J. Phys. Chem. A **2008,** *112,* 11677–11687 **11677**

Thermodynamics of Heterogeneous Crystal Nucleation in Contact and Immersion Modes

Y. S. Djikaev[†] **and E. Ruckenstein***

Department of Chemical and Biological Engineering, SUNY at Buffalo, Buffalo, New York 14260

Received: April 11, 2008; Revised Manuscript Received: August 5, 2008

One of the most intriguing problems of heterogeneous crystal nucleation in droplets is its strong enhancement in the contact mode (when the foreign particle is presumably in some kind of contact with the droplet surface) compared to the immersion mode (particle immersed in the droplet). Heterogeneous centers can have different nucleation thresholds when they act in contact or immersion modes. The underlying physical reasons for this enhancement have remained largely unclear. In this paper we present a model for the thermodynamic enhancement of heterogeneous crystal nucleation in the contact mode compared to the immersion one. To determine if and how the surface of a liquid droplet can thermodynamically stimulate its heterogeneous crystallization, we examine crystal nucleation in the immersion and contact modes by deriving and comparing with each other the reversible works of formation of crystal nuclei in these cases. The line tension of a three-phase contact gives rise to additional terms in the formation free energy of a crystal cluster and affects its Wulff (equilibrium) shape. As an illustration, the proposed model is applied to the heterogeneous nucleation of hexagonal ice crystals on generic macroscopic foreign particles in water droplets at $T = 253$ K. Our results show that the droplet surface does thermodynamically favor the contact mode over the immersion one. Surprisingly, the numerical evaluations suggest that the line tension contribution (from the contact of three water phases (vapor−liquid−crystal)) to this enhancement may be of the same order of magnitude as or even larger than the surface tension contribution.

1. Introduction

The size, composition, and phases of aerosol and cloud particles affect the adiative and chemical properties[1,2] of clouds and hence have a great impact on Earth's climate as a whole. On the other hand, the composition, size, and phases of atmospheric particles are determined by the rate at and mode in which these particles form and evolve.[2−4]

Water constitutes an overwhelmingly dominant chemical species that participates in atmospheric processes. Consequently, great importance is attributed to studying aqueous aerosols and cloud droplets as well as their phase transformations. In a number of important cases, atmospheric particles appear to freeze homogeneously.[4−6] For example, the conversion of supercooled water droplets into ice at temperatures below about −30 °C is known to occur homogeneously, mainly because the concentrations of the observed ice particles in the clouds often exceed the number densities of preexisting particles capable of nucleating ice.[4,5] Also, it has been suggested that aqueous nitric acid-containing cloud droplets in the polar stratosphere freeze into nitric acid hydrates via homogeneous nucleation.[6] Understanding how nitric acid clouds form and grow in the stratosphere is a topic of current interest because such clouds participate in the heterogeneous chemistry that leads to springtime ozone depletion over the polar regions.[2]

However, most phase transformations in aqueous cloud droplets occur as a result of heterogeneous nucleation on preexisting macroscopic particles, macromolecules, or even ions.[3] Heterogeneous nucleation of ice on a microscopic foreign particle can be considered as a result of the adsorption of water molecules on a substrate which serves as a template. If the substrate stimulates the adsorption of water molecules in a configuration close enough to the crystalline structure of ice, then the energy barrier between phases is substantially reduced.[7] Recent work on the heterogeneous nucleation of ice in the atmosphere is motivated by the evidence, primarily from modeling studies, that heterogeneous freezing may significantly impact the radiative properties, in both the visible and infrared regions, of cirrus clouds. The leading candidates for heterogeneous nucleating centers are the mineral dusts (fly ash and metallic particles) and emissions from aircraft, primarily soot.[8−10] Interest in cirrus clouds motivated several laboratory studies as well.[11,12] They showed that the presence of various foreign inclusions shifts the apparent freezing temperature of droplets upward by as much as 10 °C.

