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Driving Force in First-Order Phase Transitions and Its Application to Gas Hydrate Nucleation from a Single Phase

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Classical nucleation theories of general application are taken as starting point to analyze the driving force for multicomponent gas hydrate nucleation from a single homogeneous phase. It is shown that the ratio between the specific surface energy and the critical radius of nucleation has a single value irrespective of the analyzed driving force expression. From this result, two driving force expressions for multicomponent gas hydrate nucleation are derived in the context of the so-called generalized nucleation theory, and it is demonstrated that the driving force for gas hydrates can be estimated using the same information given for the determination of the incipient formation points of the dispersed phase from a saturated phase. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 2433–2447, 2009

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Introduction

Gas hydrates are crystalline solids that are composed of water and organic small gas molecules. If these crystals form from natural gas components, the crystalline solids are called natural gas hydrates. The inorganic compounds called solid hydrates are ionic solids, whereas natural gas hydrates are nonstecheometric compounds whose composition depends on the operating temperature and pressure. Natural gas hydrates represent a potential problem for natural gas production, because gas hydrate accumulations block pipelines and equipments.[1] However, they also represent an attractive way of storing large quantities of gases.[2,3] Besides, it is believed that vast amounts of hydrocarbons are trapped in gas hydrate deposits.[4] To be able to deal with these applications, it is necessary to study the gas hydrates from different standpoints, of which the gas hydrate nucleation is of great significance.

In phase transitions of first order,[5] inclusions of a dispersed phase emerge and grow up at the expense of a

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homogeneous metastable phase until a thermodynamically stable state is reached by the system, where the resultant phases have intensive properties different from the respective quantities of the original metastable phase. The equilibrium coexistence between two macroscopic phases, the dispersed and continuous 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 homogeneous metastable phase. Nucleation theory is divided into kinetics and thermodynamics. Kinetics deals with the rate at which the phenomenon takes place and thermodynamics is devoted to its energetic requirements by the nucleation work, which is the most important parameter to be determined by nucleation theories. This work is defined as the energetic barrier that has to be overcome by molecular clusters to form inclusions of the dispersed phase inside the metastable phase. Although there are several ways to obtain the nucleation work,[6] the theories derived from the Gibbs' approach,[7] better known as classical theories, are still used due to their simplicity and in some instances, good results.

The continuous change of intensive properties throughout the interfacial region in a nonhomogeneous system is the first issue that has to be overcome by a classical theory, because homogeneous phases in internal equilibrium are required from the classical thermodynamic standpoint. To deal with this matter, Gibbs introduced a mathematical dividing surface in his work about equilibrium of heterogeneous substances.[7] This dividing surface is an artificial border inserted into the interfacial region by an arbitrary but convenient mathematical condition, and hence the phases constructed by such insertion are artificial phases, which are commonly called hypothetical phases. In the classical Gibbs' approach, the hypothetical phase enclosed by the dividing surface and surrounded by the continuous phase accounts for an inclusion of the dispersed phase. The differences between the properties of the actual system and the respective properties of the hypothetical phases are the so-called surface excess quantities.

The inclusion of the dispersed phase corresponding to the nucleation work, the well-known critical inclusion of the dispersed phase, comes from the search for stationary points of an appropriate thermodynamic potential, and a characteristic radius, the critical radius, determines its size. The critical inclusion is regarded as a tiny entity (a cluster of few molecules) when it is compared with the original metastable phase such that the usual assumption is to treat the intensive variables of the metastable phase as constant during dispersed phase formation. This assumption characterizes the nucleation process and it is the starting point for either classical or nonclassical nucleation theories.

Despite an exhaustive discussion about the nucleation phenomenon and its mathematical description for long, contradictory assertions are commonly found in the literature, even in the context of the classical nucleation theories. The existence of such disagreements is related, on the one hand, to the lack of opportunities to study nucleation phenomena directly from experiments, and on the other hand, to the absence of a satisfactory, in all respects, molecular theory. Several topics have been involved in the discussion, for example, the terms in the free-energy expression,[8] the necessary equilibrium conditions to be solved,[9] the proper dividing surface together with its connection with the specific surface energy,[10] the type of stationary point to which the nucleation work represents,[11] etc. In the case of the nucleation work, various authors consider the nucleation work as a maximum of the free-energy surface,[12,13] whereas others consider that the nucleation work corresponds to a saddle point.[8,14,15] The consensus is, however, to regard the nucleation work as an unstable equilibrium state of the free-energy surface. Similarly, a significant number of driving force equations has been suggested in the literature, and even though all they express a measure of the degree of metastability of the original homogeneous phase, there are discrepancies about the best way of calculating such degree of metastability. The problem of finding the driving force becomes more complicated when gas hydrate nucleation is involved in the discussion, because additional driving force expressions are proposed in this specific case.[13,16,17] The importance of the driving force lies in the fact that the nucleation work is an inverse function of the driving force. In this work, driving force expressions of general application are applied to the multicomponent gas hydrate nucleation from a single homogeneous phase. In addition, a complete derivation of the driving force expression given by both the revised nucleation theory (RNT)[8,14,18] and the generalized nucleation theory (GNT)[11,19] is presented in order to clarify the assumptions under which nucleation is tackled from the classical standpoint.

Thermodynamic Potential for an Isothermal-Closed System

Most driving force expressions of general application are defined from the corresponding necessary equilibrium conditions of nucleation, which, in turn, are determined by taking partial derivatives with respect to the independent variables of an appropriate thermodynamic potential of the system under consideration. Hence, the construction of such thermodynamic potential is the first task that has to be performed by a theory. This construction starts with the description of the system under study, which, in the current work, is an isothermal-closed system with E components, total volume V_t, total number of moles N_t, and temperature T. At first, the system is composed of a single homogeneous metastable phase with pressure P_I. Once the nucleation process has taken place, the system is composed of two macroscopic phases: the dispersed and continuous phases whose intensive properties are different from the respective quantities of the original metastable phase. In view of the fact that the necessary equilibrium conditions are given by specific thermodynamic states (stationary points) of the thermodynamic potential, the mathematical search for such stationary points requires, therefore, that the thermodynamic potential can account for not only equilibrium states but also nonequilibrium states. The main problem with such generalized thermodynamic potential is that extensions to nonequilibrium states of the classical thermodynamics are controversial by definition, because the classical thermodynamics arises from characterizing systems at equilibrium conditions or close to. Several authors have already performed the construction of thermodynamic potentials for equilibrium and nonequilibrium states of the nucleation process, where the intensive properties of the metastable phase are assumed constant, as mentioned before. There, an explicit modification of the fundamental thermodynamic relations is proposed[11,19,20] or a hypothetical force field is applied to the nonequilibrium inclusions of the dispersed phase so that the inclusions and the metastable phase can be assumed to be separately in internal equilibrium.[14,21] In what follows, the force-field approach will be used to obtain a generalized thermodynamic potential of the free-energy change in a closed-isothermal system, but thermodynamic states from nucleation to evolved macroscopic inclusions of the dispersed phase inside the continuous phase will be considered.

In this work, the Nishioka and Kusaka's approach is taken as starting point,[22] where the fundamental equation in its differential form for the internal energy U of one nonequilibrium cluster of the dispersed phase is:

$$dU = TdS^* + \sum_{i=1}^{E} \mu_{i\mathrm{d}}^* dN_{i\mathrm{d}}^* + \sum_{i=1}^{E} \mu_{i\mathrm{c}}^* dN_{i\mathrm{c}}^* - P_{\mathrm{c}} \eta R_{\mathrm{sph}}^2 dR_{\mathrm{sph}} + \eta d\varphi. \tag{1}$$

Here, S is the entropy, μ denotes the chemical potential, N is the number of moles, P is the pressure, η accounts for the interfacial contributions to the free energy, and φ represents the angle of a conical region intersected by a mathematical sphere with radius R_{sph}, whose center coincides with the center of the dispersed phase cluster. Although the radius R_{sph} is an arbitrary constant, it is supposed to be large enough so that the surrounding interfacial region is entirely included inside the sphere. The subscript i denotes the ith component, the superscript * indicates the bulk properties of the actual system far from the interfacial region, and the subscripts d and c refer to the dispersed and continuous phases, respectively. Although Eq. 1 is exact, it has the disadvantage that the last two terms depend on mathematical variables, which cannot be obtained experimentally. Therefore, it is necessary to rewrite Eq. 1 into a more practical expression, for which the classical Gibbs' approach is used. Once the dividing surface is inserted into the actual system, every term in Eq. 1 is rewritten as the difference between the values of the actual system and those of the hypothetical phases constructed by such insertion. Following Nishioka and Kusaka and Nishioka,[22,23] this difference for the mechanical work term is:

$$\eta d\varphi + \left\lfloor P_{\mathrm{c}} (dV_{\mathrm{c}})_{R_{\mathrm{sph}}} + P_{\mathrm{d}} dV_{\mathrm{d}} \right\rfloor = \sigma dA + \chi dr. \tag{2}$$

The subscript R_{sph} indicates that the radius of the sphere is kept constant. Here, σ represents the specific surface energy, V denotes the volume, r indicates the location of the dividing surface, and A is its surface area. Although χ is the strain energy connected with changes of the curvature, it is usually conceived as a degree of freedom to place the dividing surface. In Eq. 2, the first term on the right-hand side represents the surface work associated with changes in the surface area, and the latter term accounts for the strain work due to changes in the curvature of the dividing surface keeping invariant its surface area. Similarly, the difference for the chemical work terms is introduced as

$$\left(\sum_{i=1}^{E} \mu_{i\mathrm{d}}^* dN_{i\mathrm{d}}^* + \sum_{i=1}^{E} \mu_{i\mathrm{c}}^* dN_{i\mathrm{c}}^* \right) - \left(\sum_{i=1}^{E} \mu_{i\mathrm{d}} dN_{i\mathrm{d}} + \sum_{i=1}^{E} \mu_{i\mathrm{c}} dN_{i\mathrm{c}} \right) = \sum_{i=1}^{E} \mu_{i\mathrm{s}} dN_{i\mathrm{s}} \tag{3}$$

