq. 10 in terms of the intensive properties of both hypothetical phases, that is, Eq. 10 can be rewritten into the well-known expression

$$x_{i\mathrm{d}} P_{\mathrm{d}} \phi_{i\mathrm{d}} = x_{i\mathrm{c}} P_{\mathrm{c}} \phi_{i\mathrm{c}}, \tag{23}$$

where fugacity coefficients are defined as $\phi_{ij} \equiv f_{ij}/x_{ij}P_j$, with f_{ij} as the fugacity of the component i in the hypothetical phase j. Although formally unchanged with respect to the commonly used equilibrium expressions, Eq. 23 is written in terms of the intensive properties of the hypothetical phases. From Eqs. 9 and 23, the equilibrium ratio K_i^{curve} can be defined as[34]:

$$K_i^{\mathrm{curve}} \equiv \frac{x_{i\mathrm{c}}}{x_{i\mathrm{d}}} = \frac{P_{\mathrm{d}}}{P_{\mathrm{c}}} \frac{\phi_{i\mathrm{d}}}{\phi_{i\mathrm{o}}} = \left(1 + \frac{2\sigma}{rP_{\mathrm{c}}}\right) \frac{\phi_{i\mathrm{d}}}{\phi_{i\mathrm{c}}} = \left(1 + \frac{2\sigma}{rP_{\mathrm{c}}}\right) K_i. \tag{24}$$

Here, the dividing surface is the surface of tension again ($\chi = 0$). K_i^{curve} depends on the fugacity coefficients ratio of the dispersed and continuous phases, $K_i = \phi_{i\mathrm{d}}/\phi_{i\mathrm{c}}$. This equilibrium ratio is a measure of the molar distribution of the component i between two given phases at equilibrium conditions for planar dividing surfaces; the higher this ratio becomes, the larger the mole fraction of the component i in the continuous phase is in the specific case of Eq. 24. It is important to highlight that $K_i^{\mathrm{curve}} = K_i$, when $r \to \infty$, that is, they coincide with each other for planar dividing surfaces, and hence the ratio K_i^{curve} physically expresses the same as K_i but for curved dividing surfaces.

Considering that mole fractions are the experimental variables handled in Eqs. 23 and 24, it is advisable to rewrite Eq. 21 as follows:

$$z_{i\mathrm{h}} N_{\mathrm{h}} = x_{i\mathrm{c}} N_{\mathrm{c}} + \lambda x_{i\mathrm{d}} N_{\mathrm{d}}; i = 1, \ldots, E, \tag{25}$$

where $z_{i\mathrm{h}} = N_{i\mathrm{h}}/N_{\mathrm{h}}$ accounts for the combined mole fraction of both hypothetical phases. Then, the substitution of Eqs. 22 and 24 into Eq. 25 results in

$$x_{i\mathrm{d}} = \frac{z_{i\mathrm{h}}}{1 + \alpha\left(K_i^{\mathrm{curve}} - 1\right)}; i = 1, \ldots, E. \tag{26}$$

This expression, along with Eq. 24, allows the calculation of compositions of both hypothetical phases, where the hypothetical molar phase fraction α is defined as

$$\alpha \equiv \frac{N_{\mathrm{c}}}{N_{\mathrm{h}}}. \tag{27}$$

It is important to notice that the number of inclusions λ disappears from Eq. 26, that is, the inclusion composition does not rely directly on the number of inclusions inside the system. If Eq. 26 is inserted into Eq. 17, and the same is performed for the composition of the continuous phase, then the results can be combined to yield

$$\Psi(\alpha, r) \equiv \sum_{i=1}^{E} x_{i\mathrm{c}} - \sum_{i=1}^{E} x_{i\mathrm{d}} = \sum_{i=1}^{E} \frac{z_{i\mathrm{h}}(K_i^{\mathrm{curve}} - 1)}{1 + \alpha(K_i^{\mathrm{curve}} - 1)} = 0. \tag{28}$$

This expression, along with the volume constraint,[19] allows the determination of the hypothetical molar phase fraction α and the inclusion size r at constant K_i for the equilibrium coexistence between the dispersed phase inclusions and the continuous phase. Equation 28 is the so-called the Rachford-Rice equation,[12–16] but in terms of the intensive properties of the hypothetical phases. The Rachford-Rice equation has been widely used to calculate the mass distribution between two phases when the interfacial contributions are negligible for equilibrium calculations. However, it is important to emphasize that these circumstances are only specific situations in the present formalism, because the interfacial contributions are negligible only when either $N_{i\mathrm{s}} \to 0$ or $r \to \infty$ in accordance with Eqs. 22 and 24. From the mathematical point of view, Eq. 28 provides thermodynamic states where the general necessary equilibrium conditions are satisfied: maxima, minima, and saddle points. The exact thermodynamic nature of these stationary points is beyond the scope of this work. Hence, it is not possible to be certain that the numerical result of Eq. 28 corresponds to a stable state (minimum of the free energy),[35] as mentioned previously. However, the aim is to distinguish between critical inclusions in the nucleation process and other macroscopic inclusions at equilibrium conditions, which can be of either stable or unstable nature. Hereafter, r_{E} represents radii calculated from Eq. 28, and r_{C} accounts for the critical radius of nucleation as given by Eq. 18.

Determination of the Surface Excess Quantities

According to Eq. 28, the two-phase equilibrium problem relies on the combined mole fraction of both hypothetical phases $z_{i\mathrm{h}}$, which, in turn, is calculated from the hypothetical number of moles $N_{i\mathrm{h}}$. Thus, we have that the hypothetical number of moles plays a central role in the present formalism, or more accurately the surface excess number of moles, in accordance with Eqs. 21 and 22. In what follows, the Gibbs adsorption isotherm as given by Eq. 6 will be used as starting point to obtain generalized expressions for calculating the surface excess number of moles.

Bearing in mind that the Gibbs adsorption isotherm is a fundamental differential relation between the excess quantities of the system governed by Eq. 4, the Gibbs adsorption isotherm should also be written in terms of the same independent variables $N_{i\mathrm{d}}$, $N_{i\mathrm{c}}$ and V_{d}. Thus, taking the partial derivatives of Eq. 6 with respect to $N_{i\mathrm{d}}$, $N_{i\mathrm{c}}$ and V_{d}, we have that

$$\sum_{i=1}^{E} N_{i\mathrm{s}} \left(\frac{\partial \mu_{i\mathrm{s}}}{\partial N_{k\mathrm{d}}}\right)_{N_{k\mathrm{c}}, V_{\mathrm{d}}, N_{j\mathrm{d}}, j \neq k} + A \left(\frac{\partial \sigma}{\partial N_{k\mathrm{d}}}\right)_{N_{k\mathrm{c}}, V_{\mathrm{d}}, N_{j\mathrm{d}}, j \neq k} = \chi \left(\frac{\partial r}{\partial N_{k\mathrm{d}}}\right)_{N_{k\mathrm{c}}, V_{\mathrm{d}}, N_{j\mathrm{d}}, j \neq k}; k = 1, \ldots, E, \tag{29}$$

$$\sum_{i=1}^{E} N_{i\mathrm{s}} \left(\frac{\partial \mu_{i\mathrm{s}}}{\partial N_{k\mathrm{c}}}\right)_{N_{k\mathrm{d}}, V_{\mathrm{d}}, N_{j\mathrm{c}}, j \neq k} + A \left(\frac{\partial \sigma}{\partial N_{k\mathrm{c}}}\right)_{N_{k\mathrm{d}}, V_{\mathrm{d}}, N_{j\mathrm{c}}, j \neq k} = \chi \left(\frac{\partial r}{\partial N_{k\mathrm{c}}}\right)_{N_{k\mathrm{d}}, V_{\mathrm{d}}, N_{j\mathrm{c}}, j \neq k}; k = 1, \ldots, E, \tag{30}$$

and

$$\sum_{i=1}^{E} N_{i\mathrm{s}} \left(\frac{\partial \mu_{i\mathrm{s}}}{\partial V_{\mathrm{d}}}\right)_{N_{k\mathrm{d}}, N_{k\mathrm{c}}} + A \left(\frac{\partial \sigma}{\partial V_{\mathrm{d}}}\right)_{N_{k\mathrm{d}}, N_{k\mathrm{c}},} = \chi \left(\frac{\partial r}{\partial V_{\mathrm{d}}}\right)_{N_{k\mathrm{d}}, N_{k\mathrm{c}}}. \tag{31}$$