Most investigators targeted particulates as the primary heterogeneous ice nucleating centers in the atmosphere. Recently, however, increasing attention is payed to the role of films of high-molecular-weight organic compounds located on droplets. Such compounds are emitted into the atmosphere, especially in regions that are influenced by biomass burning.[13] It was reported, for example, that the films of long-chain alcohols and some other organic species can catalyze ice nucleation in droplets at a supercooling of only 1 °C.[14,15]

So far, the physical mechanism underlying heterogeneous crystal nucleation in droplets remains rather obscure.[2] As an additional mystery, many heterogeneous centers have different nucleation thresholds when they act in different modes, contact or immersion, indicating that the mechanisms may be actually different for the different modes. In the contact mode, the ice-nucleating particle contacts the water droplet, i.e., touches or intersects its surface, whereas in the immersion mode the particle is immersed in the water droplet (Figure 1).[2,16] The same particle can trigger the freezing of a supercooled water droplet at a higher temperature in the contact mode than in the immersion one.[2,16,17]

---

* Corresponding author. Phone: (716) 645-2911, ext 2214. Fax: (716) 645-3822. E-mail: feaeliru@acsu.buffalo.edu.

[†] E-mail: idjikaev@eng.buffalo.edu..

10.1021/jp803155f CCC: $40.75

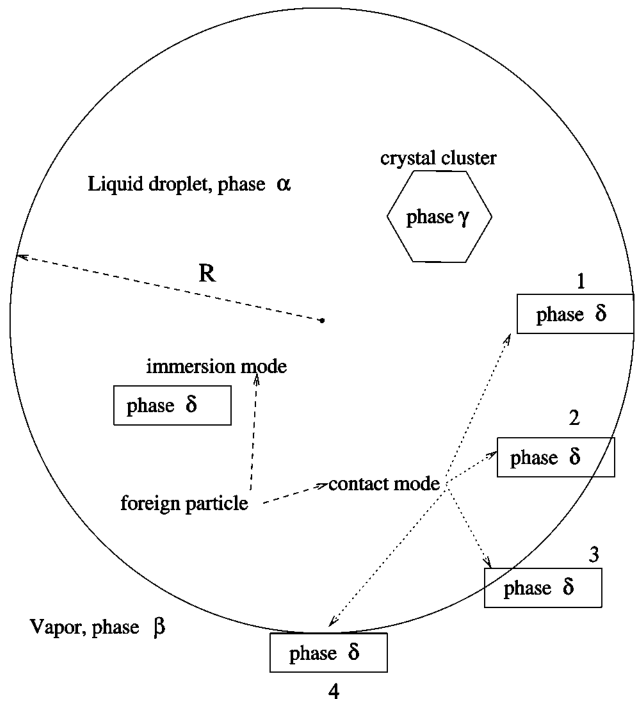

Figure 1. Heterogeneous crystal nucleation in a liquid droplet surrounded by vapor: "immersion" mode, the crystal cluster forms with one of its facets on a foreign particle, completely immersed in a liquid droplet, i.e., all other crystal facets interface the liquid; "contact" mode, the foreign particle is in contact with the droplet surface; the cluster forms with one of the crystal facets on the particle, another facet at the liquid−vapor interface, and all other facets making the "crystal−liquid" interface. Cases 1 through 4 represent a few of possible variations of the "foreign particle−droplet surface" contact.

The cause of this enhancement is unknown, but it provides a hint that the water surface could be of special interest in ice nucleation. Several investigators have put forward conjectures on the mechanism of contact nucleation, all of which depend on the contact of a particle impinging upon the droplet surface from air.[2] One of the hypotheses is based on the partial solubility of small solid particles whereby the active sites at the surface of a particle are subject to erosion after it becomes immersed in water.[18,19] Another hypothesis suggests[20] that only those particles enhance nucleation in the contact mode which exhibit a strong affinity for water. During the initial contact with the droplet (before the equilibrium adsorption is achieved) such particles might strongly lower the free energy barrier to ice nucleation at its surface. Another interesting explanation[21] suggests that the contact mode enhancement of crystal nucleation is due to the mechanically forced rapid spreading of water along a hydrophobic solid surface which forces its local wetting and thereby temporarily creates local high interface-energy zones increasing the probability of crystal nucleation. While acceptable for some particular cases, all those explanations have some inconsistencies and limitations, and so far no rigorous (and general enough) theoretical model of this phenomenon has been proposed.

