

Thermodynamics of crystal nucleation in multicomponent droplets: Adsorption, dissociation, and surface-stimulated nucleation

Y. S. Djikaev^{a)}

NRC Associateship, NASA Ames Research Center, Moffett Field, California 94035

A. Tabazadeh

NASA Ames Research Center, Earth Sciences Division, Moffett Field, California 94035

H. Reiss

Department of Chemistry and Biochemistry, University of California–Los Angeles, Los Angeles, California 90095

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We extend our previous work on crystallization of unary liquids [Djikaev *et al.*, *J. Phys. Chem. A* **106**, 10247 (2002)] to multicomponent systems and develop the Gibbsian thermodynamics of the crystallization of multicomponent liquid solutions (bulk as well as droplets). Our treatment takes into account the possibility of formation of a solid phase from a nonstoichiometric liquid solution (noncongruent solidification). Using the capillarity approximation and taking into account both dissociation and surface adsorption effects, we derive the reversible work of formation of a crystal nucleus in homogeneous and pseudoheterogeneous modes (the density difference between crystal and liquid phases is also taken into account). In the former mode, the nucleus forms homogeneously within the (supercooled) bulk liquid solution, while in the latter mode, it forms “pseudoheterogeneously” at the liquid–vapor interface. Comparison of the works of formation in the two modes provides an inequality which must hold in order for pseudoheterogeneous crystal nucleation to be thermodynamically favored over the homogeneous process. As for unary systems, this inequality is identical to the condition of partial wetting of at least one crystal facet by its melt, i.e., the effects of adsorption and dissociation do not explicitly alter the thermodynamic condition for surface-stimulated crystallization in multicomponent systems. These effects do play an important role in determining the crystal nucleation mode, because they contribute to the liquid–vapor and liquid–solid surface tensions that enter the condition of partial wetting. The influence of these effects on the freezing behavior of droplets is expected to depend on the droplet size. © 2003 American Institute of Physics. [DOI: 10.1063/1.1559034]

I. INTRODUCTION

Crystallization process in pure systems has long been assumed to initiate within the volume of the supercooled phase.^{1–3} However, it has been known for some time, from a number of molecular dynamics simulations on small clusters,⁴ that the crystalline nucleus most often appears to form at or very near the surface layer. In addition, there is now evidence from analysis of laboratory data that the nucleation of ice⁵ in supercooled water droplets and the nucleation of hydrates of nitric acid⁶ in concentrated aqueous nitric acid droplets may also initiate at the droplet surface layer. Thus there is some support from analyses of laboratory data on the freezing of supercooled solution droplets that crystallization in some single component (ice–water) and binary systems (aqueous nitric acid–hydrates) may initiate at the droplet surface.

In a recent paper⁷ we presented a thermodynamic theory, based on the capillarity approximation, for the reversible work of formation of a crystal nucleus in a supercooled

single component melt. We evaluated and compared the work of nucleus formation at the melt surface to that within its volume in order to determine the condition under which surface nucleation is thermodynamically favored over bulk phase nucleation. This thermodynamic condition⁷ is identical to the condition of partial wetting (nonzero contact angle) of at least one of the crystal facets by the melt. In other words, if a liquid only partially wets at least one of the facets of the crystal nucleus, then the initiation of the crystal nucleation in this single component system is thermodynamically favored on the surface of the melt compared to crystal nucleation within its bulk.

The observed behavior of crystallization in the ice–water system⁵ provides some support for the validity of the partial wetting criterion as an indicator of the thermodynamic favorability of surface as opposed to volume nucleation in single-component systems. Optical studies on the surface melting of ice show that water only partially wets the ice surface,⁸ which may help to explain why ice nucleation in supercooled water appears to initiate at the surface layer.⁵ Furthermore, molecular dynamic simulations⁴ of crystallization in small clusters, in many single component systems, clearly show evidence for the appearance of the crystalline

^{a)} Author to whom correspondence should be addressed. Electronic mail: djikaev@chem.ucla.edu

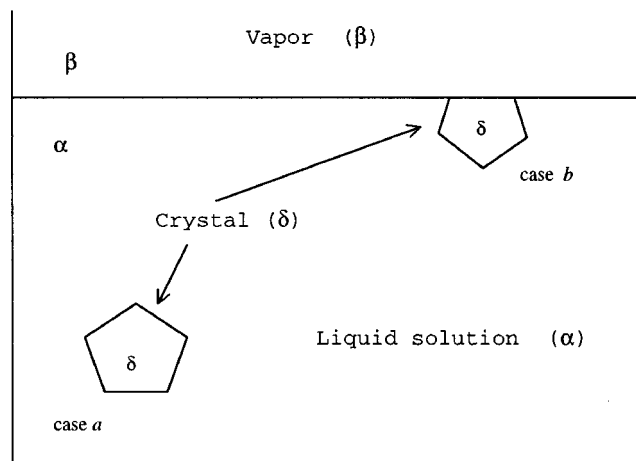


FIG. 1. Multicomponent liquid solution in a container. (a) Homogeneous crystal formation within the solution. (b) Pseudoheterogeneous crystal formation at its interface with the vapor mixture.

nucleus near or at the surface layer. Besides thermodynamics, kinetic factors also play an important role in determining the mode of crystallization. In this study we only focus on the thermodynamics of the crystallization process.

In this paper we extend our previous treatment⁷ to multicomponent systems in an attempt to determine the thermodynamic condition(s) under which surface nucleation is favored over the volume process. In a multicomponent system, a mixture of vapors of several components replaces the simple vapor of a single-component system. The thermodynamics will be complicated not only by the presence of several components, but also by the need to consider the surface adsorption of all components as well as their dissociation into ions.⁹

It should be noted that there is currently some indirect laboratory evidence for aqueous nitric acid⁶ that crystallization in this binary system appears to initiate at the surface layer. The analysis presented in Ref. 6 suggests that the rate of the crystal nucleation process is most likely governed by the rate of nucleus formation at the surface of the melt. In contrast, according to the classical theory of homogeneous crystal nucleation, the nucleation rate is determined only by the rate of nucleus formation within the volume of the melt.

II. THERMODYNAMICS OF CRYSTAL NUCLEATION IN MULTICOMPONENT SOLUTIONS

Going beyond our previous work,⁷ we will now study crystallization in a liquid multicomponent solution either in a container (Fig. 1) or in droplets (Fig. 2) in equilibrium with the corresponding vapor mixture. Crystallization will take place in the liquid solution if it is in a metastable (supercooled) state.