Similarly to Eq. 3 where the connection between the surface excess number of moles and the respective properties of both hypothetical phases is proposed, it is necessary here to suggest how the remaining excess quantities, the specific surface energy and the surface excess chemical potentials, are connected with the intensive properties of the hypothetical phases. At this point, we are free to suggest any connection arbitrarily; hence, in this work, we assume that the specific surface energy is a function of the inclusion curvature and the molar densities of both hypothetical phases as follows:

$$d\sigma = \left(\frac{\partial \sigma}{\partial r}\right)_{\rho_{i\mathrm{d}}, \rho_{i\mathrm{c}}} dr + \sum_{i=1}^{E} \left(\frac{\partial \sigma}{\partial \rho_{i\mathrm{d}}}\right)_{r, \rho_{ic}, \rho_{j\mathrm{d}}, j \neq i} d\rho_{i\mathrm{d}} + \sum_{i=1}^{E} \left(\frac{\partial \sigma}{\partial \rho_{ic}}\right)_{r, \rho_{i\mathrm{d}}, \rho_{j\mathrm{c}}, j \neq i} d\rho_{ic} \tag{32}$$

Here, $\rho_{ij} \equiv N_{ij}/V_j$ is the molar density of the component i in the hypothetical phase j. Although the specific surface energy may be identified with either the continuous phase or the dispersed phase alone, Eq. 32 is proposed because we are interested in possible changes of the properties of both hypothetical phases. Similarly, other concentration units may substitute molar densities; the molar densities are selected here, because they are directly related to the independent variables of the system. Indeed, physical and chemical arguments are needed to establish the exact relation between the specific surface energy and a particular system. However, Eq. 32 is general enough to include most particular cases considered from other standpoints. For instance, it is commonly assumed in vapor-liquid systems that the specific surface energy is independent of the composition of the vapor phase and the inclusion curvature, but it is considered as a function of the composition of the liquid phase. From these assumptions, the first term and one of the other two terms on the right-hand side of Eq. 32 would be canceled out in this particular case. Bearing this in mind, we have that Eq. 32 may be used to obtain the partial derivatives of the specific surface energy with respect to the independent variables of the system required in Eqs. 29–31 as follows:

$$\left(\frac{\partial\sigma}{\partial N_{k\mathrm{d}}}\right)_{N_{k\mathrm{c}},V_\mathrm{d},N_{j\mathrm{d}},j\neq k} = \left(\frac{\partial\sigma}{\partial r}\right)_{\rho_{i\mathrm{d}},\rho_{i\mathrm{c}}}\left(\frac{\partial r}{\partial N_{k\mathrm{d}}}\right)_{N_{k\mathrm{c}},V_\mathrm{d},N_{j\mathrm{d}},j\neq ki} + \left(\frac{\partial\sigma}{\partial\rho_{kd}}\right)_{r,\rho_{k\mathrm{c}},\rho_{j\mathrm{d}},j\neq k}\left(\frac{\partial\rho_{k\mathrm{d}}}{\partial N_{k\mathrm{d}}}\right)_{N_{k\mathrm{c}},V_\mathrm{d},N_{j\mathrm{d}},j\neq k}, + \left(\frac{\partial\sigma}{\partial\rho_{k\mathrm{c}}}\right)_{r,\rho_{k\mathrm{d}},\rho_{j\mathrm{c}},j\neq k}\left(\frac{\partial\rho_{k\mathrm{c}}}{\partial N_{k\mathrm{d}}}\right)_{N_{k\mathrm{c}},V_\mathrm{d},N_{j\mathrm{d}},j\neq k} \tag{33}$$

$$\left(\frac{\partial\sigma}{\partial N_{k\mathrm{c}}}\right)_{N_{k\mathrm{d}},V_\mathrm{d},N_{j\mathrm{c}},j\neq k} = \left(\frac{\partial\sigma}{\partial r}\right)_{\rho_{i\mathrm{d}},\rho_{i\mathrm{c}}}\left(\frac{\partial r}{\partial N_{k\mathrm{c}}}\right)_{N_{k\mathrm{d}},V_\mathrm{d},N_{j\mathrm{c}},j\neq k} + \left(\frac{\partial\sigma}{\partial\rho_{k\mathrm{d}}}\right)_{r,\rho_{k\mathrm{c}},\rho_{j\mathrm{d}},j\neq k}\left(\frac{\partial\rho_{k\mathrm{d}}}{\partial N_{k\mathrm{c}}}\right)_{N_{k\mathrm{d}},V_\mathrm{d},N_{j\mathrm{c}},j\neq k} + \left(\frac{\partial\sigma}{\partial\rho_{k\mathrm{c}}}\right)_{r,\rho_{k\mathrm{d}},\rho_{j\mathrm{c}},j\neq k}\left(\frac{\partial\rho_{k\mathrm{c}}}{\partial N_{k\mathrm{c}}}\right)_{N_{k\mathrm{d}},V_\mathrm{d},N_{j\mathrm{c}},j\neq k} \tag{34}$$

and

$$\left(\frac{\partial\sigma}{\partial V_\mathrm{d}}\right)_{N_{k\mathrm{d}},N_{k\mathrm{c}}} = \left(\frac{\partial\sigma}{\partial r}\right)_{\rho_{i\mathrm{d}},\rho_{i\mathrm{c}}}\left(\frac{\partial r}{\partial V_\mathrm{d}}\right)_{N_{k\mathrm{d}},N_{k\mathrm{c}}} + \sum_{i=1}^{E}\left(\frac{\partial\sigma}{\partial\rho_{i\mathrm{d}}}\right)_{r,\rho_{i\mathrm{c}},\rho_{j\mathrm{d}},j\neq i}\left(\frac{\partial\rho_{i\mathrm{d}}}{\partial V_\mathrm{d}}\right)_{N_{k\mathrm{d}},N_{k\mathrm{c}}} + \sum_{i=1}^{E}\left(\frac{\partial\sigma}{\partial\rho_{i\mathrm{c}}}\right)_{r,\rho_{i\mathrm{d}},\rho_{j\mathrm{c}},j\neq i}\left(\frac{\partial\rho_{i\mathrm{c}}}{\partial V_\mathrm{n}}\right)_{N_{k\mathrm{d}},N_{k\mathrm{c}}} \tag{35}$$

As the result of the geometrical relation $V_\mathrm{d} = 4\pi r^3/3$, $(\partial r/\partial V_\mathrm{d})_{N_{k\mathrm{d}},N_{k\mathrm{c}}} = 1/A$ and considering that the dispersed phase volume is held constant in Eqs. 33 and 34, $(\partial r/\partial N_{k\mathrm{d}})_{N_{k\mathrm{c}},V_\mathrm{d},N_{j\mathrm{d}},\, j\neq k} = 0$ and $(\partial r/\partial N_{k\mathrm{c}})_{N_{k\mathrm{d}},V_\mathrm{d}N_{j\mathrm{c}},\, j\neq k} = 0$. On the other hand, we have that $(\partial\rho_{k\mathrm{d}}/\partial N_{k\mathrm{c}})_{N_{k\mathrm{d}},V_\mathrm{d},N_{j\mathrm{c}},\ j\neq k} = 0$ because both the number of moles and the volume of the dispersed phase are kept constant in Eq. 34. Besides, from the definition $\rho_{ij} \equiv N_{ij}/V_j$, we also have that $(\partial\rho_{k\mathrm{d}}/\partial N_{k\mathrm{d}})_{N_{k\mathrm{c}},V_\mathrm{d},N_{j\mathrm{d}},j\neq k} = 1/V_d$ and $(\partial\rho_{i\mathrm{d}}/\partial V_\mathrm{d})_{N_{k\mathrm{d}},N_{k\mathrm{c}}} = -\rho_{i\mathrm{d}}/V_\mathrm{d}$. Similarly,$(\partial\rho_{k\mathrm{c}}/\partial N_{k\mathrm{d}})_{N_{k\mathrm{c}},V_\mathrm{d},N_{j\mathrm{d}},\ j\neq k} = 0$, $(\partial\rho_{k\mathrm{c}}/\partial N_{k\mathrm{c}})_{N_{k\mathrm{d}},V_\mathrm{d},N_{j\mathrm{c}},}j \neq k = 1/V_c$, and $(\partial\rho_{i\mathrm{c}}/\partial V_\mathrm{d})_{N_{k\mathrm{d}},N_{k\mathrm{c}}} = -\rho_{i\mathrm{c}}/V_\mathrm{c}$. From these partial derivatives, Eqs. 33, 34, and 35 simplify to