Moreover, the difference for the entropic terms can be written as

$$dS^* - (dS_{\mathrm{c}} + dS_{\mathrm{d}}) = dS_{\mathrm{s}}. \tag{4}$$

In the previous expressions, the subscript s denotes the so-called surface excess quantities, which, together with the two terms on the right-hand side in Eq. 2, may be called merely excess quantities. The substitution of Eqs. 2–4 into Eq. 1 results in

$$dU = TdS + \sum_{i=1}^{E} \mu_{i\mathrm{d}} dN_{i\mathrm{d}} + \sum_{i=1}^{E} \mu_{i\mathrm{c}} dN_{i\mathrm{c}} + \sum_{i=1}^{E} \mu_{i\mathrm{s}} dN_{i\mathrm{s}} - P_{\mathrm{c}} dV_{\mathrm{c}} - P_{\mathrm{d}} dV_{\mathrm{d}} + \sigma dA + \chi dr, \tag{5}$$

where $S = S_{\mathrm{c}} + S_{\mathrm{d}} + S_{\mathrm{s}}$. The above equation can be integrated in order to derive the Euler's fundamental equation:[14]

$$U = TS + \sum_{i=1}^{E} \mu_{i\mathrm{d}} N_{i\mathrm{d}} + \sum_{i=1}^{E} \mu_{i\mathrm{c}} N_{i\mathrm{c}} + \sum_{i=1}^{E} \mu_{i\mathrm{s}} N_{i\mathrm{s}} - P_{\mathrm{c}} V_{\mathrm{c}} - P_{\mathrm{d}} V_{\mathrm{d}} + \sigma A. \tag{6}$$

This equation is the sought expression for the internal energy of the system in terms of both hypothetical phases and the respective excess quantities. In addition to Eq. 6, it can be shown from Eq. 5 and the first fundamental equation for the phase j

$$dU_j = TdS_j + \sum_{i=1}^{E} \mu_{ij} dN_{ij} - P_j dV_j, \tag{7}$$

that the following expression has to be satisfied by the excess quantities:[19]

$$dU_{\mathrm{s}} = TdS_{\mathrm{s}} + \sum_{i=1}^{E} \mu_{i\mathrm{s}} dN_{i\mathrm{s}} + \sigma dA + \chi dr. \tag{8}$$

Integrating Eq. 8, then taking the differential of the resulting equation, and comparing with the same Eq. 8, the well-known Gibbs adsorption isotherm is obtained:

$$\sum_{i=1}^{E} N_{i\mathrm{s}} d\mu_{i\mathrm{s}} + A d\sigma = \chi dr. \tag{9}$$

Here, $\mu_{i\mathrm{s}}$ is the surface excess chemical potential. Equations 8 and 9 are fundamental relations between excess quantities; particularly Eq. 8 looks similar to Eq. 7. Hence, the excess quantities may be conceived as state functions of an "interfacial phase," better known as interface. This has been the most usual treatment given to the surface excess quantities. However, it is important to bear in mind that the excess quantities are mathematical corrections to the hypothetical phases because of introducing the dividing surface into the actual system. To be precise, unlike any other phase, the interface cannot be thermodynamically defined by itself. It is necessary, therefore, to propose connections between excess quantities and the hypothetical phases. This point is crucial for all excess quantities and determines the final expressions for the equilibrium coexistence between both hypothetical phases, we will return to this point later. In accordance with all above ideas, the word interface will be used for simplicity from now on.

Although the thermodynamic potential given by Eq. 5 describes both equilibrium and nonequilibrium states for inclusions from nucleation to macroscopic scales, the constraints for the system under consideration have not been taken into account yet. For an isothermal-closed system, these constraints are given by the volume constraint

$$V_{\mathrm{t}} = V_{\mathrm{d}} + V_{\mathrm{c}} \tag{10}$$

and by the mass constraints

$$N_{i\mathrm{t}} - (N_{i\mathrm{d}} + N_{i\mathrm{c}}) = N_{i\mathrm{s}}; \quad i = 1, \ldots, E \tag{11}$$

for the total number of moles of the component i in the system N_{it}. The former constraint establishes that the total volume is finite, and though the latter constraint is frequently conceived as a conventional mass balance, it actually defines the surface excess number of moles N_{is}. By this reason, Eq. 11 represents the mathematical correction to the combined number of moles of both hypothetical phases with respect to the actual total number of moles of the system. At this point, it is important to notice that the Helmholtz free energy F is the suitable thermodynamic potential for representing changes of state inside an isothermal–isochoric-closed system. Bearing this in mind and combining Eqs. 6, 10, and 11 together with the expression for the free energy of the homogeneous metastable phase $F_{\mathrm{I}} = \sum_{i=1}^{E} \mu_{i\mathrm{I}} N_{i\mathrm{t}} - P_{\mathrm{I}} V_{\mathrm{t}}$, the free-energy change between an arbitrary nonhomogeneous state and the homogeneous initial state of an isothermal-closed system is given by

$$\Delta F + \sum_{i=1}^{E} (\mu_{i\mathrm{d}} - \mu_{i\mathrm{I}}) N_{i\mathrm{d}} + \sum_{i=1}^{E} (\mu_{i\mathrm{c}} - \mu_{i\mathrm{I}}) N_{i\mathrm{c}} + \sum_{i=1}^{E} (\mu_{i\mathrm{s}} - \mu_{i\mathrm{I}}) N_{i\mathrm{s}} + V_{\mathrm{d}}(P_{\mathrm{I}} - P_{\mathrm{d}}) + V_{\mathrm{c}}(P_{\mathrm{I}} - P_{\mathrm{c}}) + \sigma A. \tag{12}$$

Here, the subscript I denotes conditions before the appearance of the dispersed phase inclusions, that is, the metastable phase. The second and fifth terms vanish for the nucleation process because of the assumption of constant intensive variables of the original metastable phase, that is, the intensive properties of the continuous phase coincide with the respective quantities of the homogeneous metastable phase in the limit of nucleation. This point will be tackled in detail in the following sections. By definition, the properties of both hypothetical phases and the excess quantities in Eq. 12 are dependent on the choice of the positions of the dividing surface, but the free-energy change of the system is independent of it.

Although the necessary partial derivatives in the search for stationary points can be directly calculated from Eq. 12, it is advisable for analytical purposes to derive the total differential of Eq. 12, given that in this way, the independent variables and the partial derivatives can be explicitly recognized. Thus, if the differential of Eq. 12 is calculated and the resulting expression is combined, on the one hand, with the Gibbs-Duhem equation for each one of the hypothetical phases, and on the other hand, with the differential forms of Eqs. 10 and 11: $dV_{\mathrm{d}} = -dV_{\mathrm{c}}$ and $dN_{i\mathrm{s}} = -(dN_{i\mathrm{d}} + dN_{i\mathrm{c}})$, then the following fundamental equation is obtained:

$$d(\Delta F) = \sum_{i=1}^{E} (\mu_{i\mathrm{d}} - \mu_{i\mathrm{c}}) dN_{i\mathrm{d}} + \sum_{i=1}^{E} (\mu_{i\mathrm{s}} - \mu_{i\mathrm{c}}) dN_{i\mathrm{s}} + \left(P_{\mathrm{c}} - P_{\mathrm{d}} + \frac{2\sigma}{r}\right) dV_{\mathrm{d}} + A d\sigma + \sum_{i=1}^{E} N_{i\mathrm{s}} d\mu_{i\mathrm{s}}. \tag{13}$$

In the above relation, a spherical geometry is assumed, and hence r represents both the position of the dividing surface and the inclusion radius. For a given position of the dividing surface, a fixed spherical geometry implies that the inclusion curvature changes only due to changes in the inclusion size. It is important to notice that the last two terms are connected through Eq. 9, and therefore, Eq. 13 can be equivalently written as

$$d(\Delta F) = \sum_{i=1}^{E} (\mu_{i\mathrm{d}} - \mu_{i\mathrm{c}}) dN_{i\mathrm{d}} + \sum_{i=1}^{E} (\mu_{i\mathrm{s}} - \mu_{i\mathrm{c}}) dN_{i\mathrm{s}} + \left(P_{\mathrm{c}} - P_{\mathrm{d}} + \frac{2\sigma}{r} + \frac{\chi}{A}\right) dV_{\mathrm{d}}. \tag{14}$$

Equations 13 and 14 are general and exact because neither the dividing surface has been located nor it has been set up how the surface excess chemical potentials and the specific surface energy are related to the state variables of the hypothetical phases. In an isothermal–isochoric-closed system, Eqs. 13 and 14 represent the total differential of the Helmholtz free-energy change between the homogeneous metastable phase and an arbitrary state formed by two phases, for example, the stable equilibrium coexistence between the evolved macroscopic inclusions of the dispersed phase and the continuous phase. Assumptions about the connection between the excess quantities and both hypothetical phases as well as the basic assumption of constant intensive properties of the metastable phase in the above fundamental equations give rise to the different necessary equilibrium conditions of nucleation and the corresponding driving force expressions.

Necessary Equilibrium Conditions

In an isothermal-closed system, the coefficients of the independent variables $N_{i\mathrm{d}}$, $N_{i\mathrm{s}}$, and V_{d} in Eq. 14 give directly the required partial derivatives of the free-energy change for determining the necessary equilibrium conditions between the dispersed and continuous phases. Strictly speaking, however, the surface excess numbers of moles are mathematical corrections, as discussed before. Hence, they cannot be independent variables of the system by themselves, but as the differential form of Eq. 11 establishes the connection between these excess quantities and the hypothetical phases, it is a matter of experimental or theoretical convenience the set of independent variables in Eq. 14. For instance, $N_{i\mathrm{d}}$, $N_{i\mathrm{c}}$, and V_{d} may be selected instead of $N_{i\mathrm{d}}$, $N_{i\mathrm{s}}$, and V_{d} without changing the general character of Eq. 14. Therefore, the general necessary equilibrium conditions from nucleation to stable equilibrium states are

$$\left[\frac{\partial(\Delta F)}{\partial N_{i\mathrm{d}}}\right]_{N_{i\mathrm{s}},V_{\mathrm{d}},N_{j\mathrm{d}},j\neq i} = \mu_{i\mathrm{d}} - \mu_{i\mathrm{c}} = 0, \tag{15}$$

$$\left[\frac{\partial(\Delta F)}{\partial N_{i\mathrm{s}}}\right]_{N_{i\mathrm{d}},V_{\mathrm{d}},N_{j\mathrm{s}},j\neq i} = \mu_{i\mathrm{s}} - \mu_{i\mathrm{c}} = 0, \tag{16}$$

and

$$\left[\frac{\partial(\Delta F)}{\partial V_{\mathrm{d}}}\right]_{N_{i\mathrm{d}},N_{i\mathrm{s}}} = P_{\mathrm{c}} - P_{\mathrm{d}} + \frac{2\sigma}{r} + \frac{\chi}{A} = 0. \tag{17}$$

Equations 15 and 16 are the well-known equalities of chemical potentials, and Eq. 17 is the generalized Laplace equation. The first two equations can be combined in order to yield,

$$\mu_{i\mathrm{s}} = \mu_{i\mathrm{d}} = \mu_{i\mathrm{c}}. \tag{18}$$

This equation provides not only necessary equilibrium conditions but also the connection between the surface excess chemical potentials and the hypothetical phases. This equation states constant chemical potentials 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. It is important to emphasize that Eqs. 17 and 18 are general equilibrium conditions that remain valid irrespective of the proposed relation between the specific surface energy and the hypothetical phases.