The formation of a crystal may occur either (1) within the bulk liquid or in the interior of the droplet, or (2) at the interface of the bulk liquid or droplet with the surrounding medium. Focusing on the freezing of liquid drops in the atmosphere (or other fluid media), we will not be interested in the crystal nucleation at “liquid–container” interfaces, but

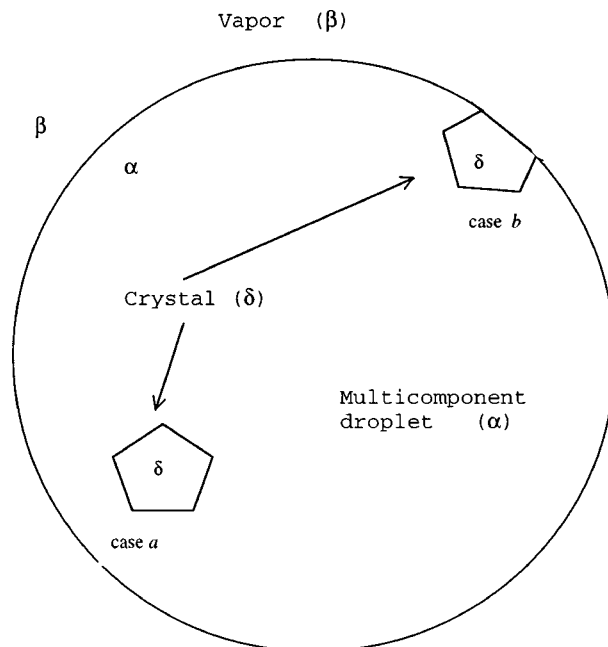


FIG. 2. Multicomponent liquid droplet in a vapor mixture. (a) Homogeneous crystal formation within the droplet. (b) Pseudoheterogeneous crystal formation at its interface.

only at a “liquid–vapor” interface. We will use the classical Gibbsian thermodynamics to derive the reversible works of crystal nucleus formation (1) *within* the bulk liquid or droplet and (2) *at* the liquid–vapor interface of the bulk liquid or droplet. These will be compared in order to specify the conditions under which the surface-stimulated crystallization is thermodynamically favored over the volume process.

For single component systems we showed⁷ that the thermodynamic condition for surface-stimulated crystal nucleation is identical to the condition of partial wetting of at least one crystal facet by its own melt. That condition is

$$\sigma_{\lambda}^{vs} - \sigma^{vl} < \sigma_{\lambda}^{ls}, \quad (1)$$

where the double superscripts vs , vl , and ls indicate the interfaces vapor–solid, vapor–liquid, and liquid–solid, respectively, the σ 's are the corresponding surface tensions, and λ indicates a particular facet of the crystal nucleus.

As we will show below, the condition for surface-stimulated crystal nucleation in multicomponent liquids has the same form as that in unary liquids. However, the physical implications of this condition and underlying phenomena are now significantly more complicated than in unary systems. They will be indicated as our theoretical development unfolds.

We consider the case when the liquid solution (whether bulk or in droplets) remains in equilibrium with the vapor mixture at all times. If the chemical potentials of all the components in the vapor phase are fixed, so are those in the liquid solution. Under such conditions, the composition of the liquid solution remains constant during crystal nucleation. Often, however, a liquid solution freeze into a solid of fixed composition, that is independent of a variable solution composition. (For example, nitric acid hydrates can crystallize from an aqueous nitric acid solution of variable compo-

sition.) If the composition of the liquid solution differs from that of the solid phase, material must be exchanged between the vapor mixture and the liquid solution to maintain equilibrium. This exchange of material can lead to a change in the vapor and liquid volumes (note that the total volume of the system is fixed). Thus, *unlike* the situation in Ref. 7 dealing with crystallization in single-component liquids, it is now necessary to consider the vapor mixture as a part of our system in order to take into account the possibility of formation of a solid phase of fixed composition from a multicomponent solution of arbitrary (nonstoichiometric) composition.

For convenience, the work of formation will be calculated in the canonical ensemble (i.e., N, V, T ensemble, where N is the constant total number of molecules, V is the constant volume, and T is the constant temperature in the system). Strictly speaking, in this ensemble it is not possible to fix the chemical potentials of the vapor mixture, since its volume and number of molecules can vary during crystallization. In the thermodynamic limit, however, since the crystalline nucleus is usually very small compared to the bulk liquid solution, the relative inaccuracy in the free energy due to such variations tends to zero, and the reversible work of formation of a crystal particle does not depend on the choice of the ensemble (for more detailed discussion of this issue see, e.g., Ref. 10).

Assuming the crystallization process to be isothermal,^{7,11} the reversible work of crystal nucleus formation, W , can be found as the difference between F_{fin} , the Helmholtz free energy of the system in its final state (vapor+liquid+crystal), and F_{in} , the Helmholtz free energy in the initial state (vapor+liquid):

$$W = F_{fin} - F_{in}. \quad (2)$$

A. Formation of a crystal within a bulk multicomponent solution or a multicomponent droplet

Consider a bulk liquid n -component solution in a container (Fig. 1) whose upper surface is in equilibrium with the corresponding vapor mixture.

We will use superscripts α, β , and δ to denote quantities in the liquid solution, vapor mixture, and crystal nucleus, respectively. Double Greek superscripts will denote quantities at the corresponding interfaces. The contribution to the free energy of the system from the liquid–container interfaces will not be considered since we are interested in crystallization of “free” volumes of multicomponent solutions.

In accordance with the Gibbsian thermodynamics of multicomponent multiphase systems,¹² the system in the initial state is regarded as consisting of three distinct subsystems: Liquid phase α (multicomponent solution) of uniform density, vapor phase β (vapor mixture) also of uniform density, and dividing surface $\alpha\beta$ between them. In the final state, the system consists of the liquid phase α , vapor phase β , solid phase δ (crystal), and the dividing surfaces $\alpha\beta$ (liquid–vapor) and $\alpha\delta$ (liquid–solid).

The composition of the liquid solution (and eventually of the solid phase) can be characterized by the composite variable $\chi^\alpha \equiv \{\chi_1^\alpha, \chi_2^\alpha, \dots, \chi_{n-1}^\alpha\}$ representing the set of $n-1$ independent stoichiometric mole fractions defined by

$$\chi_i^\alpha = N_i^\alpha / \sum_{i=1}^n N_i^\alpha \quad (i=1, \dots, n).$$

Clearly, $\chi_1^\alpha + \dots + \chi_n^\alpha = 1$.

Since some components of the liquid solution may dissociate into ions, it is also useful to introduce mole fractions based on the assumption of complete dissociation. Denote by z_i the number of ions into which a molecule of component i dissociates in the solution (the corresponding quantity for the $\alpha\beta$ -interface will be denoted by $z_i^{\alpha\beta}$), and define x_i as

$$x_i^\alpha = N_i^\alpha / \sum_{i=1}^n z_i N_i^\alpha \quad (i=1, \dots, n).$$

For components which do not dissociate, $z_i = z_i^{\alpha\beta} = 1$. Clearly, $z_1 x_1^\alpha + \dots + z_n x_n^\alpha = 1$. Note that z_i and $z_i^{\alpha\beta}$ may differ from each other. For example, in aqueous nitric acid solution a nitric acid molecule dissociates into two ions within the bulk, whereas at the surface nitric acid is adsorbed in a molecular form.⁹ Thus, in this case $z_{NA} = 2$, while $z_{NA}^{\alpha\beta} = 1$ (NA stands for nitric acid).