$$\left(\frac{\partial\sigma}{\partial N_{k\mathrm{d}}}\right)_{N_{k\mathrm{c}},V_\mathrm{d},N_{j\mathrm{d}},j\neq k} = \frac{1}{V_\mathrm{d}}\left(\frac{\partial\sigma}{\partial\rho_{k\mathrm{d}}}\right)_{r,\rho_{k\mathrm{c}},\rho_{j\mathrm{d}},j\neq k}, \tag{36}$$

$$\left(\frac{\partial\sigma}{\partial N_{k\mathrm{c}}}\right)_{N_{k\mathrm{d}},V_\mathrm{d},N_{j\mathrm{c}},j\neq k} = \frac{1}{V_\mathrm{c}}\left(\frac{\partial\sigma}{\partial\rho_{k\mathrm{c}}}\right)_{r,\rho_{k\mathrm{d}},\rho_{j\mathrm{c}},j\neq k}, \tag{37}$$

and

$$\left(\frac{\partial\sigma}{\partial N_\mathrm{d}}\right)_{N_{k\mathrm{d}},N_{k\mathrm{c}}} = \frac{1}{A}\left(\frac{\partial\sigma}{\partial r}\right)_{\rho_{i\mathrm{d}},\rho_{i\mathrm{c}}} - \frac{1}{V_\mathrm{d}}\sum_{i=1}^{E}\rho_{i\mathrm{d}}\left(\frac{\partial\sigma}{\partial\rho_{i\mathrm{d}}}\right)_{r,\rho_{i\mathrm{c}},\rho_{j\mathrm{d}},j\neq i} + \frac{1}{V_\mathrm{c}}\sum_{i=1}^{E}\rho_{i\mathrm{c}}\left(\frac{\partial\sigma}{\partial\rho_{i\mathrm{c}}}\right)_{r,\rho_{i\mathrm{d}},\rho_{j\mathrm{c}},j\neq i}. \tag{38}$$

From which, Eqs. 29, 30, and 31 reduce to

$$\sum_{i=1}^{E} N_{i\mathrm{s}}\left(\frac{\partial\mu_{i\mathrm{s}}}{\partial N_{k\mathrm{d}}}\right)_{N_{k\mathrm{c}},V_\mathrm{d},N_{j\mathrm{d}},j\neq k} + \frac{3}{r}\left(\frac{\partial\sigma}{\partial\rho_{k\mathrm{d}}}\right)_{r,\rho_{k\mathrm{c}},\rho_{j\mathrm{d}},j\neq k} = 0; k = 1,\ldots,E, \tag{39}$$

$$\sum_{i=1}^{E} N_{i\mathrm{s}}\left(\frac{\partial\mu_{i\mathrm{s}}}{\partial N_{k\mathrm{c}}}\right)_{N_{k\mathrm{d}},V_\mathrm{d},N_{j\mathrm{c}},j\neq k} + \frac{3}{r}\frac{V_\mathrm{d}}{V_\mathrm{c}}\left(\frac{\partial\sigma}{\partial\rho_{k\mathrm{c}}}\right)_{r,\rho_{k\mathrm{d}},\rho_{j\mathrm{c}},j\neq k} = 0; k = 1,\ldots,E, \tag{40}$$

and

$$\sum_{i=1}^{E} N_{i\mathrm{s}}\left(\frac{\partial\mu_{i\mathrm{s}}}{\partial V_\mathrm{d}}\right)_{N_{k\mathrm{d}},N_{k\mathrm{c}}} - \frac{3}{r}\sum_{i=1}^{E}\left[\rho_{i\mathrm{d}}\left(\frac{\partial\sigma}{\partial\rho_{i\mathrm{d}}}\right)_{r,\rho_{i\mathrm{c}},\rho_{j\mathrm{d}},j\neq i} - \frac{V_\mathrm{d}}{V_\mathrm{c}}\rho_{i\mathrm{c}}\left(\frac{\partial\sigma}{\partial\rho_{i\mathrm{c}}}\right)_{r,\rho_{i\mathrm{d}},\rho_{j\mathrm{c}},j\neq i}\right] = \frac{\chi}{A} - \left(\frac{\partial\sigma}{\partial r}\right)_{\rho_{i\mathrm{d}},\rho_{i\mathrm{c}}}. \tag{41}$$

Before going forward, it is worth highlighting from Eq. 41 that, if the actual system is kept unchanged, then

$$\left(\frac{\partial\sigma}{\partial r}\right)_{\rho_{i\mathrm{c}},\rho_{i\mathrm{d}}} = \frac{\chi}{A} = \left[\frac{d\sigma}{dr}\right], \tag{42}$$

where $[d\sigma/dr]$ is the well-known notional derivative.[30] Considering that the position of the dividing surface can be arbitrarily set through χ ($\chi = 0$ in the case of the surface of tension), the notional derivative accounts for changes of the specific surface energy with respect to the mathematical variation of the position of the dividing surface. The notional derivative affects only the description of the system, and therefore does not correspond to any physical change. On the other hand, in nucleation, the critical inclusion is considered as a tiny entity in comparison with the metastable-continuous phase; hence, the ratio of volumes in Eqs. 40 and 41 vanishes in this case. These equations suggest therefore that the specific surface energy derivative with respect to composition of the continuous phase should be removed from such expressions in the limit of nucleation. This might justify why this derivative does not appear in classical nucleation theories. However, this derivative becomes important for evolved macroscopic phases at equilibrium conditions, as will be seen immediately.

At this point, the surface excess chemical potentials μ_{is} are the only excess quantities whose relation with the hypothetical phases is missing. In the same way as the specific surface energy and the surface excess number of moles, the surface excess chemical potentials should be considered as a function of both hypothetical phases. However, in the problem of finding non-equilibrium inclusions in the context of classical nucleation theories, these excess quantities have been set equal to the respective quantities of either the continuous or the dispersed phases. In the former case, it is argued that the continuous phase is the only macroscopic phase during dispersed phase formation, and therefore the only phase with well-defined properties in advance,[6,26] whereas the latter case is justified by considering faster molecular diffusion inside the dispersed phase than the molecular diffusion from the continuous phase to the dispersed phase.[7,28] In this work, beyond the practical and theoretical consequences of these assumptions, we are interested in describing stable and unstable equilibrium states, where the surface excess chemical potentials must be equal to the respective quantities of both hypothetical phases, as shown by Eq. 10. Therefore, we are free to set up either $\mu_{is} = \mu_{ic}$ or $\mu_{is} = \mu_{id}$ without making assumptions about the physical behavior of the hypothetical phases. Thus, if $\mu_{is} = \mu_{ic}$, Eq. 39 leads to the conclusion that

$$\left(\frac{\partial \sigma}{\partial \rho_{k\mathrm{d}}}\right)_{r,\rho_{k\mathrm{c}},\rho_{j\mathrm{d}},j\neq k} = 0; k = 1, \ldots, E, \tag{43}$$

because $(\partial \mu_{ic}/\partial N_{k\mathrm{d}})_{N_{k\mathrm{c}},V_\mathrm{d},N_{j\mathrm{d}},j\neq k=0}$ as the result of keeping constant the volume and the number of moles of the continuous phase in the differentiation ($dV_\mathrm{c} = -dV_\mathrm{d}$). Equation 43 states that the specific surface energy derivatives with respect to the composition of the dispersed phase vanish as long as $\mu_{is} = \mu_{ic}$. If now the Maxwell equation

$$\left(\frac{\partial \mu_{ic}}{\partial V_\mathrm{c}}\right)_{N_c} = v_{ic} \Bigg/ \left(\frac{\partial V_\mathrm{c}}{\partial P_\mathrm{c}}\right)_{N_c} \tag{44}$$

is regarded together with the following thermodynamic relations:

$$\left(\frac{\partial \mu_{ic}}{\partial N_{k\mathrm{c}}}\right)_{V_\mathrm{c},N_i,i\neq k} = \left(\frac{\partial \mu_{ic}}{\partial N_{k\mathrm{c}}}\right)_{P_\mathrm{c},N_i,i\neq k} - v_{i\mathrm{c}} v_{k\mathrm{c}} \Bigg/ \left(\frac{\partial V_\mathrm{c}}{\partial P_\mathrm{c}}\right)_{N_\mathrm{c}} \tag{45}$$