As a related problem, recently a thermodynamic theory was developed[22,23] that determines the condition under which the surface of a droplet can stimulate homogeneous crystal nucleation therein so that the homogeneous formation of a crystal nucleus with one of its facets at the droplet surface (surface-stimulated mode) is thermodynamically favored over its formation with all the facets within the liquid phase (volume-based mode). For both unary and multicomponent droplets, that condition has the form of an inequality which coincides with the condition of partial wettability of at least one of the facets of the crystal nucleus by its own melt.[24] This effect was experimentally observed for several systems,[25,26] including water−ice[27] at temperatures at or below 0 °C.

Clearly, the mode of crystal nucleation is most likely determined by both thermodynamic and kinetic factors. However, the partial wettability of a solid by its melt and the confining constraint may help to explain why, in molecular dynamics simulations of various kinds of supercooled liquid droplets,[28,29] crystal nuclei appear preferentially close to the surface. Since smaller droplets have a higher surface-to-volume ratio, the per-droplet nucleation rate in small droplets tends to be higher than those in the bulk. Hence it is experimentally easier to observe the crystallization of aerosols, having a large collective surface area, than those having a large volume. Recent experiments[17] on the heterogeneous freezing of water droplets in both immersion and contact modes have also provided evidence that the rate of crystal nucleation in the contact mode is much higher because the droplet surface may stimulate heterogeneous crystal nucleation in a way similar to the enhancement of the homogeneous process.

In this paper we extend the approach, previously developed in refs 22 and 23, to heterogeneous crystal nucleation on a solid particle (in both immersion and contact modes) and present a thermodynamic model thereof in the framework of the classical nucleation theory (CNT) using the capillarity approximation. Our main thrust is to demonstrate that line tensions associated with three-phase contact lines involved in the process may play as important a role as the surface tensions. Taking into account the line tension effects, a set of modified Wulff's relations (which determine the equilibrium shape of a crystal cluster) is obtained. For particular cases where a cluster of hexagonal ice (Ih) forms with its basal facet on a foreign particle in the immersion and contact modes, we present the works of formation of a cluster as explicit functions of its single variable of state (e.g., its radius or number of molucules therein). Our thermodynamic analysis suggests that, indeed, the droplet surface can thermodynamically enhance crystal nucleation in the contact mode compared to the immersion mode. Whether this occurs or not for a particular foreign particle is determined, however, by the interplay between the surface tensions and line tensions involved in this process.

The paper is structured as follows. In section 2 we derive and compare with each other the expressions for the free energy of formation of a crystal nucleus on a solid (say, dust) particle in the immersion and contact modes. For the sake of simplicity, in this work we consider only unary systems, i.e., pure water droplets, but the generalization to multicomponent droplets can be carried out as well. Only one kind of foreign nucleating centers is considered, namely, those completely wettable by water. In section 3 the model is applied to the formation of crystal clusters of hexagonal ice (Ih) on a foreign solid particle. In the immersion mode, one of the basal facets of an Ih cluster is formed on the foreign particle. In the contact mode, the same basal facet is formed on the foreign particle and, in addition, a prismal facet (assumed to be only partially wettable by water) at the droplet surface. In these cases, explicit expressions for the works of formation of a crystal cluster are presented as functions of just one variable of state of the cluster. Numerical evaluations are discussed in section 4, and the results and conclusions are summarized in section 5.