Marking the quantities for component i by the corresponding subscript, indicating the initial values of all quantities by the subscript “0,” and using the Gibbs method of dividing surfaces, one can write the Helmholtz free energy of the n -component system in the initial state as

$$F_{in} = \sum_{i=1}^n N_{i0}^\beta \mu_i^\beta(P_{i0}^\beta, T) + \sum_{i=1}^n z_i N_{i0}^\alpha \mu_i^\alpha(P_0^\alpha, \chi_0^\alpha, T) + \sum_{i=1}^n z_i^{\alpha\beta} N_{i0}^{\alpha\beta} \mu_i^{\alpha\beta}(\Gamma_0) - P_0^\beta V_0^\beta - P_0^\alpha V_0^\alpha + \sigma_0^{\alpha\beta} a^{\alpha\beta}, \quad (3)$$

where N^β and $\mu^\beta(P_i^\beta, T)$ are the number of molecules and chemical potential in the vapor mixture of volume V^β and total pressure $P^\beta = \sum_i P_i^\beta$ (partial pressure of component i is denoted by P_i^β), while N^α and $\mu^\alpha(P^\alpha, \chi^\alpha, T)$ are the number of molecules and chemical potential in the solution of volume V^α , pressure P^α , and composition χ^α . Note that for components that dissociate in the solution or at the interface, the corresponding chemical potentials should be understood as mean ionic chemical potentials. The third term on the right-hand side of Eq. (3) represents the contribution to the free energy F_{in} from the excess numbers of molecules, $N^{\alpha\beta}$, attributed to the dividing surface. The chemical potentials $\mu^{\alpha\beta}(\Gamma^{\alpha\beta})$ at the dividing surface are functions of the composite variable $\Gamma^{\alpha\beta} = \{\Gamma_1^{\alpha\beta}, \dots, \Gamma_n^{\alpha\beta}\}$ where $\Gamma_i^{\alpha\beta} = N_i^{\alpha\beta}/a^{\alpha\beta}$ ($i=1, \dots, n$). The surface tension and corresponding area of the liquid–vapor interface are denoted by $\sigma_0^{\alpha\beta}$ and $a^{\alpha\beta}$, respectively. The first five terms on the right-hand side of Eq. (3) depend on the choice of the dividing surface, but the last term therein does not, and neither does the sum (i.e., the free energy itself). Moreover, neither $\sigma_0^{\alpha\beta}$ nor $a^{\alpha\beta}$ depends on the choice of the dividing surface as long as the interface is flat.

It should be noted that in electrolyte solutions, cations and anions may adsorb at the vapor–liquid interface in different proportions. However, we cannot take this effect into account within the approach chosen. As shown in Ref. 12, if

the concept of dividing surfaces is applied to an electrocapillary two-phase system in equilibrium (without external electric fields), the condition of electroneutrality must hold not only for the both homogeneous phases but also for the dividing surface. There exists another method that could allow one, at least in principle, to take account of the asymmetry of ion adsorption. It is called the multiple layer model of the interface and is also described in Ref. 12. In this model the interface between liquid and vapor phases is considered as consisting of a series of thin layers placed one on the other, each layer being of uniform composition. Although the successive layers may have finite charges associated with them, the interface is neutral as a whole. This multilayer method would be also more appropriate in the case where the thickness of the nonuniform interfacial layer is of the order of the diameter of crystal nucleus, even if there were no asymmetric ion adsorption. In the present work we study the situation when the nucleus diameter is much larger than the interface thickness.

Now consider the above system but with a crystal formed within the liquid solution (Fig. 1, case *a*). The crystal is of arbitrary shape with λ facets (Fig. 3). Hereafter, we adopt Gibbs' definition of the surface tension of a solid as given in Chap. 17 of Ref. 12. Namely, $\sigma^{\text{solid}} = f' - \sum_i s'_i \mu'_i$, where f' , s'_i , and μ'_i are the surface free energy per unit area, adsorption, and chemical potential of component i , all attributed to the dividing surface between solid and fluid. (Note that only in the case where the adsorption at the solid–fluid interfaces is neglected, the surface tension of the solid can be identified with the surface free energy per unit area.) The surface area and surface tension of the facet j will be denoted by A_j and σ_j , respectively. (Anisotropic interfacial energies are particularly important in determining the character of the nucleation process.) The Helmholtz free energy of the system in this “final” state is (from now on we omit the limits of sums over i keeping in mind that i takes on values from 1 to n)

$$\begin{aligned}
 F_{fin} = & \sum_i N_i^\beta \mu_i^\beta(P_i^\beta, T) + \sum_i z_i N_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\alpha, T) \\
 & + \sum_i z_i^{\alpha\beta} N_i^{\alpha\beta} \mu_i^{\alpha\beta}(\Gamma^{\alpha\beta}, T) + \sum_i \nu_i \mu_i^\delta(P^\delta, \chi^\delta, T) \\
 & + \sum_i \sum_{j=1}^{\lambda} z_{ij}^{\alpha\delta} N_{ij}^{\alpha\delta} \mu_{ij}^{\alpha\delta}(\Gamma_j^{\alpha\delta}, T) - P^\beta V^\beta - P^\alpha V^\alpha \\
 & - P^\delta V^\delta + \sum_{j=1}^{\lambda} \sigma_j^{\alpha\delta} A_j^{\alpha\delta} + \sigma^{\alpha\beta} a^{\alpha\beta}, \quad (4)
 \end{aligned}$$

where in the fourth term ν_i and $\mu_i^\delta(P^\delta, \chi^\delta, T)$ are the number of molecules and chemical potential of component i in the solid particle formed within the liquid, P^δ being the pressure within the crystal, V^δ its volume, and χ^δ its composition defined as a set $\{\chi_1^\delta, \chi_2^\delta, \dots, \chi_{n-1}^\delta\}$ of stoichiometric mole fractions $\chi_i^\delta = \nu_i / \sum_{i=1}^n \nu_i$ ($i = 1, \dots, n$). The fifth term on the right-hand side of Eq. (4) represents the contribution to F_{fin} from adsorption at the liquid–solid interface. The number of ions, into which a molecule of component i dissociates, when adsorbed at the facet j , is indicated by $z_{ij}^{\alpha\delta}$. The total

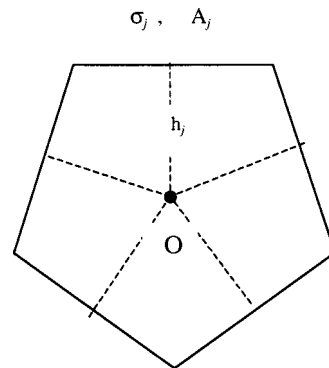


FIG. 3. An equilibrium crystal with λ facets, the surface area and surface tension of the facet i being A_j and σ_j , respectively; h_j is the distance from the facet j to the reference point O (see the text for more detail).

number of molecules, chemical potential, and adsorption of component i at facet j are denoted by N_{ij} , μ_{ij} , and $\Gamma_{ij}^{\alpha\delta}$, respectively (the double superscripts specify the interface). The composite variable $\Gamma_j^{\alpha\delta}$ is the set of adsorptions $\{\Gamma_{1j}^{\alpha\delta}, \dots, \Gamma_{nj}^{\alpha\delta}\}$ of all components. In the case of two dividing surfaces the numbers of molecules at each surface is defined by introducing a *mathematical* surface that lies between two dividing surfaces in the region of uniform density. This mathematical surface should split the whole system in two parts (with known number of molecules), such that in each part there is only one dividing surface. Thus the usual definitions^{10,12} of excess numbers of molecules and adsorptions at the dividing surfaces can be given. The *physical* surface of the crystal is usually sharp on an atomic scale, so that the contribution of the fifth term on the right-hand side of Eq. (4) to F_{fin} can be expected to be relatively small and the size of the crystal is determined by the set ν_1, \dots, ν_n . The area of the liquid–vapor interface does not change, but the surface tension $\sigma^{\alpha\beta}$ may change due to changes in the adsorption $\Gamma^{\alpha\beta}$.