and

$$\left(\frac{\partial \mu_{ic}}{\partial N_{k\mathrm{c}}}\right)_{P_\mathrm{c},N_i,\, i\neq k} = \frac{1}{N_\mathrm{c}} \sum_{l=1}^{E-1} \left(\frac{\partial \mu_{ic}}{\partial x_{l\mathrm{c}}}\right)_{P_\mathrm{c}} (\delta_{kl} - x_{i\mathrm{c}}) \tag{46}$$

substitution of Eqs. 43–46 into Eqs. 40 and 41 leads to

$$\sum_{i=1}^{E} N_{is} \left[\left(\frac{\partial \tilde{V}_\mathrm{c}}{\partial P_\mathrm{c}}\right)_{N_\mathrm{c}} \sum_{l=1}^{E-1} \left(\frac{\partial \mu_{ic}}{\partial x_{l\mathrm{c}}}\right)_{P_\mathrm{c}} (\delta_{kl} - x_{l\mathrm{c}}) - v_{i\mathrm{c}} v_{k\mathrm{c}} \right] = -A \left(\frac{\partial \ln \tilde{V}_\mathrm{c}}{\partial P_\mathrm{c}}\right)_{N_\mathrm{c}} \left(\frac{\partial \gamma}{\partial \rho_{k\mathrm{c}}}\right)_{\rho_\mathrm{d},\rho_{j\mathrm{c}},k\neq j}; k = 1, \ldots, E \tag{47}$$

and

$$\sum_{i=1}^{E} N_{is} v_{ic} = A \left(\frac{\partial \ln \tilde{V}_\mathrm{c}}{\partial P_\mathrm{c}}\right)_{N_\mathrm{c}} \sum_{j=1}^{E} \rho_{j\mathrm{c}} \left(\frac{\partial \gamma}{\partial \rho_{j\mathrm{c}}}\right)_{\rho\mathrm{d},\rho_{k\mathrm{c}},k\neq j}. \tag{48}$$

The symbol δ_{kl} denotes the Kronecker delta functions, $\tilde{V}_\mathrm{c} = V_\mathrm{c}/N_\mathrm{c}$ is the molar volume of the continuous phase, v_{ic} the partial molar volume of the component i in the continuous phase, and x_{ic} the respective mole fraction. In the aforementioned equations, the dividing surface is located by setting $\chi = 0$ again, and the capillary approximation ($\sigma \approx \gamma$) is used. This approximation uses the specific surface energy of planar interfaces γ for curved interfaces σ, which means that the specific surface energy does not depend explicitly on the inclusion size. The $E + 1$ Eqs. 47 and 48 are the final expressions of the Gibbs adsorption isotherm, which can be used to calculate the surface excess number of moles in an isothermal-isochoric-closed system. However, only E linearly independent equations are needed for the E unknown quantities (one for each component). It was found by numerical computations that Eq. 48 is a linear combination of the E Eq. 47 because the same values were obtained no matter whether $E - 1$ Eqs. 47 and 48 are considered in the calculations or just the E Eq. 47. It is important to stress that, in the specific case of nucleation, this system of equations is not defined, because the intensive properties of the continuous phase are set equal to the respective quantities of the metastable phase, in accordance with Eqs. 10 and 11. Therefore, this system of equations should not be used to calculate the surface excess number of moles for the nucleation process; it should be used only for equilibrium states between evolved phases. Finally, even though the aforementioned equations are derived for a system with just one inclusion, they remain valid for a system with several inclusions, because the surface area inclusion and the surface excess number of moles are the only properties depending directly on the number of inclusions.

Similarly, if now $\mu_{is} = \mu_{id}$ is assumed, it turns out that $(\partial \mu_{id}/\partial N_{k\mathrm{c}})_{N_{k\mathrm{d}},V_\mathrm{d},N_{j\mathrm{c}},\, j\neq k} = 0$, because the volume and the number of moles of the dispersed phase are held constant in the differentiation, that is, from Eq. 40 we obtain that

$$\left(\frac{\partial \sigma}{\partial \rho_{k\mathrm{c}}}\right)_{r,\rho_{k\mathrm{d}},\rho_{j\mathrm{c}},j\neq k} = 0; k = 1, \ldots, E. \tag{49}$$

Unlike Eq. 43, Eq. 49 shows that the specific surface energy derivative with respect to the composition of the continuous phase vanishes as long as $\mu_{is} = \mu_{id}$. If Eq. 49 is taken instead of Eq. 43, by a similar procedure to Eqs. 47 and 48, we obtain that

$$\sum_{i=1}^{E} N_{is} \left[\left(\frac{\partial \tilde{V}_\mathrm{d}}{\partial P_\mathrm{d}}\right)_{N_\mathrm{d}} \sum_{l=1}^{E-1} \left(\frac{\partial \mu_{id}}{\partial x_{l\mathrm{d}}}\right)_{P_\mathrm{d}} (\delta_{kj} - x_{l\mathrm{d}}) - v_{i\mathrm{d}} v_{k\mathrm{d}} \right] = -A \left(\frac{\partial \ln \tilde{V}_\mathrm{d}}{\partial P_\mathrm{d}}\right)_{N_\mathrm{d}} \left(\frac{\partial \gamma}{\partial \rho_{k\mathrm{d}}}\right)_{\rho_\mathrm{c},\rho_{j\mathrm{d}},k\neq j}; k = 1, \ldots, E \tag{50}$$

along with

$$\sum_{i=1}^{E} N_{is} v_{id} = A \left(\frac{\partial \ln \tilde{V}_\mathrm{d}}{\partial P_\mathrm{d}}\right)_{N_\mathrm{d}} \sum_{j=1}^{E} \rho_{j\mathrm{d}} \left(\frac{\partial \gamma}{\partial \rho_{j\mathrm{d}}}\right)_{\rho_\mathrm{c},\rho_{k\mathrm{d}},k\neq j}. \tag{51}$$

Here, $\tilde{V}_\mathrm{d} = V_\mathrm{d}/N_\mathrm{d}$ denotes the molar volume of the dispersed phase, v_{id} the partial molar volume of the component i in the dispersed phase, and x_{id} the corresponding mole fraction. As observed, these equations are the same as those given by Eqs. 47 and 48, but in terms of the intensive properties of the dispersed phase. Unlike the system of equations given by Eqs. 47 and 48, this system of equations can be used for the nucleation process because the intensive properties of the dispersed phase are allowed varying arbitrarily, that is, all the partial derivatives are nonzero in Eqs. 50 and 51. Therefore, to set μ_{is} equal to μ_{id} is the only option left to calculate the surface excess number of moles in the case of nucleation. However, the two options, $\mu_{is} = \mu_{ic}$ or $\mu_{is} = \mu_{id}$, may be considered for the stable equilibrium states between evolved macroscopic inclusions of the dispersed phase and the continuous phase.

So far, the surface of tension has been the only dividing surface taken into account; however, other dividing surfaces may be considered, one of them is the so-called König's dividing surface[36] or just "K" dividing surface,[28] which is set by

$$\sum_{i=1}^{E} N_{is} v_{ij} = 0. \tag{52}$$

The subscript j accounts for either the continuous or the dispersed phases. It has been proved that this dividing surface match the surface of tension as long as the specific surface energy is independent of the curvature.[7,28] In this work, this assumption has been taken implicitly through the capillary approximation in Eqs. 48 and 51. As observed from these same equations, however, this condition is not enough for the surface of tension to coincide with the König's dividing surface. Furthermore, it turns out that this assertion is correct, if and only if, at least one of the following conditions is additionally fulfilled: The reference hypothetical phase is incompressible or the specific surface energy does not depend on composition. It is worth underlining that just one condition has to be satisfied for these dividing surfaces to coincide with each other. If one assumes, for example, incompressibility of the reference phase, other effects, no matter how large, will not modify the equality between these two dividing surfaces. Finally, from the previous systems of equations, it follows that the aforementioned conditions not only establish when the two dividing surfaces coincide with each other but also, under what conditions the surface excess number of moles are unimportant for the equilibrium calculations. For instance, if the specific surface energy is independent of composition, the surface excess number of moles can be ignored in calculations.