The revised nucleation theory (RNT)

As mentioned above, the nucleation process is characterized by the existence of so small inclusions such that it is assumed that the initial state of the continuous phase, the homogeneous metastable phase, is not altered by the emergence of inclusions of the dispersed phase. This condition leads, on one hand, to the constant chemical potential of the continuous phase

$$\mu_{i\mathrm{c}} = \mu_{i\mathrm{I}}, \tag{19}$$

and, on the other hand, to constant pressure of the continuous phase,

$$P_{\mathrm{c}} = P_{\mathrm{I}}. \tag{20}$$

In other words, the intensive properties of the continuous phase are kept constant and set equal to the respective quantities of the metastable phase. These assumptions can be introduced into Eqs. 17 and 18, with which the necessary equilibrium conditions for the specific case of nucleation are given by

$$P_{\mathrm{I}} - P_{\mathrm{d}} + \frac{2\sigma}{r_{\mathrm{C}}} + \frac{\chi}{A} = 0 \tag{21}$$

and

$$\mu_{i\mathrm{s}} = \mu_{i\mathrm{d}} = \mu_{i\mathrm{I}}. \tag{22}$$

Here, r_{C} represents the critical radius of the dispersed phase, which is defined as the inclusion size from which inclusions grow up spontaneously at the expense of the metastable phase, and hence smaller inclusions dissipate into the metastable phase. As mentioned before, this critical inclusion corresponds to a stationary point of an appropriate thermodynamic potential, Eqs. 21 and 22 in the case of RNT. These necessary equilibrium conditions can be transformed into a more practical expression governing the composition of the critical inclusion[8,14,18,24]:

$$\frac{\Delta\mu_i}{v_{i\mathrm{d}}} = \frac{\Delta\mu_j}{v_{j\mathrm{d}}} = \frac{2\sigma}{r_{\mathrm{C}}}. \tag{23}$$

Here, $v_{i\mathrm{d}}$ is the partial molar volume of the component i in the critical inclusion of the dispersed phase. In this expression, a constant ratio between thermodynamic properties for every component is shown, where the numerators are defined as

$$\Delta\mu_i = \mu_{i\mathrm{d}}(P_{\mathrm{I}}, x_{1\mathrm{d}}, \ldots, x_{E\mathrm{d}}) - \mu_{i\mathrm{I}}(P_{\mathrm{I}}, z_{1\mathrm{t}}, \ldots, z_{E\mathrm{t}}) \qquad i = 1, \ldots, E. \tag{24}$$

The numerators are the driving forces of RNT, where $z_{i\mathrm{t}}$ refers to the total mole fraction of the component i in the homogeneous metastable phase. Although Eq. 23 is a general expression, the incompressibility of the dispersed phase is assumed in its derivation. Assuming that the thermodynamic state of the metastable phase is known, Eq. 23 forms a system of $E - 1$ equations with $E - 1$ unknown quantities: The independent mole fractions $x_{i\mathrm{d}}$ of component i in the critical inclusion of the dispersed phase.

In the derivation of Eq. 23, the position of the dividing surface is located by setting $\chi = 0$, the well-known surface of tension. This dividing surface can equivalently be defined by the so-called notional derivate,[25] which satisfies

$$\left[\frac{d\sigma}{dr}\right] = \frac{\chi}{A}. \tag{25}$$

Considering that the position of the dividing surface may be arbitrarily set by χ, Eq. 25 accounts for the specific surface energy derivative with respect to the mathematical variation of the position of the dividing surface. In other words, the notional derivative affects only the description of the system, and does not correspond to physical changes. Hence, the surface of tension denotes a stationary point of such mathematical description, which corresponds to a minimum.[10]

In addition to Eq. 23, Eq. 22 may equally be expressed in terms of experimental variables by using the so-called fugacity $\boldsymbol{f_{ij}}$ of the component i in the phase j, which obeys the following relation:

$$(d\mu_{ij} = RTd \ln f_{ij})_{\mathrm{T},N_{ij}}. \tag{26}$$

In this equation, R denotes the universal gas constant. The fugacity was originally introduced to overcome those mathematical singularities for the chemical potential when an ideal gas behavior is regarded. This provides an appropriate way to characterize a phase when the pressure is an independent variable. Another useful property defined from the fugacity is the so-called fugacity coefficient ϕ_{ij}, which is defined as follows:

$$\phi_{ij} = \frac{f_{ij}}{x_{ij}P_j}. \tag{27}$$

Here, x_{ij} denotes the mole fraction of the component i in the phase j. According to the condition $\lim\limits_{P_j \to 0} \phi_{ij} = 1$, the fugacity coefficient is a nonideality measure, because any gas behaves as an ideal one as long as the pressure goes to zero. If the fugacity coefficient is approximately equal to one, an ideal gas is present in the system. Otherwise, a real gas, a liquid, or even a solid should be considered. Thus, if Eqs. 26 and 27 are combined for both hypothetical phases and the resulting expressions are introduced into Eq. 22, we have that

$$K_i^{\mathrm{curve}} \equiv \frac{z_{i\mathrm{t}}}{x_{i\mathrm{d}}} = \frac{P_\mathrm{d}}{P_\mathrm{I}}\frac{\phi_{i\mathrm{d}}}{\phi_{i\mathrm{I}}} = \left(1 + \frac{2\sigma}{r_\mathrm{C}P_\mathrm{I}}\right)\frac{\phi_{i\mathrm{d}}}{\phi_{i\mathrm{I}}} = \left(1 + \frac{2\sigma}{r_\mathrm{C}P_\mathrm{I}}\right)K_i. \tag{28}$$

Here, Eq. 21 is used to substitute the ratio $P_\mathrm{d}/P_\mathrm{I}$ and the surface of tension is used again. Equation 28 is similar to the equation proposed by Shapiro and Stenby for the capillary condensation,[26] except for the metastability condition of the original homogeneous phase. As observed, K_i^{curve} depends on the fugacity coefficients ratio of the dispersed and metastable phases $K_i = \phi_{i\mathrm{d}}/\phi_{i\mathrm{I}}$. This ratio, the so-called equilibrium constant, indicates how the component i distributes between two given phases with planar dividing surfaces at equilibrium conditions. The higher this ratio becomes, the higher the mole fraction is in the metastable phase. It is important to highlight that $K_i^{\mathrm{curve}} = K_i$ as long as $r \to \infty$, that is, they coincide for planar dividing surfaces. Therefore, the ratio K_i^{curve} physically expresses the same as K_i but for curved dividing surfaces.

It is interesting to notice from Eq. 28 that the following ratios have to be satisfied:

$$\frac{z_{i\mathrm{t}}\phi_{i\mathrm{I}}}{x_{i\mathrm{d}}\phi_{i\mathrm{d}}} = \frac{z_{j\mathrm{t}}\phi_{j\mathrm{I}}}{x_{j\mathrm{d}}\phi_{j\mathrm{d}}} = \frac{P_\mathrm{d}}{P_\mathrm{I}} = \left(1 + \frac{2\sigma}{r_\mathrm{C}P_\mathrm{I}}\right). \tag{29}$$

If the component E is chosen as a reference component, we obtain from this equation that

$$\frac{z_{i\mathrm{t}}\phi_{i\mathrm{I}}(z_{1\mathrm{t}}, \ldots, z_{E\mathrm{t}}, P_\mathrm{I})}{x_{i\mathrm{d}}\phi_{i\mathrm{d}}(x_{1\mathrm{d}}, \ldots, x_{E\mathrm{d}}, P_\mathrm{d})} - \frac{z_{E\mathrm{t}}\phi_{E\mathrm{I}}(z_{1\mathrm{t}}, \ldots, z_{E\mathrm{t}}, P_\mathrm{I})}{x_{E\mathrm{d}}\phi_{E\mathrm{d}}(x_{1\mathrm{d}}, \ldots, x_{E\mathrm{d}}, P_\mathrm{d})} = 0; \quad i = 1, \ldots, E-1 \tag{30}$$

and

$$\frac{P_\mathrm{d}}{P_\mathrm{I}} - \frac{z_{E\mathrm{t}}\phi_{E\mathrm{I}}(z_{\mathrm{It}}, \ldots, z_{E\mathrm{t}}, P_\mathrm{I})}{x_{E\mathrm{d}}\phi_{E\mathrm{d}}(x_{1\mathrm{d}}, \ldots, x_{E\mathrm{d}}, P_\mathrm{d})} = 0. \tag{31}$$

Assuming that the homogeneous metastable phase is known, Eqs. 30 and 31 form a system of E equations with E unknown quantities: The $E - 1$ mole fractions in the critical inclusion of the dispersed phase and the respective pressure. The mole fraction of the component E in the critical inclusion is calculated from

$$\sum_{i=1}^{E} x_{i\mathrm{d}} = 1. \tag{32}$$

As in the case of Eq. 23, Eqs. 30 and 31 do not depend on excess quantities. This system of equations is, however, more general because it does not rely on the incompressibility assumption.