Equation (4) allows the composition of the solid phase to differ from that of the liquid solution. Thus during crystallization the vapor mixture and liquid solution have to continually adjust the equilibrium between them if χ_0^α differs from χ^δ (as is often the case with freezing of aqueous nitric acid into nitric acid hydrates). Since we work in the closed NVT ensemble, the composition of the liquid solution may change as it freezes, and so may the vapor (and hence the liquid) pressures. In addition, the density of the liquid may differ from that of the solid. If it does, the crystal formation will induce a change in the volume of the vapor phase. The volume change can affect the partial pressures in the vapor mixture (and the pressure in the liquid), which in turn can induce a change in the liquid composition. However, all the above changes can be neglected at the stage of crystal nucleation where the sizes of crystal particles are still so small that the following conditions are fulfilled

$$\Delta V^{\alpha\delta} \ll V_0^\beta, \quad \Delta \nu_i \ll N_{i0}^\beta \quad (i = 1, \dots, n), \quad (5)$$

where $\Delta V^{\alpha\delta} = \sum_i \nu_i |v_i^\delta - v_i^\alpha|$ is the difference in the total volume occupied by the crystal molecules before and after crystal formation, and $\Delta \nu_i = |\chi_i^\delta - \chi_i^\alpha| (1 - \chi_i^\alpha)^{-1} \sum_i \nu_i$ is the number of molecules of component i exchanged between the

vapor mixture and liquid solution (the solution composition is bound to be constant, hence such exchange occurs if the compositions χ_i^δ and χ_{i0}^α differ from each other). Note that $\Delta v_i \rightarrow v_i$ as $\chi_i^\delta \rightarrow 1$ which corresponds to a single component system.

Under conditions (5), one can assume that

$$P_i \equiv P_i^\beta = P_{i0}^\beta, \quad P \equiv P^\beta = P_0^\beta (= P^\alpha = P_0^\alpha), \quad (6)$$

$$\chi^\alpha = \chi_0^\alpha, \quad \Gamma_i = \Gamma_{i0}, \quad N_i^{\alpha\beta} = N_{i0}^{\alpha\beta},$$

with $P^\beta \equiv \sum_i P_i^\beta$. Clearly, these equalities hold automatically in PVT or μVT ensembles (in the latter if the vapor mixture is ideal). Note that we do not neglect possible changes in the volume of the vapor or liquid phases occurring as material is exchanged between them and as a result of the density difference in the liquid and solid phases. As a matter of fact, in the thermodynamic limit the contributions to the free energy change arising from the inconstancy of pressure, chemical potentials, etc. cancel due to Gibbs–Duhem relation and Gibbs adsorption equation.¹⁰

Given Eqs. (2)–(4) and (6), one can show that

$$W = \sum_i v_i [\mu_i^\delta(P^\delta, \chi^\delta, T) - z_i \mu_i^\alpha(P^\alpha, \chi^\alpha, T)]$$

$$+ \sum_i \sum_{j=1}^{\lambda} N_{ij}^{\alpha\delta} [z_{ij}^{\alpha\delta} \mu_{ij}^{\alpha\delta}(\Gamma_j^{\alpha\delta}, T) - z_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\alpha, T)]$$

$$- V^\delta(P^\delta - P^\alpha) + \sum_{j=1}^{\lambda} \sigma_j^{\alpha\delta} A_j^{\alpha\delta}. \quad (7)$$

Since usually both $P^\alpha \ll P^\delta - P^\alpha$ and $\Delta V^{\alpha\delta} \ll V^\delta$, the term $P^\alpha \Delta V^{\alpha\delta}$ on the right-hand side of Eq. (7) has been neglected. It is at least two orders of magnitude smaller than $(P^\delta - P^\alpha)V^\delta$. The neglected term would represent the work involved in the change of volume of the vapor mixture upon the formation of the crystal within the liquid. Such a change may occur because of the density difference between liquid and solid phases.

Above, we have assumed that mechanical effects within the crystal (e.g., stresses) reduce to an isotropic pressure P^δ , which is related to the fluid pressure P^α by the Laplace equation for crystals^{1,12}

$$P^\delta - P^\alpha = \frac{2\sigma_j^{\alpha\delta}}{h_j} \quad (j=1, \dots, \lambda), \quad (8)$$

where h_j is the distance from facet j to such a point O within the crystal that (see Fig. 3)

$$\frac{\sigma_1^{\alpha\delta}}{h_1} = \frac{\sigma_2^{\alpha\delta}}{h_2} = \dots = \frac{\sigma_\lambda^{\alpha\delta}}{h_\lambda}. \quad (9)$$

These equalities are called Wulff's relations (see, e.g., Refs. 1 and 12) and they determine the equilibrium shape of the crystal, known as the Wulff form.

Making use of Eqs. (8) and (9), one can represent Eq. (7) as

$$W = \sum_i v_i [\mu_i^\delta(P^\alpha, \chi^\delta, T) - z_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\alpha, T)]$$

$$+ \sum_i \sum_{j=1}^{\lambda} N_{ij}^{\alpha\delta} [z_{ij}^{\alpha\delta} \mu_{ij}^{\alpha\delta}(\Gamma_j^{\alpha\delta}, T) - z_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\alpha, T)]$$

$$+ \sum_{j=1}^{\lambda} \sigma_j^{\alpha\delta} A_j^{\alpha\delta}. \quad (10)$$

In this equation, the first term represents the excess Gibbs free energy of the molecules in the bulk crystal with respect to their free energy in the liquid state. This term is related to the partial molecular enthalpy of fusion of all components $\Delta H_i(\chi^\delta) < 0$ by (see, e.g., Ref. 13)

$$\mu_i(P^\alpha, \chi^\delta) - z_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\alpha)$$

$$= - \int_{T_0}^T \Delta H_i(\chi^\delta) \frac{dT}{T} + kT z_i^\alpha \ln \frac{x_i^\delta f_i(\chi^\delta)}{x_i^\alpha f_i(\chi^\alpha)}, \quad (11)$$

where T_0 is the melting temperature of the bulk solid and the argument of ΔH_i indicates that ΔH_i in Eq. (11) corresponds to the case in which the solid and liquid phases have the same composition (congruent melting). The second term on the right-hand side of Eq. (11) is equal to the difference $z_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\delta) - z_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\alpha)$ and represents to contribution arising from the noncongruent melting (crystallization) effects. If $\chi^\alpha = \chi^\delta$, this contribution vanishes. The partial molecular enthalpy of fusion for composition χ is defined as

$$\Delta H_i(\chi) = H_i^\delta - H_i^\alpha \quad (12)$$

with $H_i = (\partial H / \partial v_i)_{P, T, v \neq v_i}$ and H being the total enthalpy of the system undergoing freezing or fusion and having the same composition χ in both the solid and liquid phases. Depending on whether or not the molecules of component i dissociate into ions in the solution, $f_i^\alpha(\chi)$ is either its activity coefficient or mean ionic activity coefficient in a solution of composition χ . The quantity x_i^δ is defined by analogy with x_i^α : $x_i^\delta = v_i^\delta / \sum_{i=1}^n z_i v_i^\delta$ ($i=1, \dots, n$).