Algorithm for Calculating the Equilibrium Radius

The generalized scheme to predict the equilibrium radius is based on the commonly used algorithms for the flash problem,[12–16] where the mass distribution of the equilibrium coexistence between two phases is calculated for a given z_{it}, T and P. In terms of the present notation, these approaches provide the molar phase fraction and the respective mole fractions of two actual phases at equilibrium conditions with planar dividing surfaces. To incorporate the interfacial contributions into this sort of two-phase equilibrium problem, new quantities were needed: the dispersed phase pressure, the equilibrium radius, the number of inclusions in the system, and the surface excess number of moles. This gives $E + 3$ additional quantities to be determined, bearing in mind that the specific surface energy is a dependent variable. On the other hand, we have the generalized Laplace's equation Eq. 9, the volume constraint Eq. 19, and the Gibbs adsorption isotherm in the form of either Eq. 47 or Eq. 50, that is, we have $E + 2$ new equations that are incorporated into the two-phase equilibrium problem. Thus, we are left with one degree of freedom for the two-phase equilibrium problem to be defined unambiguously. From a mathematical standpoint, any variable can be chosen as independent variable; however, none of them is an experimentally controllable variable. Hence, for analytical purposes, we are free to choose any variable as independent variable. Among the variables mentioned above, the number of inclusions in the system is the only quantity that is not connected with the interfacial region directly. By this reason, this quantity will be regarded as an additional degree of freedom for the calculation of two-phase equilibrium states where interfacial contributions are taken into account. The generalized scheme of the algorithm is summarized as follows

1. Given T, N_{t},V_{t},z_{it},λ.
2. Run two-phase flash calculations, using as initial estimates $P_{\mathrm{c}} = P_{\mathrm{c}}(T, \tilde{V}_{\mathrm{t}}, z_{1,\mathrm{t}}, \ldots, z_{E\mathrm{t}})$, $N_{is} = 0$ and $\gamma = 0$, with which Eq. 28 and related expressions are reduced to the conventional two-phase flash problem, that is, $P_{\mathrm{d}} = P_{\mathrm{c}}, z_{i\mathrm{h}}, = z_{i\mathrm{t}}, N_{\mathrm{h}} = N_{\mathrm{t}}$ and $K_i^{\mathrm{curve}} = K_i$.
3. Using the intensive properties from the two-phase flash problem, calculate the total number of moles of both hypothetical phases with the expressions $N_{\mathrm{d}} = N_{\mathrm{t}}(1 - \alpha)/(\lambda + \lambda^2 N_{\mathrm{s}}/N_{\mathrm{h}})$ and $N_{\mathrm{c}} = N_{\mathrm{h}} - \lambda N_{\mathrm{d}}$. On he other hand, calculate the molar volume of the dispersed phase $\tilde{V}_{\mathrm{d}} = \tilde{V}_{\mathrm{d}}(T, P_{\mathrm{d}}, x_{1\mathrm{d},\ldots,}x_{\mathrm{Ed}})$, the specific surface energy and the respective derivatives $\gamma = \gamma(T, P_{\mathrm{d}}, P_{\mathrm{c}}, x_{1\mathrm{d}}, \ldots, x_{\mathrm{E}d}, x_{1\mathrm{c}}, \ldots, x_{\mathrm{Ec}})$.
4. Determine the total volume of the dispersed phase $V_{\mathrm{d}} = N_{\mathrm{d}} \tilde{V}_{\mathrm{d}}$, the molar volume of the continuous phase $\tilde{V}_{\mathrm{c}} = (V_{\mathrm{t}} - \lambda V_{\mathrm{d}})/N_{\mathrm{c}}$, and the respective equilibrium radius $r_{\mathrm{E}} = \sqrt[3]{3V_{\mathrm{d}}/4\pi}$.
5. Calculate the surface excess number of moles $N_{is} = N_{is}(T, P_{\mathrm{d}}, P_{\mathrm{c}}, x_{1\mathrm{d}}, \ldots, x_{\mathrm{E}d}, x_{1\mathrm{c}}, \ldots, x_{\mathrm{Ec}}, A)$ using $A = 4\pi r_{\mathrm{E}}^2$, and then calculate N_{h} together with the respective mole fractions $z_{i\mathrm{h}}$.
6. Run two-phase flash calculations with the incorporation of the interfacial contributions, Eq. 28 and related expressions, using $P_{\mathrm{c}} = P_{\mathrm{c}}(T, \tilde{V}_{\mathrm{c}}, x_{1\mathrm{c}}, \ldots, x_{E\mathrm{c}})$ and $P_{\mathrm{d}} = P_{\mathrm{c}} + 2\gamma/r_{\mathrm{E}}$. Finally, return to step three until convergence of all variables.

To be able to compare the predicted equilibrium radius with experimental data, the current formalism deals, on the one hand, with the fact that the number of inclusions is not an experimentally controllable variable and, on the other hand, with the fact that size-distributions are observed in the experiments rather than a single size.[4,5] These theoretical limitations may be overcome by including the well-known population balance into the description of the two-phase equilibrium problems. The population-balance technique is used to account for both the size and the number of inclusions, and it parallels other balance approaches such as material and energy balances. In the context of classical nucleation theories, the corresponding treatment gives rise to the so-called equilibrium cluster size distributions.[2,7] These issues will be the concern of future works; however, for time being, the predicted equilibrium radius in this work may be understood as an average equilibrium radius of such size distributions.

Application of the Modified Rachford-Rice Equations to Nucleation

In principle, the equations derived earlier in this work allow the determination of any equilibrium state for first-order phase transitions, where interfacial contributions are important such as nucleation. Hence, it should be possible to derive the results of classical nucleation theories from Eq. 28 and associated expressions. To prove this statement, first Eq. 28 is evaluated at $\alpha = 1$, with which we have that

$$-\Psi(1, r_{\mathrm{E}}) = \sum_{i=1}^{E} \frac{z_{i\mathrm{h}}}{K_i^{\mathrm{curve}}} - 1 = 0. \tag{53}$$

This equation is the same as the expression inside the parenthesis from Eq. 18, with the exception of the combined mole fraction $z_{i\mathrm{h}}$ and K_i^{curve}. The continuous phase is a hypothetical phase in Eq. 53, whereas the homogeneous metastable phase is present in Eq. 18. At this point, it is worth pausing to explain what $\alpha = 1$ indicates. As can be seen from Eq. 27, α is defined as the molar phase fraction of the hypothetical continuous phase with respect to the combined moles of both hypothetical phases; thus, $\alpha = 1$ leads to $N_{\mathrm{c}} = N_{\mathrm{h}}$. If this result is inserted into Eq. 22, it follows that $N_{\mathrm{d}} = 0$, that is, the system is formed by the hypothetical continuous phase entirely. From this result and the system of equations given by either Eq. 47 or Eq. 50, we have that $N_{is} = 0$ because $A = 0$ in the absence of dispersed phase. In other words, if there is no a dispersed phase, there is no surface excess number of moles. This conclusion is also reached by taking the derivatives of the Gibbs adsorption isotherm with respect to the mole fraction of the dispersed phase. In this case, the following expression can be derived for two-component systems:[7,28,37]

$$N_{is} = \frac{4\pi r^3 \frac{d\gamma}{dx_{2\mathrm{d}}}}{\frac{v_{i\mathrm{d}}}{v_{j\mathrm{d}}}\left[r\left(\frac{\partial \Delta\mu_{j\mathrm{d}}}{\partial x_{2\mathrm{d}}}\right) + 2\gamma\left(\frac{\partial v_{j\mathrm{d}}}{\partial x_{2\mathrm{d}}}\right)\right] - \left[r\left(\frac{\partial \Delta\mu_{i\mathrm{d}}}{\partial x_{2\mathrm{d}}}\right) + 2\gamma\left(\frac{\partial v_{i\mathrm{d}}}{\partial x_{2\mathrm{d}}}\right)\right]}; \quad i = 1, 2; i \neq j, \tag{54}$$

where $\Delta\mu_i \equiv \mu_{i\mathrm{d}}(P_1, x_{1\mathrm{d}}, \ldots, x_{E\mathrm{d}}) - \mu_{i\mathrm{I}}(P_{\mathrm{I}}, z_{1\mathrm{t},} \ldots, z_{E\mathrm{t}})$. Considering that the thermodynamic properties derivatives with respect to composition of the dispersed phase are finite in general, it can be seen by inspection that the limit of Eq. 54 is zero as $r \rightarrow 0$. It is important to stress that this conclusion is based on the capillary approximation, where the specific surface energy does not depend explicitly on the curvature. From this result and Eq. 21, we find that $N_{is} = 0$ leads to $N_{i\mathrm{h}} = N_{i\mathrm{t}}$, and in consequence to $z_{i\mathrm{h}} = z_{i\mathrm{t}}$. Thus, if there is no dispersed phase, the properties of the hypothetical system coincide with the properties of the actual system in its homogeneous initial state (the metastable phase), that is, $\mu_{i\mathrm{I}} = \mu_{i\mathrm{c}}$ and $P_{\mathrm{I}} = P_{\mathrm{c}}$, which are the basic assumptions of nucleation theories as given by Eqs. 11 and 12. Finally, it can be verified that Eq. 18 arises from Eq. 53 as long as $z_{i\mathrm{h}} = z_{i\mathrm{t}}$; therefore, the unstable equilibrium state of nucleation may be defined from Eq. 28 at $\alpha = 1$.