Once the critical inclusion composition and the respective pressure have been calculated from the above system of equations, the critical inclusion size and the specific surface energy are the only unknown quantities in Eq. 29. A useful relation between these surface quantities and the system of equations given by Eqs. 30 and 31 can be obtained by inserting Eq. 28 into Eq. 32 to yield

$$\frac{2\sigma}{r_\mathrm{C}} = P_\mathrm{I}\left(\sum_{i=1}^{E}\frac{z_{i\mathrm{t}}}{K_i} - 1\right) \equiv \Phi. \tag{33}$$

From this equation, it is important to highlight that the expression on the right-hand side relies only on the intensive properties of the critical inclusion and the corresponding metastable phase. Hence, the use of Eqs. 30 and 31 implies that this expression is independent of any surface quantity, including the surface excess energy and the critical radius themselves. Furthermore, the value of this expression does not rely on assumptions about the connection between the specific surface energy and the intensive properties of both hypothetical phases, because the necessary equilibrium conditions, Eqs. 21 and 22, are independent of such connection. By this same reason, this assertion remains valid, if the well-known capillary approximation is used to determine the specific surface energy. This approximation uses the interfacial tension over planar interfaces γ to determine the specific surface energy over curved interfaces σ, which means that the specific surface energy does not rely explicitly on the inclusion curvature. The other implication of Eqs. 30 and 31 in the expression on the right-hand side of Eq. 33 lies in the fact that the intensive properties of the critical inclusion are determined, in turn, from a known metastable phase. This means that this expression relies only on the intensive properties of such metastable phase. By this reason, the ratio $2\sigma/r_{\mathrm{C}}$ on the left-hand side of Eq. 33 relies only on the metastable thermodynamic state of the original homogeneous phase as well, that is, the ratio between these surface quantities is only dependent on the bulk properties of the metastable phase. From this discussion, it follows that the ratio between the specific surface energy and the critical radius has a single value for a given metastable phase at equilibrium conditions, irrespective of the used method to determine the specific surface energy.

It is worth highlighting that the expression inside the parenthesis on the right-hand side of Eq. 33 is nothing but the commonly used expression for determining the incipient new-phase formation points on the binodal curve.[27,28] For instance, this expression determines the dew pressure of a saturated vapor in vapor–liquid systems when it is set equal to zero. Thus, we have that $2\sigma/r_{\mathrm{C}} \to 0$ close to the binodal curve, which implies that either $\sigma \to 0$ or $r_{\mathrm{C}} \to \infty$. The latter condition stands out because the incipient formation points of the dispersed phase on the binodal curve may be conceived as a nucleation process with planar interfaces, and therefore the incipient formation points of the dispersed phase can be estimated using the same expressions from the binodal curve to the spinodal curve. A critical inclusion with infinite radius is a mathematical concept that is controversial from the physical point of view, because an infinite metastable phase would be required for the intensive properties of such metastable phase to remain unvarying during dispersed phase nucleation. However, it is important to underline that this infinite radius arises from the condition $2\sigma/r_{\mathrm{C}} \to 0$ on the binodal curve, that is, it is not defined by itself. Thus, bearing in mind that the ratio $2\sigma/r_{\mathrm{C}}$ is related to the degree of metastability of the original phase via Eq. 33, an infinite critical radius physically expresses merely that such degree of metastability vanishes on the binodal curve.

The generalized nucleation theory (GNT)

Unlike Eq. 14, the specific surface tension and the surface excess chemical potentials appear as independent variables in Eq. 13. This situation represents a theoretical problem, because they cannot be treated as independent variables of the system; they are mathematical corrections, as discussed before. Hence, it is required to propose the connections between these excess quantities with the hypothetical phases in advance, before proceeding with the search for stationary points. If, as a postulate, the surface excess chemical potentials are set equal to the respective quantities of the continuous phase $\mu_{is} = \mu_{i\mathrm{c}}$ and Eq. 19, one basic assumption for the nucleation process, is applied, then the surface excess chemical potentials are equal to the respective values of the metastable phase, that is, $\mu_{is} = \mu_{i\mathrm{I}}$. These assumptions may be used to cancel out the second and last terms on the right-hand side in Eq. 13, and thus the surface excess chemical potentials and the surface excess number of moles disappear as independent variables. On the other hand, if the relation between the specific surface energy and the hypothetical phases is proposed to be

$$d\sigma = \left(\frac{\partial \sigma}{\partial r}\right)_{\rho_{i\mathrm{d}},\rho_{i\mathrm{c}}} dr + \sum_{i=1}^{E}\left(\frac{\partial \sigma}{\partial \rho_{i\mathrm{d}}}\right)_{r,\rho_{i\mathrm{c}},\rho_{j\mathrm{d}},j\neq i} d\rho_{i\mathrm{d}} + \sum_{i=1}^{E}\left(\frac{\partial \sigma}{\partial \rho_{i\mathrm{c}}}\right)_{r,\rho_{i\mathrm{d}},\rho_{j\mathrm{c}},j\neq i} d\rho_{i\mathrm{c}}, \quad (34)$$

where $\rho_{ij} = N_{ij}/V_j$ is the molar density of the ith component in the jth hypothetical phase, then the total differential of the specific surface energy $d\sigma$ may be eliminated from Eq. 13. Finally, if the postulates of nucleation theories, Eqs. 19 and 20, are used again, all the intensive variables of the continuous-metastable phase are fixed, with which the corresponding derivatives vanish and Eq. 13 transforms into

$$d(\Delta F) = \sum_{i=1}^{E}\left[\mu_{i\mathrm{d}} - \mu_{i\mathrm{I}} + \frac{3}{r}\left(\frac{\partial \sigma}{\partial \rho_{i\mathrm{d}}}\right)_{V_{\mathrm{d}},\rho_{i\mathrm{c}},\rho_{i\mathrm{d}},i\neq j}\right] dN_{i\mathrm{d}} + \left[P_{\mathrm{I}} - P_{\mathrm{d}} + \frac{2\sigma}{r} + \left(\frac{\partial \sigma}{\partial r}\right)_{\rho_{i\mathrm{d}},\rho_{i\mathrm{c}}} - \frac{3}{r}\sum_{i=1}^{E}\rho_{i\mathrm{d}}\left(\frac{\partial \sigma}{\partial \rho_{i\mathrm{d}}}\right)_{V_{\mathrm{d}},\rho_{i\mathrm{c}},\rho_{i\mathrm{d}},i\neq j}\right] dV_n \quad (35)$$

In Eq. 35, the excess quantities have been eliminated as independent variables, and therefore the stationary points can be obtained by setting directly the partial derivatives with respect to the remaining independent variables equal to zero, that is,[11,15,19,20]

$$\left[\frac{\partial(\Delta F)}{\partial N_{i\mathrm{d}}}\right]_{V_{\mathrm{d}},N_{j\mathrm{d}},j\neq i} = \mu_{i\mathrm{d}} - \mu_{i\mathrm{I}} + \frac{3}{r_{\mathrm{C}}}\left(\frac{\partial \sigma}{\partial \rho_{i\mathrm{d}}}\right)_{V_{\mathrm{d}},\rho_{i\mathrm{c}},\rho_{j\mathrm{d}},i\neq j} = 0 \quad (36)$$

and

$$\left[\frac{\partial(\Delta F)}{\partial V_{\mathrm{d}}}\right]_{N_{i\mathrm{d}}} = P_{\mathrm{I}} - P_{\mathrm{d}} + \frac{2\sigma}{r_{\mathrm{C}}} + \left(\frac{\partial \sigma}{\partial r}\right)_{\rho_{i\mathrm{d}},\rho_{i\mathrm{c}}} + \sum_{i=1}^{E}\rho_{i\mathrm{d}}(\mu_{i\mathrm{d}} - \mu_{i\mathrm{I}}) = 0. \quad (37)$$

These stationary points are basic results of GNT and give the conditions under which the critical inclusion emerges. The above derivations are just one possible way to obtain these results; consequently, the above approach does not necessarily coincide with assumptions and steps from other procedures. However, the derivations exposed in this work illustrate that the different necessary equilibrium conditions of nucleation may be derived from the same approach based on: a generalized thermodynamic potential for first-order phase transitions, the basic assumption of constant intensive properties of the metastable phase, and, if it is required, assumptions about the connection between the excess quantities and hypothetical phases.

In the above equations, the derivative $(\partial\sigma/\partial r)_{\rho_{i\mathrm{d}},\rho_{i\mathrm{c}}}$ accounts for the specific surface energy derivative with respect to the inclusion curvature (size of the inclusion when composition is constant) and not with respect to the position of the dividing surface. This real derivative coincides with the notional derivative as long as the so-called König's dividing surface is used or the surface excess chemical potentials are kept fixed.[14,29] In this work, the latter condition is fulfilled via $\mu_{is} = \mu_{i\mathrm{I}}$, and thus if the surface of tension is used again, this derivative vanishes from Eq. 37. Therefore, the surface of tension transforms Eq. 37 into

$$\frac{2\sigma}{r_\mathrm{C}} = P_\mathrm{d} - P_\mathrm{I} + \sum_{i=1}^{E} \rho_{id}(\mu_{i\mathrm{I}} - \mu_{id}) \equiv \Pi, \tag{38}$$

where Π is the driving force of GNT. Although Eq. 24 defines E driving forces (one for each component), Eq. 38 expresses the driving force through just one quantity.

In the previous section, it was shown that the ratio between the specific surface energy and the critical radius is fixed for a given thermodynamic state of the metastable phase, irrespective of the used method to calculate the specific surface energy. If this statement is a general result of nucleation, the ratio $2\sigma/r_\mathrm{C}$ calculated from Eq. 38 should take a single value for a given metastable phase and be equal to the ratio $2\sigma/r_\mathrm{C}$ calculated from Eq. 33, in spite of the connection between the specific surface energy and the hypothetical phases suggested by Eq. 34. In other words, the following postulate may be stated:

$$\frac{2\sigma}{r_\mathrm{C}} = \Pi = \Phi, \tag{39}$$

which comes from a comparison of the Eq. 33 with Eq. 38. In addition, if the surface of tension is used in Eq. 21, a comparison of the resulting expression with Eq. 39 results in

$$\frac{2\sigma}{r_\mathrm{C}} = \Pi = \Phi = P_\mathrm{d} - P_\mathrm{I} \equiv \Delta P. \tag{40}$$

Here, ΔP is the overpressure of the metastable phase, which has been suggested as another measure of the degree of metastability of the original homogeneous phase.[30] According to the postulate given by Eq. 40, the ratio $2\sigma/r_\mathrm{C}$ is a unique quantity that is independent of the classical driving force expression and that establishes, therefore, the connection between the different formalisms. If this assertion is correct, then it should be possible to obtain the same results irrespective of the driving force expression taken as starting point. In what follows, this assertion will be proved for the driving force expressions in gas hydrate nucleation.