If in the temperature range between T and T_0 the partial enthalpy of fusion ΔH_i does not change significantly, Eq. (11) takes the form

$$\mu_i^\delta(P^\alpha, \chi^\delta) - z_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\alpha)$$

$$= - \Delta H_i \ln \Theta + kT z_i^\alpha \ln \frac{x_i^\delta f_i(\chi_i^\delta)}{x_i^\alpha f_i(\chi_i^\alpha)}, \quad (13)$$

with $\Theta = T/T_0$. Substituting Eq. (13) into Eq. (10), we get

$$W = - \sum_i v_i \left(\Delta H_i \ln \Theta - kT z_i^\alpha \ln \frac{x_i^\delta f_i(\chi_i^\delta)}{x_i^\alpha f_i(\chi_i^\alpha)} \right)$$

$$+ \sum_i \sum_{j=1}^{\lambda} N_{ij}^{\alpha\delta} [z_{ij}^{\alpha\delta} \mu_{ij}^{\alpha\delta}(\Gamma_j^{\alpha\delta}, T) - z_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\alpha, T)]$$

$$+ \sum_{j=1}^{\lambda} \sigma_j^{\alpha\delta} A_j^{\alpha\delta}. \quad (14)$$

Introduce a characteristic linear size (“radius”) r and a characteristic surface tension $\sigma^{\alpha\delta}$ for a crystal surrounded by its melt as

$$r = \left[\frac{3}{4\pi} \sum v_i v_i^\delta \right]^{1/3}, \quad \sigma^{\alpha\delta} = \frac{1}{4\pi R^2} \sum_{j=1}^{\lambda} \sigma_j^{\alpha\delta} A_j^{\alpha\delta}. \quad (15)$$

If the crystal had a spherical shape, it would have a radius r and a surface tension $\sigma^{\alpha\delta}$.

As usual, define a critical crystal (nucleus) as a crystal that is in unstable equilibrium with the surrounding fluid. It follows from Eqs. (14) and (15) that the characteristic radius r_* of the crystal nucleus is

$$r_* = 2\sigma^{\alpha\delta} v_i \left(\Delta H_i(\chi^\delta) \ln \Theta - kT z_i^\alpha \ln \frac{x_i^\delta f_i(\chi_i^\delta)}{x_i^\alpha f_i(\chi_i^\alpha)} \right)^{-1} \quad (16)$$

(hereafter the subscript “*” indicates quantities corresponding to the nucleus). The work of crystal formation W as a function of r attains its maximum at $r=r_*$. For the solid phase to form, the radius of the critical crystal cannot be infinite or negative. Therefore, for any given χ^δ the condition

$$\Delta H_i(\chi^\delta) \ln \Theta - kT z_i^\alpha \ln \frac{x_i^\delta f_i(\chi_i^\delta)}{x_i^\alpha f_i(\chi_i^\alpha)} \geq 0 \quad (17)$$

determines the phase diagram and phase coexistence curve in the plane $T-\chi^\alpha$. In other words, for every χ^α the equality in Eq. (17) determines the upper limit of the temperature range in which a finite-size critical crystal of fixed composition χ^δ can form in the liquid solution of variable composition χ^α .

Equations (8) and (9) along with the geometric relation $V^\delta = \frac{1}{3} \sum_j h_j A_j$ allow one to show that

$$V^\delta (P^\delta - P^\alpha) = \frac{2}{3} \sum_{j=1}^{\lambda} \sigma_j^{\alpha\delta} A_j^{\alpha\delta}. \quad (18)$$

By virtue of Eq. (18) and (7), the reversible work of formation of the (critical) crystal nucleus can be written in the form

$$W_* = \frac{1}{3} \sum_{j=1}^{\lambda} \sigma_j^{\alpha\delta} A_j^{\alpha\delta}, \quad (19)$$

or, alternatively, as

$$W_* = \frac{1}{2} V_*^\delta (P_*^\delta - P^\alpha). \quad (20)$$

In what follows, Eq. (20) will be very useful.

Next, consider the case of a crystal, that forms not in the bulk liquid solution, but within a liquid droplet of multicomponent solution [Fig. 2(a)] itself surrounded by the vapor mixture. The reasoning here is almost identical to the preceding if, again, we assume the conditions in Eq. (5) to be fulfilled at least at the stage of crystal nucleation [for droplets, that are usually small compared to the vapor phase, both conditions in Eq. (5) hold]. The Helmholtz free energies of the system in the initial and final states (F_{in} and F_{fin} , respectively) are now given by slightly modified Eqs. (3) and (4). Namely, the pressure P^α in Eqs. (3) and (4) is now given by the Laplace equation $P^\alpha = P_0^\alpha = P + 2\sigma^{\alpha\beta}/R$, where R is the radius of the droplet, and the liquid–vapor interface area

is now equal to the surface area of the droplet $a_R^{\alpha\beta} = 4\pi R^2$ [since both conditions in Eq. (5) hold, not only are all the equalities in Eq. (6) again valid, but also the radius R and hence surface area $a_R^{\alpha\beta}$ can be assumed to remain constant during crystal nucleation]. Keeping this in mind, one can show that all the above equations, including Eqs. (19) and (20) for the reversible work W_* , remain unchanged.

B. Formation of a crystal at the liquid–vapor interface

Assuming that there are no foreign particles in the system and omitting consideration of crystallization at the liquid–container interface, we will focus on “pseudoheterogeneous” crystal nucleation at the liquid–vapor interface.

First, consider a bulk solution in a container (Fig. 1) whose upper surface is in contact with the vapor mixture (recall that we work in NVT ensemble, where the total number of molecules, volume, and temperature of the whole system are constant). In the “initial” state, there is no crystal particle in the liquid solution. In the “final” state there is a crystal nucleus with one facet placed at the liquid–vapor interface [Fig. 1(b)]. We will assign the subscript “ λ ” to this particular facet. The Helmholtz free energy of the system in its initial state is given by Eq. (3), while in the final state it is

$$\begin{aligned} F_{fin} = & \sum_i N_i^\beta \mu_i^\beta(P_i^\beta, T) + \sum_i z_i N_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\alpha, T) \\ & + \sum_i z_i^{\alpha\beta} N_i^{\alpha\beta} \mu_i^{\alpha\beta}(\Gamma^{\alpha\beta}, T) + \sum_i v_i \mu_i^\delta(P^\delta, T) \\ & + \sum_i \left[\sum_{j=1}^{\lambda-1} z_{ij}^{\alpha\delta} N_{ij}^{\alpha\delta} \mu_{ij}^{\alpha\delta}(\Gamma_j^{\alpha\delta}, T) \right. \\ & \left. + N_{i\lambda}^{\beta\delta} \mu_{i\lambda}^{\beta\delta}(\Gamma_\lambda^{\beta\delta}, T) \right] - P^\beta V^\beta - P^\alpha V^\alpha - P^\delta V'^\delta \\ & + \sum_{j=1}^{\lambda-1} \sigma_j^{\alpha\delta} A_j^{\alpha\delta} + \sigma_\lambda^{\beta\delta} A_\lambda^{\beta\delta} + \sigma^{\alpha\beta} (a^{\alpha\beta} - A_\lambda^{\beta\delta}), \quad (21) \end{aligned}$$

where V'^δ is the volume of a crystal formed pseudoheterogeneously. The fifth term on the right-hand side of Eq. (21) takes into account that the adsorption of vapor on the solid surface may differ from the adsorption of liquid on the solid (and that there is no dissociation in the vapor phase).