The aforementioned discussion implies that the amount of mass inside the critical inclusions is so small that the composition of the metastable phase does not change, no matter how many inclusions are present. Hence, we have that the critical inclusion may also be understood as follows:

$$r_{\mathrm{C}} = \lim_{\alpha \to 1} r_{\mathrm{E}}(\alpha). \tag{55}$$

The critical radius is established as a limit because there must be inclusions to define a radius. Equation 55 leads to the conclusion that the determination of the critical inclusion of nucleation from Eq. 28 is similar to the determination of incipient new-phase formation points of a saturated phase. The difference lies in the definition of the molar phase fraction α; the molar phase fraction is defined from hypothetical phases in this work, whereas actual phases are used in the conventional definition of the molar phase fraction, that is, the difference lies in the incorporation of interfacial contributions into the conventional Rachford-Rice expressions. Another important implication of Eq. 53 lies in the effect of the interfacial region on the metastable phase properties. According to the respective argument, it does not matter how large the interfacial region becomes with respect to the bulk of the critical inclusion; in nucleation, the interfacial region has to be small enough with respect to the metastable phase for the corresponding properties not to be altered by its presence. This is the reason for why the excess surface quantities do not play any role in the determination of the intensive properties of the critical inclusion, at least, in the context of the Gibbs' approach.

Work to Form the Dispersed Phase

Once the equilibrium conditions have been established, the required work to form one inclusion of the dispersed phase with the continuous phase is obtained by substitution of Eqs. 9 and 10 into Eq. 1. If the surface of tension is used again, then this work is given by

$$W = \sum_{i=1}^{E} (\mu_{i\mathrm{c}} - \mu_{i\mathrm{I}})N_{i\mathrm{t}} + (P_{\mathrm{I}} - P_{\mathrm{c}})V_{\mathrm{c}} + \frac{4}{3}\pi r_{\mathrm{E}}^2\sigma. \tag{56}$$

Here, the first and second terms represent the chemical and volumetric contributions because of the change of state of the metastable-continuous phase, respectively. The last term is the surface work performed by the inclusion, which, in the case of the nucleation process, is called nucleation work $W_n = 4\pi r_{\mathrm{C}}^2\sigma/3$. The nucleation work is defined as the energetic barrier that has to be overcome by a molecular cluster to form an inclusion of the dispersed phase inside the homogeneous metastable phase. The surface work in Eq. 56 comes from combining the volume work and the surface work of one inclusion, fourth and sixth terms in Eq. 1, respectively. As observed, the nucleation work is retrieved from Eq. 56, if Eqs. 11 and 12 hold, that is, if fixed intensive properties of the metastable-continuous phase are assumed. Therefore, the conventional classical nucleation work implies neither chemical nor volume work of the original metastable phase. Although Eq. 56 accounts for the process work for just one inclusion, it is easy to show that its last term differs by a constant factor given by λ, when λ identical inclusions are considered.

Numerical Applications

To illustrate the results obtained previously, the equilibrium coexistence between macroscopic drops and a continuous vapor as well as the corresponding drop-nucleation is studied for hydrocarbon mixtures. To calculate the specific surface energy required in equilibrium calculations, the well-known Macleod-Sudgen correlation, better known as the Parachor model, is an appropriate model here, because it relies on the density of both liquid and vapor phases. Zuo and

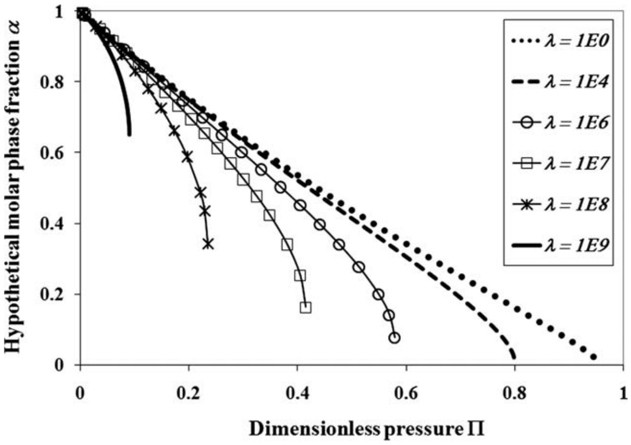

Figure 1. Effect of the number of drops on the hypothetical molar phase fraction for the equilibrium coexistence of drops into a vapor phase formed by propane, isobutane and butane with total molar composition in the system of 0.3, 0.3, and 0.4, respectively.

Stenby[38] fitted this model to hydrocarbon mixtures calculating vapor and liquid densities by using the Soave-Redlich-Kwong equation of state (SRK),[39] which, in turn, is also used here to calculate the fugacity coefficients. According to the Parachor model, the specific surface energy over planar interfaces is estimated by

$$\gamma = (\Theta_l - \Theta_v)^{3.66}. \tag{57}$$

Here, the subscripts l and v denote liquid and vapor phases, respectively. Θ is the so-called parachor which is calculated from

$$\Theta_j = \frac{1}{\rho_j} \sum_{k=1}^{C} \sum_{i=1}^{C} \rho_{i\hat{j}} \rho_{kj} \theta_{ik} \tag{58}$$

with

$$\theta_{ik} = \frac{\theta_i + \theta_k}{2}(1 - \varepsilon_{ik}), \tag{59}$$

where ε_{ik} is a symmetric binary interaction parameter ($\varepsilon_{ik} = \varepsilon_{kt}$), which is set equal to zero in this work. Zuo and Stenby suggested the following parachor correlation of pure components θ_i:

$$\theta_i = (8.21307 + 1.97473\omega_i) Tc_i^{1.03406} Pc_i^{0.82636}. \tag{60}$$

The units of the critical temperature T_C, the critical pressure P_C, and θ are K, bar and cm^3/mol(mN/m)$^{1/3.66}$, respectively. The symbol ω_i represents the acentric factor of the component i.

Equilibrium between macroscopic drops and a continuous vapor

Table I. Critical Properties

	Temperature, K	Pressure, MPa	Acentric factor
Propane	369.83	4.248	0.152
n-Butane	425.12	3.796	0.200
i-Butane	407.85	3.640	0.186

Figure 1 shows the hypothetical molar phase fraction α for the equilibrium coexistence of macroscopic drops into a vapor phase formed by propane, isobutane, and butane with total molar composition z_{it} of 0.3, 0.3, and 0.4, respectively. Critical properties for propane, isobutane, and butane are given in Table 1. In Figure 2 and Figure 3, the drop radius r_E and the ratio of total hypothetical number of moles to the total number of moles in the system are depicted. These quantities are determined as a function of a dimensionless pressure Π at constant number of drops λ and 343 K. The dimensionless pressure Π is defined as

$$\prod = \frac{P_c - P^{\mathrm{bv}}}{P^{\mathrm{bl}} - P^{\mathrm{bv}}}, \tag{61}$$

where superscripts bv and bl refer to the vapor and liquid phases on the binodal curve, respectively. This dimensionless pressure ranges from 0 to 1, being equal to zero when the entire continuous phase is a vapor, and being equal to one when the entire continuous phase is a liquid; hence, Π between 0 and 1 represents liquid-vapor mixtures inside the binodal curve. In Figures 1–3, Eq. 28 and associated equations provide the intensive properties of the hypothetical phases, and the system of equations given by Eq. 47 gives the surface excess number of moles. As observed, all the curves start on the same point when Π = 0, irrespective of the number of drops (inclusions) inside the system. This point coincides with the binodal curve, where the continuous phase is a homogeneous vapor entirely; therefore, in spite of the number of drops, they are so small under binodal conditions that the hypothetical molar phase fraction is practically equal to one. This statement can be confirmed precisely from Figure 2, where the drop radius falls down asymptotically at Π = 0, that is, the drops