Driving Force Expressions for Gas Hydrate Nucleation

In the case of gas hydrate nucleation, the basic expression for the driving force in a multicomponent mixture has been defined as[13,31]

$$\Delta g = \sum_{i=1}^{E} N_{id}\Delta\mu_i. \tag{41}$$

Δg is the degree of metastability of the original homogeneous phase, and $\Delta\mu_i$ is the driving force as given by Eq. 24. Equation 41 may be conceived as an overall driving force of RNT, which can be written in terms of the ratio $2\sigma/r_\mathrm{C}$ by inserting Eq. 23 into Eq. 41, that is,

$$\Delta g = \frac{2\sigma}{r_\mathrm{C}} \sum_{i=1}^{E} N_{id} v_{id} = \frac{2\sigma}{r_\mathrm{C}} V_\mathrm{d}. \tag{42}$$

In this expression, the fundamental relation $V_\mathrm{d} = \sum_{i=1}^{E} N_{id} v_{id}$ is used. Thus, if the postulate given by Eq. 40 is used to eliminate the ratio $2\sigma/r_\mathrm{C}$ in Eq. 42, we have that

$$\Delta g = \Pi V_\mathrm{d}, \tag{43}$$

which establishes the connection between the overall driving force of RNT and the driving force of GNT. According to Eq. 43, it should be possible to derive driving force expressions for multicomponent gas hydrate nucleation from either Eq. 38 or 41. In the following treatment, driving force expressions for multicomponent gas hydrate nucleation derived from Eq. 41 will be derived again, but starting with Eq. 38, and thus proving the postulate given by Eq. 40. First, it is advisable to rewrite Eq. 38 as follows:

$$\begin{aligned} \Pi V_\mathrm{d} = {} & (P_\mathrm{d} - P_\mathrm{I})V_\mathrm{d} + RT\sum_{i=1}^{E-1} N_{id} \ln\left(\frac{f_{i\mathrm{I}}}{f_{id}}\right) + RTN_\mathrm{wd}\ln\left(\frac{f_\mathrm{wI}}{\hat{f}^{0}_\mathrm{wI}}\right) \\ & - RTN_\mathrm{wd}\ln\left(\frac{f_\mathrm{wd}}{\hat{f}^{\beta}_\mathrm{wd}}\right) - RTN_\mathrm{wd}\ln\left(\frac{\hat{f}^{\beta}_\mathrm{wd}}{\hat{f}^{0}_\mathrm{wd}}\right) - RTN_\mathrm{wd}\ln\left(\frac{\hat{f}^{0}_\mathrm{wd}}{\hat{f}^{0}_\mathrm{wI}}\right). \end{aligned} \tag{44}$$

Here, Eq. 26 is used to substitute the chemical potentials by fugacities. The subscript w, which is assigned to the last component in the summation, denotes the water component, the superscripts 0 and β indicate the liquid water state and the hypothetical empty lattice state, respectively, and $\hat{f}_{ij}$ represents the fugacity of the component i in a single component phase evaluated at the pressure of the phase j. In the above equation, the ratio $f_\mathrm{wI}/f_\mathrm{wd}$ of the water fugacities is written in terms of four separated ratios, which account for different phase transitions of water. The well-known Van der Waals and Platteeuw adsorption model[32–34]

$$\ln\left(\frac{f_\mathrm{wd}}{\hat{f}^{\beta}_\mathrm{wd}}\right) = \sum\nolimits_j v_j \ln\left(1 - \sum\nolimits_k \theta_{jk}\right) \tag{45}$$

gives the phase transition from a hypothetical empty lattice state to the gas hydrate state. In the above equation, θ_{jk} is the fractional occupancy of the component k in the cavity j, and v_j gives the number of cavities of type j. On the other hand, the phase transition between liquid water and the empty lattice state is determined from[34,35]

$$\ln\left(\frac{\hat{f}^{\beta}_\mathrm{wd}}{\hat{f}^{0}_\mathrm{wd}}\right) = \ln\left(\frac{\hat{f}^{\beta}_\mathrm{wd}}{\hat{f}^{0}_\mathrm{wd}}\right)^{\#} + \frac{(\widetilde{V}^{\beta}_\mathrm{wd} - \widetilde{V}^{0}_\mathrm{wd})}{RT}(P_\mathrm{d} - P^{\#}), \tag{46}$$

where the molar volume of water $\widetilde{V}_\mathrm{wd}$ evaluated at the dispersed phase pressure is treated as constant, and the superscript # indicates a reference state. Similarly, the phase transition from liquid water at the metastable phase pressure to liquid water at the dispersed phase pressure can be calculated from

$$\ln\left(\frac{\hat{f}^{0}_{\mathrm{wd}}}{\hat{f}^{0}_{\mathrm{wI}}}\right) = \frac{\widetilde{V}^{0}_{\mathrm{w}}}{RT}(P_{\mathrm{d}} - P_{\mathrm{I}}), \tag{47}$$

provided that the liquid water neither evaporates nor crystallizes between P_d and P_{I}. Equations 45–47 transform Eq. 44 into

$$\begin{aligned}\Pi V_{\mathrm{d}} = (P_{\mathrm{d}} - P_{\mathrm{I}})V_{\mathrm{d}} + RT\sum_{i=1}^{E-1} N_{i\mathrm{d}} \ln\left(\frac{f_{i\mathrm{I}}}{f_{i\mathrm{d}}}\right)\\ + RTN_{\mathrm{wd}} \ln\left(\frac{f_{\mathrm{wI}}}{\hat{f}^{0}_{\mathrm{wI}}}\right) - RTN_{\mathrm{wd}} \sum\nolimits_{j} v_j \ln(1 - \sum\nolimits_{k} \theta_{jk})\\ - RTN_{\mathrm{wd}}\left[\ln\left(\frac{\hat{f}^{\beta}_{\mathrm{wd}}}{\hat{f}^{0}_{\mathrm{wd}}}\right)^{\#} + \frac{(\widetilde{V}^{\beta}_{\mathrm{wd}} - \widetilde{V}^{0}_{\mathrm{wd}})}{RT}(P_{\mathrm{d}} - P^{\#})\right]\\ - N_{\mathrm{wd}}\widetilde{V}^{0}_{\mathrm{w}}(P_{\mathrm{d}} - P_{\mathrm{I}}).\end{aligned} \tag{48}$$

To simply Eq. 48, we have that the driving force will be zero on the binodal curve, where the metastability vanishes by definition. In addition, according to Eq. 33, an infinite critical radius may be conceived for a dispersed phase inclusion on the curve binodal, which means that $P_{\mathrm{d}} = P_{\mathrm{I}}$ and $f_{i\mathrm{d}} = f_{i\mathrm{I}}$ in accordance with Eqs. 36 and 37. From these considerations, Eq. 48 reduces to

$$\begin{aligned}0 = RTN_{\mathrm{wb}} \ln\left(\frac{f_{\mathrm{wb}}}{\hat{f}^{0}_{\mathrm{wb}}}\right) - RTN_{\mathrm{wb}} \sum\nolimits_{j} v_j \ln(1 - \sum\nolimits_{k} \theta_{jk\mathrm{b}})\\ - RTN_{\mathrm{wb}}\left[\ln\left(\frac{\hat{f}^{\beta}_{\mathrm{wd}}}{\hat{f}^{0}_{\mathrm{wd}}}\right)^{\#} + \frac{(\widetilde{V}^{\beta}_{\mathrm{wb}} - \widetilde{V}^{0}_{\mathrm{wb}})}{RT}(P_{\mathrm{b}} - P^{\#})\right],\end{aligned} \tag{49}$$

where the subscript b indicates properties of the dispersed phase on the binodal curve. The subtraction of Eq. 49 from Eq. 48 yields

$$\begin{aligned}\Pi V_{\mathrm{d}} = (P_{\mathrm{b}} - P_{\mathrm{I}})V_{\mathrm{d}} + RT\sum_{i=1}^{E-1} N_{i\mathrm{d}} \ln\left(\frac{f_{i\mathrm{I}}}{f_{i\mathrm{b}}}\right)\\ + RT\sum_{i=1}^{E-1} N_{i\mathrm{d}} \ln\left(\frac{f_{i\mathrm{b}}}{f_{i\mathrm{d}}}\right) + RTN_{\mathrm{wb}} \ln\left(\frac{f_{\mathrm{wI}}\hat{f}^{0}_{\mathrm{wb}}}{f_{\mathrm{wb}}\hat{f}^{0}_{\mathrm{wI}}}\right)\\ - RTN_{\mathrm{wb}} \sum\nolimits_{j} v_j \ln\left(\frac{1 - \sum_k \theta_{jk}}{1 - \sum_k \theta_{jkb}}\right) - N_{wb}\widetilde{V}^{0}_{w}(P_{\mathrm{b}} - P_{\mathrm{I}})\end{aligned} \tag{50}$$

as long as $N_{\mathrm{wb}} = N_{\mathrm{wd}}$ and $P_{\mathrm{b}} = P_{\mathrm{d}}$. Similarly, if the number of moles of the component i in the critical inclusion of the dispersed phase is set equal to the corresponding quantity on the binodal curve, that is, if $N_{i\mathrm{b}} = N_{i\mathrm{d}}$ then $\hat{f}_{i\mathrm{d}} = \hat{f}_{i\mathrm{b}}$ and $\theta_{jk} = \theta_{j\mathrm{kb}}$. Thus, Eq. 50 simplifies to

$$\begin{aligned}\Pi V_{\mathrm{d}} = (P_{\mathrm{b}} - P_{\mathrm{I}})V_{\mathrm{d}} - N_{\mathrm{wb}}\widetilde{V}^{0}_{\mathrm{w}}(P_{\mathrm{b}} - P_{\mathrm{I}})\\ + RT\sum_{i=1}^{E-1} N_{i\mathrm{b}} \ln\left(\frac{f_{i\mathrm{I}}}{f_{i\mathrm{b}}}\right) + RTN_{\mathrm{wb}} \ln\left(\frac{f_{\mathrm{wI}}\hat{f}^{0}_{\mathrm{wb}}}{f_{\mathrm{wb}}\hat{f}^{0}_{\mathrm{wI}}}\right).\end{aligned} \tag{51}$$

Finally, assuming that the mole fraction of water in the metastable phase is very close to one, that is, assuming that $f_{\mathrm{wl}} = \hat{f}^{0}_{\mathrm{wl}}$ and $f_{\mathrm{wb}} = \hat{f}^{0}_{\mathrm{wb}}$, we find that

$$\Pi V_{\mathrm{d}} = (P_{\mathrm{b}} - P_{\mathrm{I}})V_{\mathrm{d}} - N_{\mathrm{wb}}\widetilde{V}^{0}_{\mathrm{w}}(P_{\mathrm{b}} - P_{\mathrm{I}}) + RT\sum_{i=1}^{E-1} N_{i\mathrm{b}} \ln\left(\frac{f_{i\mathrm{I}}}{f_{i\mathrm{b}}}\right). \tag{52}$$

This is the driving force expression suggested by Christiansen and Sloan,[36] which is the starting point of most works about gas hydrate nucleation.