As discussed above, allowing the solid phase to have a composition different from that of the liquid solution implies the possibility of changes in the compositions and pressures of the vapor and liquid phases. These changes, however, can be again neglected if condition (5) is fulfilled which is always the case in the thermodynamic limit. Then all the equalities in Eq. (6) are again valid, except for the last, which does not hold because the area of the vapor–liquid interface decreases by A_λ . Due to equilibrium between the vapor mixture and the liquid solution, however, the change in the total numbers of surface molecules does not contribute to W' , the reversible work of *pseudoheterogeneous* formation of the crystal, given by the expression

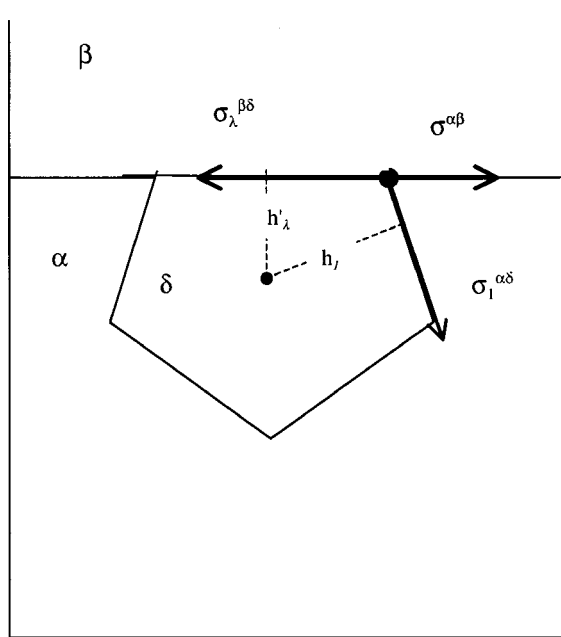


FIG. 4. Illustration to Wulff's relations (24) (for more detail see the text).

$$\begin{aligned}
 W' = & \sum_i \nu_i [\mu_i^\delta(P^\delta, T) - z_i \mu_i^\alpha(P^\alpha, T)] \\
 & + \sum_i \left[\sum_{j=1}^{\lambda} N_{ij}^{\alpha\delta} (z_{ij}^{\alpha\delta} \mu_{ij}^{\alpha\delta}(\Gamma_j^{\alpha\delta}, T) - z_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\alpha, T)) \right. \\
 & \left. + N_{i\lambda}^{\beta\delta} (\mu_{i\lambda}^{\beta\delta}(\Gamma_\lambda^{\beta\delta}, T) - \mu_i^\beta(P_i^\beta, T)) \right] - V' \delta(P^\delta - P^\alpha) \\
 & + \sum_{j=1}^{\lambda-1} \sigma_j^{\alpha\delta} A_j^{\alpha\delta} + \sigma_\lambda^{\beta\delta} A_\lambda^{\beta\delta} - \sigma^{\alpha\beta} A_\lambda^{\beta\delta}. \quad (22)
 \end{aligned}$$

We have again neglected the work associated with the change of the volume of the vapor mixture upon freezing caused by the possible density difference between the liquid and solid phases. As discussed above, this work is several orders of magnitude smaller than the PV term retained on the right-hand side of Eq. (22).

Wulff's relations, Eq. (9), which determine the equilibrium shape of a crystal, can be regarded as a set of equilibrium conditions on the "edges" of the crystal facets. In the case where one of the facets (say, facet λ) is the crystal-vapor interface while all the other facets lie within the liquid phase (see Fig. 4), the equilibrium conditions on the edges of this facet are given by

$$\frac{\sigma_k^{\alpha\delta}}{h_k} = \frac{\sigma_\lambda^{\beta\delta} - \sigma^{\alpha\beta}}{h'_\lambda}, \quad (23)$$

where the subscript k marks facets adjacent to λ . The net force (tension), acting along the facet λ on its edges, is equal to the difference of two tensions acting along this facet, hence the numerator on the right-hand side of Eq. (23). Thus, for this case, Wulff's relations take the form

$$\frac{\sigma_1^{\alpha\delta}}{h_1} = \frac{\sigma_2^{\alpha\delta}}{h_2} = \dots = \frac{\sigma_\lambda^{\alpha\delta} - \sigma^{\alpha\beta}}{h'_\lambda}, \quad (24)$$

and Eq. (8) becomes

$$\begin{aligned}
 P^\delta - P^\alpha &= \frac{2\sigma_j^{\alpha\delta}}{h_j} \quad (j=1, \dots, \lambda-1), \\
 P^\delta - P^\alpha &= \frac{2(\sigma_\lambda^{\beta\delta} - \sigma^{\alpha\beta})}{h'_\lambda}. \quad (25)
 \end{aligned}$$

Comparing Eqs. (9) and (24), it is clear that the height of the λ th pyramid (constructed with base on facet λ and apex at point O of the Wulff crystal) may differ from that of the crystal with all the facets in the liquid, even though all the other heights h_j ($j \neq \lambda$) are the same in both cases (as will be proven below). Thus, the shape of the crystal with one facet in contact with the vapor mixture, may differ from that in which all facets are in contact with the liquid.

Using Eqs. (24) and (25), one can rewrite Eq. (22) as

$$\begin{aligned}
 W' = & \sum_i \nu_i [\mu_i^\delta(P^\alpha, \chi^\delta, T) - z_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\alpha, T)] \\
 & + \sum_i \left[\sum_{j=1}^{\lambda} N_{ij}^{\alpha\delta} (z_{ij}^{\alpha\delta} \mu_{ij}^{\alpha\delta}(\Gamma_j^{\alpha\delta}, T) - z_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\alpha, T)) \right. \\
 & \left. + N_{i\lambda}^{\beta\delta} (\mu_{i\lambda}^{\beta\delta}(\Gamma_\lambda^{\beta\delta}, T) - \mu_i^\beta(P_i^\beta, T)) \right] \\
 & + \sum_{j=1}^{\lambda-1} \sigma_j^{\alpha\delta} A_j^{\alpha\delta} + \sigma_\lambda^{\beta\delta} A_\lambda^{\beta\delta} - \sigma^{\alpha\beta} A_\lambda^{\beta\delta}. \quad (26)
 \end{aligned}$$

Furthermore, Eq. (13) allows one to rewrite Eq. (26) in the form

$$\begin{aligned}
 W' = & - \sum_i \nu_i \left(\Delta H_i \ln \Theta - kT z_i^\alpha \ln \frac{x_i^\delta f_i(\chi_i^\delta)}{x_i^\alpha f_i(\chi_i^\alpha)} \right) \\
 & + \sum_i \left[\sum_{j=1}^{\lambda} N_{ij}^{\alpha\delta} (z_{ij}^{\alpha\delta} \mu_{ij}^{\alpha\delta}(\Gamma_j^{\alpha\delta}, T) - z_i^\alpha \mu_i^\alpha(P^\alpha, \chi^\alpha, T)) \right. \\
 & \left. + N_{i\lambda}^{\beta\delta} (\mu_{i\lambda}^{\beta\delta}(\Gamma_\lambda^{\beta\delta}, T) - \mu_i^\beta(P_i^\beta, T)) \right] \\
 & + \sum_{j=1}^{\lambda-1} \sigma_j^{\alpha\delta} A_j^{\alpha\delta} + \sigma_\lambda^{\beta\delta} A_\lambda^{\beta\delta} - \sigma^{\alpha\beta} A_\lambda^{\beta\delta}. \quad (27)
 \end{aligned}$$