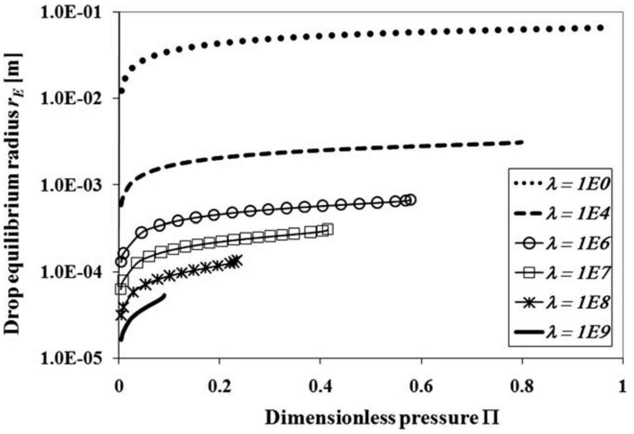

Figure 2. Effect of the number of drops on the equilibrium radius for the equilibrium coexistence of drops into a vapor phase formed by propane, isobutene and butane with total molar composition in the system of 0.3, 0.3, and 0.4, respectively.

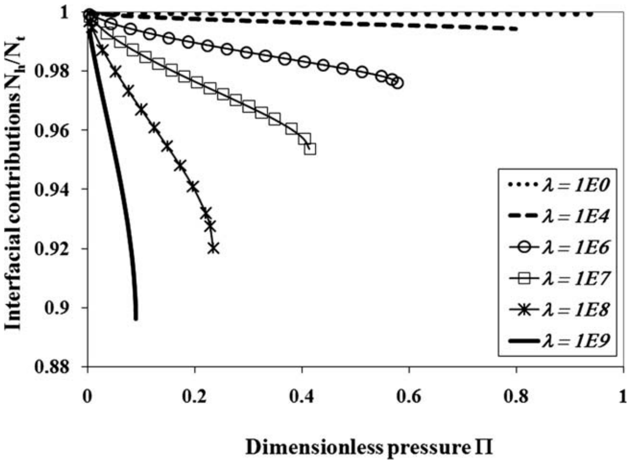

Figure 3. Effect of the number of drops on the interfacial contributions for the equilibrium coexistence of drops into a vapor phase formed by propane, isobutene and butane with total molar composition in the system of 0.3, 0.3, and 0.4, respectively.

become infinitely small in close proximity to the binodal curve. On the other hand, once the number of drops in the system is given, the more the dimensionless pressure increases, the more the hypothetical molar phase fraction of the continuous phase decreases, until a definite value is reached. It is not possible to find state variables to the right and below this point satisfying the necessary equilibrium conditions with a positive radius of drop. In other words, the equilibrium coexistence between macroscopic drops and the continuous vapor is not possible beyond this point. The respective hypothetical molar phase fraction of the dispersed phase ($\beta = 1 - \alpha$) at this point may be conceived as the maximum amount of dispersed phase that can be held within the continuous phase, and hence the corresponding drop size can be thought of as the largest one that can be fitted into the continuous phase under the given conditions. Finally, bearing in mind that the critical inclusion of nucleation can be defined from Eq. 28 as $\alpha \rightarrow 1$, it is important to highlight from Figure 1 that $\alpha < 1$ for the equilibrium states far away from the binodal curve; therefore, these equilibrium states do not represent the so-defined critical inclusion of nucleation. These equilibrium states, which can be either stable or unstable, account for the equilibrium coexistence between macroscopic drops and a continuous vapor phase, which is commonly known as fog.

It is interesting to note from Figure 2 that, even though the hypothetical molar phase fraction is a strong function of the number of drops inside the system in Figure 1, the drop radius remains almost constant far away from the binodal curve as the dimensionless pressure Π rises, while the number of drops is kept constant. These radii, on the contrary, are strongly dependent on the number of drops inside the system, at fixed dimensionless pressure Π; they become smaller with increasing drops number. The drop size is anticipated around centimeters when only one drop is set in the system, whereas the drop size is expected around micrometers when several hundreds of millions of drops are considered. These smaller radii lead to larger corrections to the total number moles of the system, as it can be observed from Figure 3, where the corrections to the hypothetical phases due to the interfacial contributions are assessed by means of the ratio of the total hypothetical number of moles to the total number of moles in the system N_h/N_t. The more different from one this ratio becomes, the more important the corrections to both hypothetical phases are due to interfacial contributions, that is, the interfacial contributions to the free energy of the entire system are negligible whenever the ratio N_h/N_t is equal to one, as can be seen from Eq. 22. Hence, it is important to notice that the ratio N_h/N_t reduces abruptly for the highest values of the number of drops inside the system as the dimensionless pressure increases, in spite of the fact that the radius is almost constant. To be precise, the interfacial contributions increase mostly because of a larger number of drops inside the system and not because of smaller inclusions. Interfacial contributions are usually considered essential only when large curvatures are present; however, Figures 2 and 3 show that interfacial contributions should be taken into account not only because of a size effect (tiny inclusions), but also because of an amount effect (enormous number of inclusions). In other words, if the interfacial contributions per drop are calculated and just one drop is taken into account, then we may conclude that the interfacial contributions to the free-energy change of the system are negligible; however, if hundreds of millions of drops are present in the system, then the interfacial contributions to the free-energy change may not be negligible. Therefore, the number of inclusions in the system is also an issue to be involved into the interfacial contributions. Finally, Figure 3 shows that the ratio N_h/N_t is approximately equal to one at $\Pi = 0$, regardless of the number of drops inside the system, because the dispersed phase inclusions and the corresponding surface area are so small that, in accordance with Eqs. 47 and 50, interfacial contributions are negligible when they are compared to volumetric contributions.

Liquid-drop nucleation from a metastable vapor phase

The critical radius calculated from Eq. 18 for liquid-drop nucleation from n-butane vapor is depicted in Figure 4 as a function of the so-called saturation ratio SR, which is defined as

$$\mathrm{SR} \equiv \frac{P_\mathrm{I}}{P_\mathrm{b}}. \qquad (62)$$

Here, P_b is the pressure on the binodal curve. The saturation ratio is a useful parameter whose purpose is to measure how far the system is from the binodal curve. For SR > 1, the vapor lies inside the binodal curve and it is named supersaturated vapor. If SR < 1 then the vapor lies outside the binodal curve and it is called subsaturated vapor. Finally, if SR $= 1$ then the vapor is a saturated vapor and it lies on the binodal curve. In Figure 4, the saturation ratio ranges from binodal to spinodal conditions of the vapor phase; thus, taking into account that the condition $\alpha \rightarrow 1$ is satisfied by Eq. 18, liquid-drop nucleation from a metastable vapor is shown in this figure. The predictions of Eq. 18 show that the

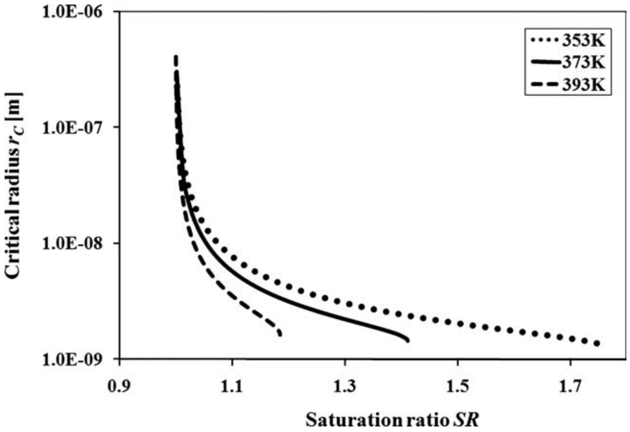

Figure 4. **Effect of temperature on the critical radius for one-drop nucleation from n-butane vapor as a function of the saturation ratio.**

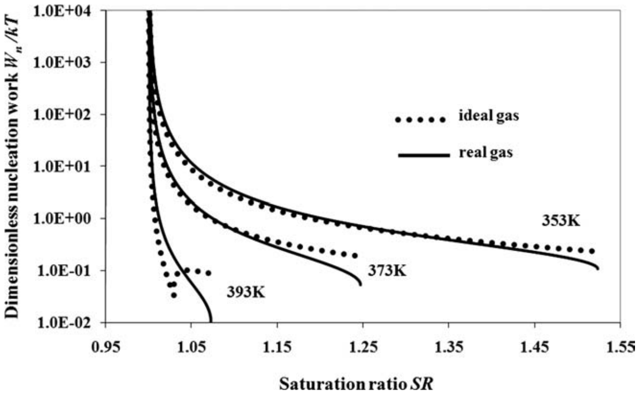

Figure 5. **Effect of the ideal-gas assumption on the dimensionless nucleation work of one drop from a vapor phase formed by propane, isobutane and butane with total molar composition in the system of 0.3, 0.3, and 0.4, respectively.**

critical radius is a weak function of temperature close to the binodal curve, whereas, on the contrary, the effect of the temperature becomes important as the saturation ratio moves away from binodal conditions. Besides, unlike the equilibrium between macroscopic phases where the radius of a drop becomes larger with increasing pressure of the continuous phase, Figure 4 shows that the critical radius of formation of a dispersed phase becomes smaller with increasing pressure of the metastable phase.