2. Free Energy of Heterogeneous Formation of Crystal Nuclei in Contact and Immersion Modes

To determine if and how the surface of a liquid droplet can thermodynamically stimulate its heterogeneous crystallization, it is necessary to consider the formation of a crystal cluster in the two modes (Figure 1). In the "immersion" mode, the crystal cluster is formed with one of its facets on a foreign particle that is completely immersed in a liquid droplet; all other crystal facets interface the liquid. In the "contact" mode, the foreign particle touches (i.e., is in contact with) the droplet surface and the cluster forms with one of the crystal facets on the particle (as in the immersion mode), another facet at the liquid−vapor interface, and all other facets making the "crystal−liquid" interface. In these two cases the reversible works of formation of a crystal nucleus (critical cluster) should be derived and compared with each other. This can be carried out in the framework of CNT for both unary and multicomponent droplets. In this paper we consider the crystallization of unary droplets.

The droplet surface can incur some deformation if its crystallization is initiated at its surface. Thus, the thermodynamic analysis of this case is considerably more complicated when compared to the case where the crystal forms at the surface of a bulk liquid. However, for large enough droplets one can assume the droplet surface to be flat and avoid the complexity of taking into account the droplet deformation upon crystallization. This assumption is reasonable under conditions relevant to the freezing of atmospheric droplets, because crystal nuclei are usually of subnanometer or nanometer size, while the droplets themselves are in submicrometer to micrometer size range. Besides, heterogeneous particles serving as nucleating centers can be considered as macroscopic particles of linear sizes much greater than the crystal nuclei; hence the part of its surface on which the crystal nucleus forms can be considered to be flat as well.

Let us consider a single-component bulk liquid. A macroscopic foreign particle is either completely immersed in the liquid or in contact with the liquid−vapor interface. Crystallization will take place in this liquid if it is in a metastable (supercooled) state. The reversible work of crystal formation, W, can be found as the difference between X_{fin}, the appropriate thermodynamic potential of the system in its final state (liquid + crystal), and X_{in}, the same potential in its initial state (liquid): $W = X_{\text{fin}} - X_{\text{in}}$. Since the density of the liquid may be different from that of the solid, the volume of the liquid may change upon crystallization if the process is not constrained to be conducted at constant volume. In such a case, strictly speaking, one cannot calculate W as the difference in the Helmholtz free energies. As an approximation, the use of the Helmholtz free energy is still acceptable since, in the thermodynamic limit (i.e., the system volume and number of molecules tend to infinity but the number density of molecules remains finite), the change in the total volume of the system is usually negligible. A better choice for the thermodynamic potential is the Gibbs free energy if the system is in contact with a pressure reservoir. However,[30] in the thermodynamic limit, the use of either the Gibbs or Helmholtz free energy or grand thermodynamic potential is acceptable for the evaluation of W.

Neglecting the density difference between liquid and solid phases and assuming the crystallization process to be isothermal, one can say that the temperature, total volume, and number of molecules in the system are constant. Thus the reversible work of formation of a crystal cluster can be evaluated as the difference between F_{fin}, the Helmholtz free energy of the system in its final state (liquid + crystal + foreign particle), and F_{in}, in its initial state (liquid + foreign particle):

$$W = F_{\text{fin}} - F_{\text{in}} \tag{1}$$

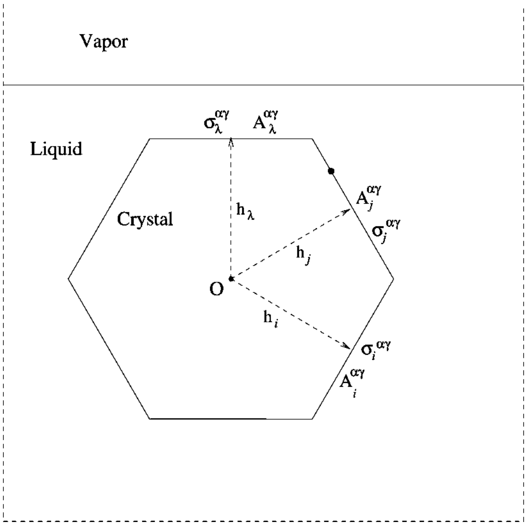

Figure 2. Illustration to Wulff's relations. The surface area and surface tension of facet i are denoted by A_i and σ_i, respectively; h is the distance from facet i to reference point O.