For the characteristic "radius" of the critical crystal formed pseudoheterogeneously one can obtain an equation similar to Eq. (16) where the surface tension $\sigma^{\alpha\delta}$ is replaced by the characteristic surface tension $\sigma^{\alpha\delta\beta}$ of the critical crystal formed pseudoheterogeneously, defined as

$$\sigma^{\alpha\delta\beta} = \frac{1}{4\pi r^2} \left(\sum_{j=1}^{\lambda-1} \sigma_j^{\alpha\delta} A_j^{\alpha\delta} + \sigma_\lambda^{\beta\delta} A_\lambda^{\beta\delta} - \sigma^{\alpha\beta} A_\lambda^{\beta\delta} \right).$$

Clearly, the use of Eq. (16) and its analogue for the "radius" of the critical crystal formed pseudoheterogeneously requires

estimates of the surface tensions of all the crystal facets in both the vapor mixture and the liquid solution, as well as an estimate of the liquid–vapor surface tension.

For an arbitrary crystal with one of its facets a solid–vapor interface, and the others solid–liquid, one can show that

$$V'^{\delta}(P^{\delta}-P^{\alpha})=\frac{2}{3}\left(\sum_{j=1}^{\lambda-1}\sigma_j^{\alpha\delta}A_j^{\alpha\delta}+\sigma_{\lambda}^{\beta\delta}A_{\lambda}^{\beta\delta}-\sigma^{\alpha\beta}A_{\lambda}^{\beta\delta}\right). \tag{28}$$

This equality allows one to write W'_* , the reversible work of formation of a critical crystal (nucleus), in the form

$$W'_*=\frac{1}{3}\left(\sum_{j=1}^{\lambda-1}\sigma_j^{\alpha\delta}A_j^{\alpha\delta}+\sigma_{\lambda}^{\beta\delta}A_{\lambda}^{\beta\delta}-\sigma^{\alpha\beta}A_{\lambda}^{\beta\delta}\right), \tag{29}$$

or, alternatively, as

$$W'_*=\frac{1}{2}V'_*(P^{\delta}_*-P^{\alpha}). \tag{30}$$

Equations (29) and (30) are similar to Eqs. (19) and (20), which correspond to homogeneous crystallization within the liquid. Along with Eq. (20), the last equation will also be important.

The analysis of the case where the crystallization begins at a drop surface can be considerably more complicated than in the above case which refers to a bulk liquid surface. This results from the deformation of the droplet if freezing is initiated at its surface [Fig. 2(b)]. However, one can show that, under the following condition (such that the area of the crystal–vapor interface is small compared to the surface area of the droplet)

$$\frac{A_{\lambda}^{\beta\delta}}{\pi R^2}\ll 1, \tag{31}$$

the formation of a crystal at the droplet surface can be considered as crystallization at the surface of a *bulk* liquid. Under conditions relevant to the freezing of atmospheric drops, crystal nuclei are usually at most of nanometer size, while the drops themselves have radii that are at least an order of magnitude larger, i.e., condition (31) is certainly satisfied. Therefore, we can use the preceding equations in the analysis of crystal nucleation at a droplet surface.

C. Comparison of the volume-based and surface-stimulated modes of crystal nucleation

As indicated above, the shape of a crystal with one facet in contact with the vapor mixture, may differ from that in which all facets are in contact with the liquid. In order to determine, which mode of crystal nucleation is thermodynamically more favorable, one has to compare the reversible works of formation of nuclei for homogeneous and pseudo-heterogeneous crystallization. To do this, it is most convenient to use Eqs. (20) and (30), which can be rewritten as

$$W_*=\frac{1}{2}V^{\delta}_*(P^{\delta}_*-P^{\alpha})_{hom}, \quad W'_*=\frac{1}{2}V'^{\delta}_*(P^{\delta}_*-P^{\alpha})_{het}, \tag{32}$$

respectively. Here, the subscripts “*hom*” and “*het*” indicate that the difference between the internal pressure of the nucleus and the external pressure might be different, depend-

ing on whether the nucleus forms homogeneously or pseudoheterogeneously (at the surface). However, by using Eq. (13) and the equilibrium condition for the nucleus, namely

$$\mu_i^{\delta}(P^{\delta},\chi^{\delta},T)-z_i^{\alpha}\mu_i^{\alpha}(P^{\alpha},\chi^{\alpha},T)=0 \quad (i=1,\dots,n),$$

and assuming the crystal to be incompressible, it is easy to show that the difference $P^{\delta}_*-P^{\alpha}$ for the crystal nucleus, in both cases, is determined by the degree of supercooling of the liquid and by the ratio of the activities of any component at compositions χ^{δ} and χ^{α} , so that

$$(P^{\delta}_*-P^{\alpha})_{het}=(P^{\delta}_*-P^{\alpha})_{hom}=\frac{1}{v_i^{\delta}}\left(\Delta H_i \ln \Theta -kTz_i^{\alpha} \ln \frac{x_i^{\delta}f_i(\chi^{\delta})}{x_i^{\alpha}f_i(\chi^{\alpha})}\right) \tag{33}$$

$(i=1,\dots,n).$

The first equality in Eq. (35) is equivalent to

$$h'_{\lambda}=\frac{\sigma_{\lambda}^{\beta\delta}-\sigma^{\alpha\beta}}{\sigma_{\lambda}^{\alpha\delta}}h_{\lambda}. \tag{34}$$

On the other hand, according to Eqs. (8), (25), and (33)

$$h_j=h'_j \quad (j=1,\dots,\lambda-1).$$

Thus, in the case of surface-stimulated nucleation, the Wulff shape of the critical crystal is obtained by simply changing the height of the λ th pyramid of the Wulff crystal nucleus corresponding to the volume process. Furthermore, by virtue of Eqs. (32) and (33),

$$\frac{W'_*}{W_*}=\frac{V'^{\delta}_*}{V^{\delta}_*}.$$

Therefore, one can conclude that if

$$\sigma_{\lambda}^{\beta\delta}-\sigma^{\alpha\beta}<\sigma_{\lambda}^{\alpha\delta}, \tag{35}$$

then $h'_{\lambda}<h_{\lambda}$, $V'^{\delta}_*<V^{\delta}_*$, and hence

$$W'_*<W_*.$$

In other words, if condition (35) is fulfilled, it is thermodynamically more favorable for the crystal nucleus to form at the surface rather than within the liquid solution.

In Ref. 7 we derived the equivalent of this condition for crystallization of unary liquids. In that paper we predicted (but did not prove) that the thermodynamic condition for surface-stimulated crystal nucleation would be similar in both unary and multicomponent systems where the possible effects of dissociation and surface adsorption have to be considered. The foregoing development fully confirms that.