On the other hand, considering that the number of water molecules and their chemical structure determine essentially the size and the properties of the hydrate inclusion, Anklam and Firoozabadi discarded the contributions to the driving force due to the change of state of the hydrate forming gases.[31] Thus, if these considerations are taken into account and an ideal solution is assumed again, Eq. 50 reduces to

$$\begin{aligned}\Pi V_{\mathrm{d}} = (P_{\mathrm{b}} - P_{\mathrm{I}})V_{\mathrm{d}} - N_{\mathrm{wb}}\widetilde{V}^{0}_{\mathrm{w}}(P_{\mathrm{b}} - P_{\mathrm{I}})\\ - RTN_{\mathrm{wb}} \sum\nolimits_{j} v_j \ln\left(\frac{1 - \sum_k \theta_{jk}}{1 - \sum_k \theta_{jk\mathrm{b}}}\right),\end{aligned} \tag{53}$$

which is the expression suggested by these authors to calculate the driving force for multicomponent gas hydrate nucleation. The assumptions involved in the derivation of Eqs. 52 and 53 coincide in essence with those given in the derivation of these equations starting with Eq. 41.[13,31] These results confirm the proposal given by Eq. 40, and therefore any expression from Eq. 40 can be used to determine the driving force for multicomponent gas hydrate nucleation.

In addition to be expressed in terms of the properties of the gas hydrates, Eqs. 52 and 53 offer the great advantage of allowing the calculation of the driving force for multicomponent gas hydrates straightforwardly, without iterative processes. On the contrary, the calculation of the driving force by any expression of Eq. 40 requires an iterative process, which consists of finding the intensive properties of the critical inclusion using, for example, the system of equations given by Eqs. 30 and 31. Despite this advantage, Eqs. 52 and 53 have the disadvantage of requiring the hydrate properties on the binodal curve, where the assumptions involved in the calculations may not coincide with those involved in the derivation of Eqs. 52 and 53. In addition, the calculation of the incipient hydrate formation point on the binodal curve may require an iterative process by itself. In this regard, the driving force expressions of Eq. 40 offer the advantage of determining the driving force without resorting to such incipient hydrate formation point. Furthermore, this two-phase equilibrium turns out to be a specific case of the driving force, as shown by Eq. 33. Finally, it is worth highlighting that the fugacity coefficients are a remarkable attribute of Eq. 33, because the fugacity coefficients may also be used in

Table 1. Geometry of Cells in Hydrate Crystal Structure I (sI)

Cavity	Small	Large
No. of cavitites/unit cell	2	6
av. Cavity radius (m)	3.95E-10	4.33E-10
Coordination number*	20	24
Volume of the unit cell (m^3)	1.73E-27	
No. of water molecules/unit cell	46	

*Number of oxygen at the periphery of each cavity.

the prediction of any stable equilibrium state where multicomponent gas hydrates are involved.[37] Therefore, the assumptions involved in the calculation of fugacity coefficients may be the only necessary assumptions to describe the equilibrium states of either nucleation or evolved macroscopic phases.

Classical Nucleation Work

The required work to form an evolved macroscopic inclusion of the dispersed phase starting with a homogeneous metastable phase in an isothermal-closed system is calculated directly from Eq. 12. In the case of nucleation, however, Eq. 12 reduces to[8,11,19–21,31]

$$\Delta F = \sum_{i=1}^{E}(\mu_{id} - \mu_{iI})N_{id} + \sum_{i=1}^{E}(\mu_{is} - \mu_{iI})N_{is} + V_d(P_I - P_d) + \sigma A, \quad (54)$$

because of Eqs. 19 and 20. It can be shown that this equation can also be derived by taking either the Gibbs free-energy change ΔG or the Grand free-energy change $\Delta\Omega$ as thermodynamic potentials,[14] that is, $\Delta F = \Delta G = \Delta\Omega$ in the limit of nucleation. In the same way as Eq. 12, the free-energy change is independent of the position of the dividing surface, but it is dependent on its curvature through the inclusion size. By inserting Eqs. 21 and 22 into Eq. 54, we have that the nucleation work W_n is given by

$$W_n = \frac{4}{3}\pi r_C^2 \gamma = \frac{16\pi\gamma^3}{3\Phi^2}. \quad (55)$$

Here, the surface of tension and the capillary approximation ($\sigma \approx \gamma$) are regarded in the derivation, together with the relations $V_d = 4\pi r_C^3/3$ and $A = 4\pi r_C^2$. The nucleation work comes from combining the volume work and the surface work of an inclusion, the last two terms in Eq. 54. Alternatively, by inserting Eqs. 17 and 18 into Eq. 12, we find that

$$W = \sum_{i=1}^{E}(\mu_{ic} - \mu_{iI})N_{it} + (P_I - P_c)V_c + \frac{4}{3}\pi r^2 \gamma. \quad (56)$$

Similar to Eq. 12, W is the required work to form an evolved macroscopic inclusion of the dispersed phase starting with a homogeneous metastable phase, but at equilibrium conditions. Here, the first and second terms account for the chemical and volumetric contributions to the work performed on the formation of the dispersed phase by the continuous-metastable phase. The nucleation work is retrieved from Eq. 56, if Eqs. 19 and 20 hold. Therefore, the conventional classical nucleation work implies neither chemical nor volume work of the continuous-metastable phase.

Equations 40 and 55 show that the critical radius and the nucleation work decreases with increasing driving force. Furthermore, in theory, the nucleation work should vanish on the spinodal curve. Although, according to Eq. 55, the same value of the nucleation work is calculated irrespective of the considered driving force expression, different approaches are suggested for the calculation of the interfacial tension. For example, the interfacial tension is regarded as a function of the molar densities of both hypothetical phases in GNT, whereas it is considered a function of the composition of the condensed phase in RNT. This is a crucial point in the determination of the nucleation work because intensive properties of the critical inclusion and the ratio $2\sigma/r_C$ rely only on the thermodynamic state of the metastable phase. This means that there is only one unknown quantity to be determined either the specific surface energy or the critical radius. However, bearing in mind that the radius of the critical inclusion is a mathematical concept, we are left only with the specific surface energy as experimental variable to be known by independent means.

Applications

To illustrate the results obtained in the previous sections, we will determine the driving force for the gas hydrate crystal structure I (sI) from a metastable phase formed by methane, carbon dioxide, and water. Relevant data for the hydrate parameters are given in Table 1 and for the methane, carbon dioxide, and water are given in Table 2. In the following examples, the critical inclusion composition and the corresponding pressure are calculated varying the metastable phase pressure at fixed temperature and composition from the binodal curve to the spinodal curve. This variation is expressed in terms of the so-called saturation ratio SR, which is defined as $SR = P_I/P_b$. The fugacity coefficients of the metastable phase are estimated using the Soave-Redlich-Kwong equation of state (SRK),[38] while the corresponding binary interaction parameters are taken from Munk and Skjold-Jørgensen.[35] Although the intensive properties of the critical inclusion can be obtained, in principle, by using Eqs. 30 and 31, this system of equations can be avoided in the particular case of gas hydrates, because the composition of the critical inclusion can be directly obtained from the

Table 2. Component Parameters

	Binary Interaction Parameters (SRK)			Kihara Parameters		
	Methane	Carbon dioxide	Water	ε/k, K	τ, m	a, m
Methane	0	0.093	0.55	154.54	3.17E-10	3.83E-11
Carbon dioxide	0.093	0	0.25	168.77	2.98E-10	6.81E-11
Water	0.55	0.25	0	n/d	n/d	n/d

fugacities of metastable phase without resorting to an iterative process. The connection between the composition of the critical inclusion and the fugacities of the metastable phase is given by

$$\theta_{kj} = \frac{C_{kj} f_{k\mathrm{I}}}{1 + \sum_{i=1}^{\mathrm{FG}} C_{ij} f_{i\mathrm{I}}}. \tag{57}$$

Here, C_{kj} denotes the Langmuir adsorption constant for the hydrate forming gas k in the cavity j. In the above equation, the summation is for all hydrate forming gases FG, excluding water. The evaluation of the Langmuir adsorption constant is performed via the integral[39]

$$C_{kj} = \frac{4\pi}{kT} \int_{0}^{R_{\mathrm{cvt}}-a} \exp\left[-\frac{\varpi(r_{\mathrm{g}})}{kT}\right] r_{\mathrm{g}}^{2} dr_{\mathrm{g}} \tag{58}$$

In this expression, k represents the Boltzmann's constant, R_{cvt} is the cell radius of the cavity, a is the radius of the spherical core, r_{g} is the distance of the guest molecule from the cavity center, and $\varpi(r_{\mathrm{g}})$ is the spherical symmetric cell potential, which is calculated from

$$\varpi(r_{\mathrm{g}}) = 2Z\varepsilon\left[\frac{\tau^{12}}{R_{\mathrm{cvt}}^{11} r_{\mathrm{g}}}\left(\delta^{10} + \frac{a}{R_{\mathrm{cvt}}} - \delta^{11}\right) - \frac{\tau^{6}}{R_{\mathrm{cvt}}^{5} r_{\mathrm{g}}}\left(\delta^{4} + \frac{a}{R_{\mathrm{cvt}}}\delta^{5}\right)\right] \tag{59}$$

and

$$\delta^{L} = \frac{1}{L}\left[\left(1 - \frac{r_{\mathrm{g}}}{R_{\mathrm{cvt}}} - \frac{a}{R_{\mathrm{cvt}}}\right)^{-L} - \left(1 + \frac{r_{\mathrm{g}}}{R_{\mathrm{cvt}}} - \frac{a}{R_{\mathrm{cvt}}}\right)^{-L}\right]. \tag{60}$$

Here, ε and τ are the respective Kihara parameters which are taken from Sloan.[39] In Eq. 57, the fugacities of the metastable phase are determined using the relation $f_{i\mathrm{d}} = f_{i\mathrm{I}} = \phi_{i\mathrm{I}} z_{i\mathrm{t}} P_{\mathrm{I}}$, which is Eq. 22 but in terms of fugacities and fugacity coefficients. The fractional occupancies from Eq. 57 allow the calculation of the composition of the critical inclusion via the equations,

$$n_k = v_1\theta_{k1} + v_2\theta_{k2} = \frac{x_{k\mathrm{d}}}{x_{\mathrm{wd}}} \tag{61}$$

and

$$x_{\mathrm{wd}} = \frac{1}{1 + \sum_{k=1}^{\mathrm{FG}} n_k}. \tag{62}$$

Once the composition of the critical inclusion has been determined, Eqs. 21 and 33 can be combined to yield,

$$\frac{P_{\mathrm{d}}}{P_{\mathrm{I}}} = \sum_{i=1}^{E} \frac{z_{i\mathrm{t}}\phi_{i\mathrm{I}}}{\phi_{i\mathrm{d}}}, \tag{63}$$

which can be solved together with Eq. 27 to obtain the critical inclusion pressure. Finally, the driving force is calculated using Eq. 33 and is expressed as either Φ or ΔP.