A common assumption in classical nucleation theories is to regard some type of ideality for obtaining a simpler description of the nucleation phenomenon. One of these assumptions is to consider that the metastable vapor phase is an ideal gas. In this work, this assumption is introduced by setting the fugacity coefficients of the metastable phase equal to one in Eqs. 15 and 16. Assuming that the metastable vapor phase behaves as both ideal and real gas, Figure 5 depicts the classical nucleation work of one drop within a metastable vapor as the ratio W_n/kT, where W_n refers to the classical nucleation work and k represents the Boltzmann's constant. In this figure, the number of critical inclusions is set equal to one, the saturation ratio ranges from the binodal curve to the spinodal curve of the vapor phase, and the same system as in Figure 1 is described. There are several interesting issues about Figure 5. First, the ideal gas assumption does not make any difference compared to the real gas case, except for conditions close to spinodal curve. This is a surprising result, because the dispersed phase pressure P_d for the ideal gas case is up to twice as high as it is for the real gas case, as can be seen from Figure 6 at 373 K. In addition, it is important to bear in mind that the equilibrium vapor pressure of the continuous phase on the binodal curve is about 22 bars at 373 K, which is a situation where the assumption of ideality is controversial. However, Figure 5 could explain why the assumption of perfect gas has been successfully used in nucleation problems. A second interesting issue comes from the fact that the W_n/kT derivative with respect to the saturation ratio is finite on the spinodal curve for the ideal gas case, but it becomes infinite for the real gas case. Often, it is claimed that classical nucleation approaches suffer from self-consistency problems, for example, the classical nucleation work does not vanish on the spinodal curve, as expected from stability considerations. However, Figure 5 shows that, for the real gas case, the classical work behavior is, at least, in qualitative agreement with the behavior expected on the spinodal curve. Similar conclusions have been obtained when the bulk properties of the critical inclusion are allowed varying arbitrarily.[40] In other words, the description of the bulk properties of both hypothetical phases may explain the classical work behavior on the spinodal curve rather than the used nucleation theory by itself. Finally, something unusual happens at 393 K, where the ideal gas curve twists up approximately at $S = 1.03$. Here, critical inclusions to the left belong to the so-called pseudo phases.[41] These pseudo phases provide well-behaved intensive properties of an invented phase when an actual phase is required under conditions where such actual phase does not exist. For instance, in order to calculate the critical radius through Eq. 18, the fugacity coefficients ratio of the

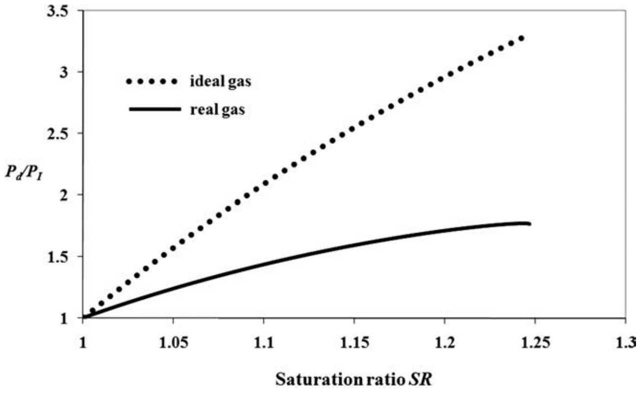

Figure 6. **Effect of the ideal-gas assumption on the dispersed phase pressure for one-drop nucleation from a vapor phase formed by propane, isobutane and butane with total molar composition in the system of 0.3, 0.3, and 0.4, respectively.**

dispersed and continuous phases is required, that is, the properties of both phases are needed. However, pressure, temperature or composition may lie on a region where one of these two phases does not exist, and therefore, the computational efforts fail without results. This is always a latent problem in equilibrium calculations. The pseudo-phase concept is a computational tool that, in the absence of a real phase, let calculations continue until convergence. In this work, the modulus of the complex compressibility factor from SRK equation of state is used to generate these pseudo phases.[42]

Conclusions

The incorporation of the surface excess number of moles and the interface curvature to the conventional Rachford-Rice equations allowed the determination of equilibrium states for first-order phase transitions from nucleation to the presence of evolved macroscopic phases by using the same classical thermodynamic framework. These generalized expressions not only provide the same information as the conventional Rachford-Rice equations, for example, the determination of incipient new-phase formation points on the binodal curve, but also provide information about equilibrium states where interfacial contributions are important such as nucleation. Thus, from these generalized expressions, it was shown that the interfacial contributions to the entire system have to be negligible for the intensive properties of the metastable phase to remain fixed during dispersed phase nucleation at equilibrium conditions, being this last statement the basic assumption of all nucleation theories. In addition, it was also shown that the number of inclusion is an important variable to be taken into account for describing the equilibrium coexistence between evolved macroscopic phases.

Finally, it was also demonstrated that the surface excess number of moles has to be a function of the intensive properties of just one hypothetical phase, from the theoretical standpoint; in particular, they are a function of the specific surface energy derivative with respect to composition and the isothermal compressibility of hypothetical phase chosen as reference phase.

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Notation

A = inclusion surface area, m^2
E = total number of components in the system
F = Helmholtz free energy, J
f_{ij} = fugacity of the component i in the phase j, MPa
K_i = equilibrium ratio of the component i over planar interfaces
K_i^{curve} = equilibrium ratio of the component i over curved interfaces
k = Boltzmann's constant, J/K
N = number of moles
P = pressure, MPa
P_{C} = critical pressure, MPa
r = location of either the dividing surface or the inclusion radius, m
r_{C} = critical radius of the dispersed phase Eq. 18, m
r_{E} = equilibrium radius of the dispersed phase Eq. 28, m
S = entropy, J/K
SR = saturation ratio Eq. 62
T = temperature, K
T_{C} = critical temperature, K
U = internal energy, J
V = volume, m^3
$\tilde{V}$ = molar volume, m^3/mol
W = required work to form an evolved inclusion at equilibrium conditions, J
W_{n} = nucleation work, J
x_{ij} = mole fraction of the component i in the phase j
$z_{i\mathrm{h}}$ = total mole fraction of component i in the hypothetical system
$z_{i\mathrm{t}}$ = total mole fraction of component i in the actual system

Greek letters

α = hypothetical molar phase fraction of the continuous phase Eq. 27
β = hypothetical molar phase fraction of the dispersed phase
χ = specific strain energy, N
δ_{kl} = Kronecker delta functions
Δ = change in a property between two thermodynamic states
ϕ_{ij} = fugacity coefficient of the component i in the phase j
γ = interfacial tension over planar interfaces, N/m
λ = number of inclusions in the system
μ_{ij} = chemical potential of the component i in the phase j, J/mol
v_{ij} = partial molar volume of the component i in the phase j, m^3/mol
Π = dimensionless pressure Eq. 61
Θ = parachor Eq. 58
θ = parachor correlation of pure components Eq. 60
ρ = molar density, mol/m^3
σ = specific surface energy, N/m
ω = acentric factor

Superscripts

bv = vapor phase at binodal conditions
bl = liquid phase at binodal conditions

Subscripts

b = properties of the dispersed and continuous phases on the binodal curve
c = continuous phase
d = dispersed phase
h = hypothetical system
I = metastable phase
i = component i
s = surface excess quantities
t = total property of the system/metastable phase

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