The inequality in Eq. (35) coincides with the condition of partial wettability of the λ th facet of a crystal of composition χ^{δ} by the liquid solution of composition χ^{α} .¹² This effect has been experimentally observed for several systems^{1,8,14} including water–ice⁸ at temperatures at or below 0 °C. In these experiments,⁸ when air was added to water vapor the partial wetting of ice by water transformed into complete wetting, but **only** for some orientations. Besides, the wettability of solids by fluids usually decreases with de-

creasing temperature.^{15,16} Since the freezing of atmospheric water drops always occurs at temperatures far below 0 °C, one can expect the partial wettability of at least some facets of water crystals even in the presence of air. Furthermore, according to Cahn,¹⁷ the perfect wetting of a solid by a liquid away from the critical point is not generally observed, i.e., condition (35) should be fulfilled for most substances. In Cahn's theory, the general restrictions on the solid phase are that its surface is sharp on an atomic scale and that interactions between surface and fluid are sufficiently short-range. Therefore, that theory can be also applied to the case where the temperature is far below the fluid critical point and the solid is of the same chemical nature as the fluid phases. If the temperature approaches the fluid critical temperature, Cahn's theory becomes inapplicable to this case. However, temperatures involved in crystallization are usually far below the critical point. All these combined with Eq. (35) help to explain why, in molecular dynamics simulations, crystallization always begins at or near a surface, and why it is easier, experimentally, to observe the crystallization of droplets of large collective surface area than that of the corresponding bulk liquid.

Inequality (35) can serve as a criterion for determining whether the formation of a solid phase of composition χ^δ in a particular supercooled liquid solution of composition χ^α will, or will not, be initiated at the surface rather than within the liquid. To implement this criterion, however, one has to have accurate and detailed information concerning the surface tension of the liquid–vapor interface as well as the surface tensions of the crystal facets both in the liquid solution and in the vapor mixture. (For a more detailed discussion of this issue see Ref. 7.)

Although our derivation of the condition of surface-stimulated crystallization in multicomponent solutions takes into account the possible surface adsorption of soluble surfactants and dissociation of some solution components, these effects are not explicitly represented in the final result [condition (35)]. Nevertheless, they are implicit therein. Actually, the bulk (internal) composition of the solution (multicomponent drop), χ^α , is determined by both the dissociation of molecules in the solution and the adsorption of surfactants at the interfaces. On the other hand, first, the surface tension $\sigma^{\alpha\delta}$ is a function of both χ^α and χ^δ , and, second, the surface tension $\sigma^{\alpha\beta}$ is a function of χ^α especially if there are surface-active components in the solution. The bulk composition of the solution (or the internal composition of the droplet) is a single-valued function of the adsorption Γ (the inverse is not in general true, because of the existence of two-dimensional phase transitions in adsorption layers of soluble surfactants¹⁸). Thus, it is clear that the surface tension $\sigma^{\alpha\beta}$ is a function of the composite variable Γ , i.e., $\sigma^{\alpha\beta} = \sigma^{\alpha\beta}(\Gamma)$, while $\sigma^{\alpha\delta} = \sigma^{\alpha\delta}(\chi^\alpha, \chi^\delta)$.

Clearly, an increase in the overall surfactant concentration in the interior of the droplet causes an increase in the surfactant concentration in the surface layer. Although this leads to a decrease in the surface tension of the droplet, $\sigma^{\alpha\beta}$, the condition of partial wetting may still hold due to the increase of the solid–liquid surface tensions of some crystal facets, $\sigma^{\alpha\delta}$. One can expect that the more the solution com-

position differs from the “packing” composition of some facet, the greater the surface tension of this facet is. Although this may not be a general rule, it is clear that the surface tension of the liquid–solid interface may nonmonotonically depend on the difference between the packing composition of a crystallographic plane and the composition of the surrounding solution. Thus, surface-stimulated crystallization may remain an important mechanism for the freezing of atmospheric droplets even at high concentrations of soluble surfactants.

Finally, it should be noted that the strength of the adsorption and dissociation effects (characteristic of multicomponent solutions) and their impact on the freezing behavior of multicomponent droplets may depend markedly on the droplet size (radius). Preliminary numerical evaluations show that the impeding effect of soluble surfactants on the surface-stimulated crystallization becomes weaker with decreasing droplet size. In a following paper¹⁹ we will present some results on the effect of adsorption at the vapor–liquid interface on the surface tension $\sigma^{\alpha\beta}$ of droplets of different sizes. The understanding of this effect combined with condition (35) will help to clarify the role of surfactants in the freezing of atmospheric droplets as well as to explain some controversial features of the observed freezing behavior of multicomponent droplets of different sizes (see, e.g., Refs. 5 and 6 and references therein).

III. CONCLUDING REMARKS

The results of previous work^{5,6} dealing with the analysis of experimental data on the freezing of atmospheric liquid aerosols suggested that the crystallization of droplets may often initiate at their surface. In addition, a number of molecular dynamics simulations of the crystallization of small droplets also showed that the process begins at or near the surface of the simulation cell.

We attempted⁷ to explain such preferential “surface” nucleation by developing the thermodynamics of the process within the framework of the capillarity approximation. In that attempt, we derived the condition that must hold in order for pseudoheterogeneous (surface) crystal nucleation to be thermodynamically favored over the volume process. That condition is identical to the condition of partial wettability of at least one crystal facet by its melt, apparently a frequent phenomenon in nature.^{1,8,14,17}

However, our previous thermodynamic treatment was restricted to crystal nucleation in single component systems, although we conjectured that it would hold in multicomponent systems and used it in the analyses of the freezing behavior of multicomponent liquids in both bulk and droplet forms.

In the present work, we have generalized our previous thermodynamic theory and have developed the Gibbsian thermodynamics of crystal nucleation in multicomponent liquid solutions (bulk as well as drops). We have derived the reversible work of formation of a crystal nucleus in two modes, homogeneous (volume-based nucleation) and pseudoheterogeneous (surface-stimulated nucleation). In the former mode, the crystal nucleus forms homogeneously within the (supercooled) bulk liquid solution, while in the

latter, it forms “pseudoheterogeneously” at the liquid–vapor interface. Rigorous account has been taken of the possible dissociation of molecules into ions and of their adsorption into the liquid–vapor interface. The comparison of the works of formation for these two modes has once again led to an inequality which must hold in order for pseudoheterogeneous (surface) nucleation to be thermodynamically favored over homogeneous (volume) nucleation. As in single-component systems, this inequality is identical to the condition of partial wettability of at least one facet of the crystal nucleus by the melt (solution). Thus the effects of adsorption and dissociation in multicomponent systems do not explicitly alter the form of the thermodynamic condition for preferential surface-stimulated crystal nucleation. However, these effects do play an important role in determining whether or not surface-stimulated nucleation is thermodynamically more favorable than volume-based process, because they influence the surface tensions of the liquid–vapor and liquid–solid interfaces which enter the condition of partial wettability. Furthermore, in the case of multicomponent droplets, the strength of these effects on freezing may depend on the droplet size.

In a following paper¹⁹ results will be presented to show how the effect of adsorption at the vapor–liquid interface affects the surface tension of droplets of different sizes. The understanding of this effect along with the condition of preferential surface-stimulated crystal nucleation should help to clarify the role of surfactants in the freezing of atmospheric multicomponent droplets and to explain some controversial features of their freezing behavior.

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