The calculation of the driving force via Eqs. 52 and 53 can be performed taking the intensive properties of the dispersed phase on the binodal curve calculated from the above procedure. In this work, however, the driving force is determined using the following expression:

$$\Pi = (P_{\mathrm{b}} - P_{\mathrm{I}})\left(1 - x_{\mathrm{wb}}\frac{\widetilde{V}_{\mathrm{w}}^{0}}{\widetilde{V}_{\mathrm{db}}}\right) + \frac{RT}{\widetilde{V}_{\mathrm{db}}}\sum_{i=1}^{E-1} x_{i\mathrm{b}} \ln\left(\frac{f_{i\mathrm{I}}}{f_{i\mathrm{b}}}\right) + \frac{RTx_{\mathrm{wb}}}{\widetilde{V}_{\mathrm{db}}}\ln\left(\frac{f_{\mathrm{wI}}\hat{f}_{\mathrm{wb}}^{0}}{f_{\mathrm{wb}}\hat{f}_{\mathrm{wI}}^{0}}\right). \tag{64}$$

The first term on the right-hand side corresponds to the mechanical contribution due to the change of the state of water, while the third term represents its chemical contribution. Similarly, the second term corresponds to the chemical contribution to the driving force due to the change of the state of the forming gases. This equation arises from dividing Eq. 51 by the critical inclusion volume and from avoiding the ideal solution assumption of Eqs. 52 and 53. Equation 64 may be considered as a representative expression of the driving force expressions that come from setting the intensive properties of the critical inclusion equal to the respective quantities on the binodal curve, and hence it should be adequate for a numerical comparison with Φ or ΔP. In Eq. 64, the molar volume of the critical inclusion is calculated from[1]

$$\widetilde{V}_{\mathrm{db}} = \frac{V_{\mathrm{cell}}\mathrm{MW}_{\mathrm{db}}NA}{M_{\mathrm{w}}\mathrm{MW}_{\mathrm{w}} + \sum_j\sum_i \theta_{ji\mathrm{b}} v_i \mathrm{MW}_{\mathrm{j}}}. \tag{65}$$

Here, V_{cell} is the volume of the unit cell, NA symbolizes Avogadro's constant, M_{w} denotes the number of water molecules per unit cell, MW_{j} represents the molar mass of the forming gas j, MW_{w} is the molar mass of water, and $\mathrm{MW}_{\mathrm{db}}$ represents the molar mass of the critical inclusion on the binodal curve, which is estimated using

$$M_{\mathrm{db}} = \frac{M_{\mathrm{w}}\mathrm{MW}_{\mathrm{w}} + \sum_j\sum_i \theta_{ji\mathrm{b}} v_i M_j}{M_{\mathrm{w}} + \sum_j\sum_i \theta_{ji\mathrm{b}} v_i}. \tag{66}$$

With regard to the molar volume of liquid water $\widetilde{V}_{\mathrm{w}}^{0}$, we have used the following expression:[40]

$$\ln(\widetilde{V}_{\mathrm{w}}^{0}) = -10.9241 + 2.5E - 4(T - 273.15) - 3.532E - 4[P_{\mathrm{b}} - 0.101325] + 1.559E - 7(P_{\mathrm{b}} - 0.101325)^{2}, \tag{67}$$

where the units of temperature and pressure are K and MPa, respectively.

Figure 1 shows the dispersed phase pressure corresponding to the critical inclusion, the metastable phase pressure and the driving force calculated from Eq. 64. In this figure, the metastable phase is a homogeneous vapor whose composition comes from the two-phase equilibrium between vapor and aqueous solution, where the pressure is set equal to the formation pressure of a sI gas hydrate at 278.15 K. In this two-phase equilibrium problem, the total molar composition is set equal to 0.4, 0.1, and 0.5 for methane, carbon dioxide,

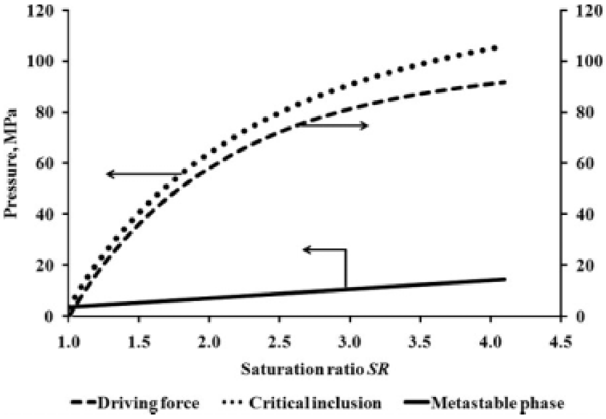

Figure 1. **Driving force Π calculated from Eq. 64 and pressures of the critical inclusion and the metastable phase for sI gas hydrate nucleation from a single homogenous vapor phase formed by methane, carbon dioxide, and water at 278.15 K.**

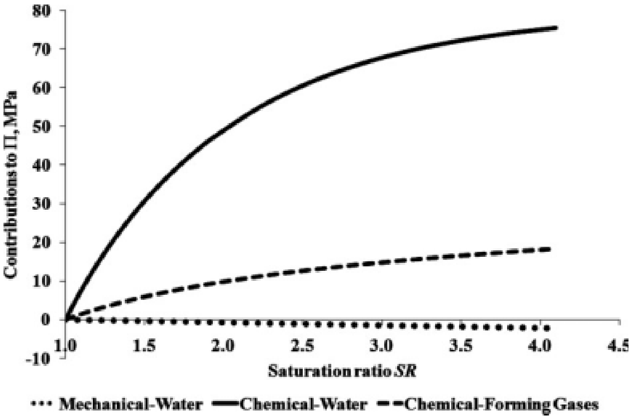

Figure 2. **Contributions to the driving force Π calculated from Eq. 64 for sI gas hydrate nucleation from a single homogenous vapor phase formed by methane, carbon dioxide, and water at 278.15 K.**

and water, respectively. Once the intensive properties of the vapor phase are calculated, the aqueous solution is discarded from the calculations so that the gas hydrate nucleation is determined from a solitary homogeneous vapor. As observed in this figure, the driving force calculated from Eq. 64 vanishes on the binodal curve ($SR = 1$) and increases monotonically up to the spinodal. Similarly, the critical inclusion pressure coincides with the metastable phase pressure on the binodal, which means the driving force calculated in the form of ΔP vanishes on this curve, in accordance with Eq. 40. If the driving force ΔP is calculated from Figure 1 far away from the binodal, we have that there is very little difference in comparison with Eq. 64 even on the spinodal curve. This is a surprising result because Eq. 64 is an expression that takes the binodal conditions as the reference state to describe the bulk properties of the critical inclusion, that is, the driving force ΔP should coincide with the driving force from Eq. 64 only at low saturation ratios. However, it has been shown that unless the intensive properties of the dispersed phase are allowed to vary arbitrarily for a given thermodynamic state of the metastable phase, different classical approaches lead to similar results far away from the binodal conditions.[41] Hence, the constant properties of a hydrate unit cell taken in the calculations (cavity radius, hydrate unit cell volume, etc.) may explain the agreement in the driving force in Figure 1. For example, these fixed values lead to molar densities almost constant with a difference of 1.3% between the binodal and spinodal curve. It has been suggested that all the hydrate properties should vary depending on the forming gas that occupies the cells, and therefore they should be a function of pressure and temperature.[40,42]

Figure 2 shows the chemical contribution of the forming gases, and the mechanical and chemical contributions of water corresponding to the driving force from Eq. 64, of which the chemical contribution of water is the most important. This contribution is usually negligible for most cases considered in the open literature, because it is usually assumed that hydrates form preferably into an aqueous phase, where the mole fraction of water is close to one because of the low solubility of the natural gas components in the liquid water. In this work, however, gas hydrate nucleation is determined starting from a vapor formed mostly by methane and carbon dioxide, where the mole fraction of water is close to zero. Hence, the contribution due to the nonideality of the solution plays an important role in this case.

The mole fractions corresponding to Figure 1 are shown in Figure 3. Although the concentration of water remains almost constant with increasing saturation ratio, the carbon dioxide and methane concentrations change continuously. This change, however, is different in each case, because the total amount of carbon dioxide reduces in the gas hydrate while the total amount of methane rises. This result

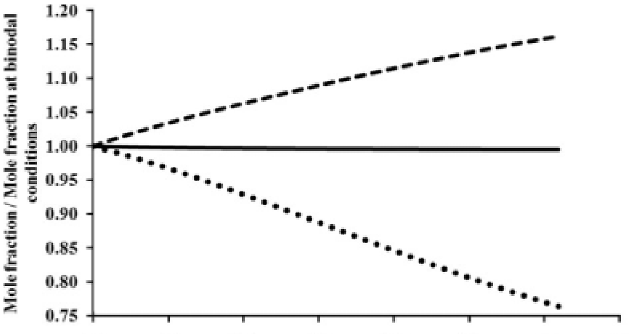

Figure 3. **Ratio between the mole fraction in the critical inclusion and the corresponding mole fraction on the binodal curve for sI gas hydrate nucleation from a single homogenous vapor phase formed by methane, carbon dioxide, and water at 278.15 K.**

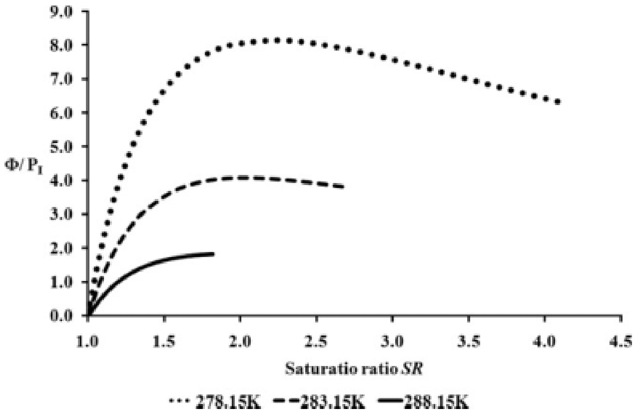

Figure 4. **Ratio between the driving force Φ and the metastable phase pressure as a function of temperature for sI gas hydrate nucleation from a single homogenous vapor phase formed by methane, carbon dioxide, and water.**

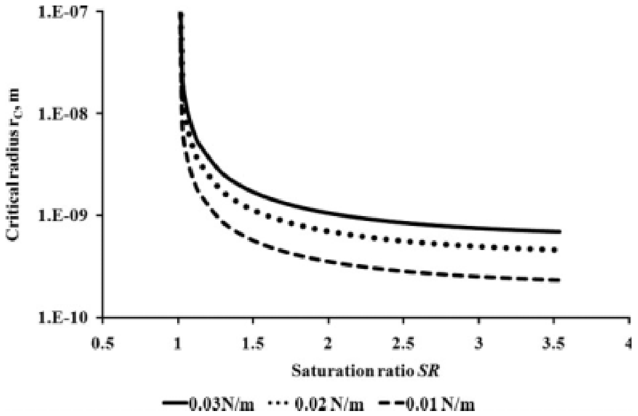

Figure 6. **Effect of the specific surface energy γ over planar interfaces on the critical radius for sI gas hydrate nucleation from a single homogenous vapor phase formed by methane, carbon dioxide, and water at 278.15 K.**

represents the displacement of carbon dioxide inside the gas hydrate cavities by methane. The opposite phenomenon, displacement of methane by carbon dioxide, has been proposed as the basic idea to confine carbon dioxide in the ocean.

In Figure 4, the driving force from Figure 1 is depicted but in the form of a ratio between the driving force Φ and the metastable phase pressure at three temperatures. As seen, the lower the temperature becomes, the higher the driving force is for a given saturation ratio, which is a logical result for a crystallization process. It is worth highlighting that a 10 K decrease leads to an increase of about four times in the driving force. This example illustrates the reason behind why the gas hydrate formation is a strong function of temperature.

Figure 5 depicts the nucleation work in the form of W_n/kT corresponding to the isotherms of Figure 4. As observed, though W_n/kT is a weak function of temperature close to the binodal curve, the effect of the temperature becomes important as the saturation ratio moves away from binodal conditions. On the other hand, the nucleation work decreases sharply at low saturation ratios, irrespective of temperature. The combination of these two effects may explain why the gas hydrate nucleation is so sensitive at small degrees of metastability. Anklam and Firoozabadi suggested that the larger derivatives of W_n/kT with respect to degree of metastability close to the binodal curve are responsible for the great scatter of experimental data at low driving forces.[31] However, the effect of temperature on the nucleation work was no taken into account in their proposal.

The critical radius and the nucleation work are shown in Figures 6 and 7 as functions of the interfacial tension. In these figures, the smaller the interfacial tension becomes, the smaller the critical radius and the nucleation work are. This result illustrates the reason behind why the nucleation work is related to the required work to form surface area inside the metastable phase. Finally, from these figures, it can be

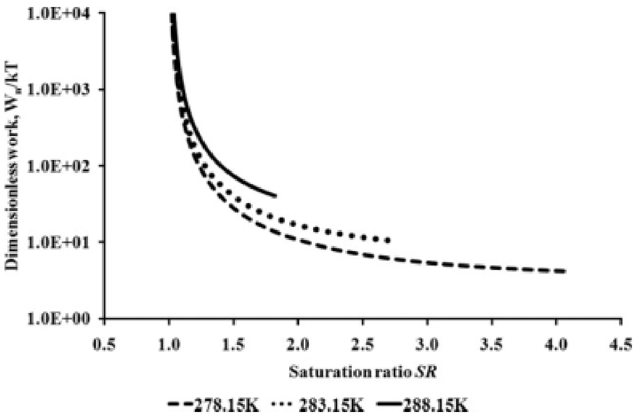

Figure 5. **Effect of temperature on the classical nucleation work of sI gas hydrate from a single homogenous vapor phase formed by methane, carbon dioxide, and water.**

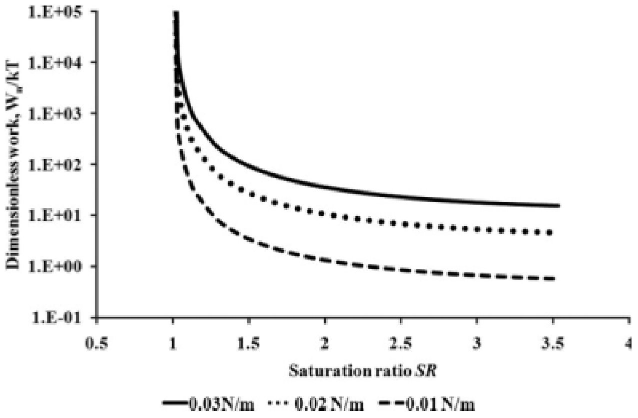

Figure 7. **Effect of the specific surface energy γ over planar interfaces on the classical nucleation work of sI gas hydrate from a single homogenous vapor phase formed by methane, carbon dioxide, and water at 278.15 K.**

numerically confirmed that the ratio $2\gamma/r_C$ is fixed for a given thermodynamic state of the metastable phase.

Conclusions

The critical inclusion of the nucleation process was described by the same expressions used for determining the incipient formation points of a new phase on the binodal curve. From this result, it was shown that the determination of the driving force of nucleation is possible without the incorporation of additional information or assumptions different from those given for the determination of the stable equilibrium state on the binodal curve. The use of the incompressibility assumption and other simplifications, however, does not give rise to a large difference in driving force for gas hydrate nucleation with respect to the general case, at least, from a numerical point of view. In addition, it was also demonstrated that the ratio between the specific surface energy and the critical radius has a single value for a given metastable phase, regardless of the suggested relation between the specific surface energy and the hypothetical phases of the system. Using this result, a connection between the basic driving force expression for multicomponent gas hydrate nucleation and the driving force expressions of general application was found. This connection allowed the determination of the driving force for gas hydrates using the driving force expressions from several classical nucleation theories. Thus, it was shown that the driving force expressions suggested by Anklam and Firoozabadi, and by Christiansen and Sloan for multicomponent gas hydrate nucleation can be obtained from the driving force expression of either the generalized nucleation theory or the revised nucleation theory.

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Notation

A = inclusion surface area, m^2
a = radius of the spherical core of the forming gas in a hydrate phase, m
C_{kj} = Langmuir adsorption constant for the forming gas k in the cavity j, MPa^{-1}
F = Helmholtz free energy, J
FG = number of hydrate forming gases
G = Gibbs free energy, J
f_{ij} = fugacity of the component i in the phase j, MPa
$\hat{f}_{ij}$ = fugacity of the component i in one-component phase at the pressure of 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
M = number of molecules per hydrate unit cell
MW = molar mass
N = number of moles
NA = Avogadro's constant, 6.023×10^{23} molecules/mol
P = pressure, MPa
R = universal gas constant, 8.314 J/mol K
r = location of the dividing surface or the inclusion radius, m
r_{C} = critical radius of the dispersed phase, m
R_{cvt} = cell radius of the cavity in a hydrate unit cell, m
r_{g} = distance of the guest molecule from the cavity center in a hydrate unit cell, m
R_{sph} = radius of the mathematical sphere in Eq. 1, m
S = entropy, J/K
SR = saturation ratio
T = temperature, K
U = internal energy, J
V = volume, m^3
$\widetilde{V}$ = molar volume, m^3/mol
V_{cell} = volume of a hydrate unit cell, m^3
W = required work to form an evolved macroscopic inclusion of the dispersed phase, J
W_{n} = nucleation work, J
x_{ij} = mole fraction of the component i in the phase j
$x_{i\mathrm{d}}$ = mole fraction of the component i in the dispersed phase d
Z = coordination number of the cavity in a hydrate unit cell
$z_{i\mathrm{t}}$ = total mole fraction of component i in the metastable phase

Greek letters

ε, τ = Kihara parameters
χ = specific strain energy, N
Δ = change in a property between two thermodynamic states
Δg = overall driving force of RNT, J
$\Delta\mu_i$ = driving force of RNT, J/mol
ΔP = overpressure of the metastable phase, MPa
Φ = generalized driving force, MPa
Ω = Grand free energy, J
ϕ_{ij} = fugacity coefficient of the component i in the phase j
γ = interfacial tension over planar interfaces, N/m
η = interfacial contributions to the free energy defined by Eq. 1, N
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 = driving force of GNT, MPa
φ = angle of a conical region intersected by a mathematical sphere with radius R_{sph}, rad
θ_{jk} = fractional occupancy of the component k in the cavity j in the hydrate unit cell
ρ = molar density, mol/m^3
σ = specific surface energy, N/m
v_j = number of cavities of type j in a hydrate unit cell
$\overline{\omega}(r_{\mathrm{g}})$ = spherical symmetric cell potential, J

Superscripts

β = hypothetical empty lattice in a hydrate unit cell
0 = liquid water
# = reference state

Subscripts

b = properties of the dispersed phase on the binodal curve
c = continuous phase
d = dispersed phase
I = metastable phase
i = component i
s = surface excess quantities
t = total property of the system/metastable phase
w = water
* = bulk properties of the actual system far from the interfacial region

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