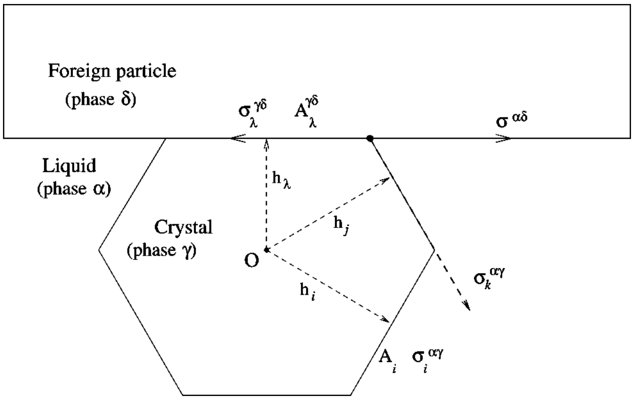

Figure 3. Heterogeneous formation of a crystal nucleus on a foreign particle completely immersed in the liquid.

2.1. Foreign Particle Completely Immersed in the Liquid. Consider a bulk liquid (in a container) whose upper surface is in contact with its vapor phase of constant pressure and temperature. A macroscopic foreign particle is completely immersed in this liquid. Clearly, for this system to be in mechanical and thermodynamic equilibrium, the particle must be completely wettable by the liquid. Upon sufficient supercooling, a crystal nucleus may form heterogeneously with one of its facets on the foreign particle. The crystal is considered to be of arbitrary shape with λ facets (Figure 2). We will assign the subscript "λ" to the facet which is in contact with the foreign particle (Figure 3).

Let us introduce the superscripts α, β, γ, and δ to denote quantities in the liquid, vapor, crystal nucleus, and foreign particle, respectively. Double superscripts will denote quantities at the corresponding interfaces, and triple superscripts at the corresponding three-phase contact lines. The surface area and surface tension of facet i ($i = 1, ..., \lambda$) will be denoted by A_i and σ_i, respectively. (Anisotropic interfacial free energies are believed to be particularly important in determining the character of the nucleation process.) Hereafter, we adopt the definition of the surface tension of a solid, σ^{solid}, as given in chapter 17 of ref 24. Namely, $\sigma^{\text{solid}} = f' + \sum_i \Gamma_i \mu'_i$, where f', Γ, and μ' 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. In the following, we will neglect the adsorption at the solid−fluid interfaces. Thus, by definition, the surface tension of the solid will be equal to the surface free energy per unit area.

Let us denote the number of molecules in the crystal cluster by ν. Neglecting the density change upon freezing, the reversible work of heterogeneous formation of the crystal (with its facet λ on the foreign particle) is given by the expression

$$W^{\text{imm}} = \nu[\mu^{\gamma}(P^{\gamma}, T) - \mu^{\alpha}(P^{\alpha}, T)] - V^{\gamma}(P^{\gamma} - P^{\alpha}) + \sum_{i=1}^{\lambda-1} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_{\lambda}^{\gamma\delta} A_{\lambda}^{\gamma\delta} - \sigma^{\alpha\delta} A_{\lambda}^{\gamma\delta} + \tau^{\alpha\gamma\delta} L^{\alpha\gamma\delta} \quad (2)$$

where μ, P, V, and T are the chemical potential, pressure, volume, and temperature, respectively, and τ is the line tension associated with a three-phase contact line[31,32] of length L. Note that hereinafter the "edge effects" (due to the edges between the adjacent "homogeneously" formed facets of the crystal) are not considered.

The necessary and sufficient conditions for the equilibrium shape (known as the Wulff form) of the crystal are represented by a series of equalities, referred to as Wulff's relations (see, e.g., ref 24), which can be regarded as a series of equilibrium conditions on the crystal "edges" formed by adjacent facets. For example, on the edge between homogeneously formed facets i and $i + 1$ the equilibrium condition is

$$\frac{\sigma_i^{\alpha\gamma}}{h_i} = \frac{\sigma_{i+1}^{\alpha\gamma}}{h_{i+1}} \qquad (i = 1, \ldots, \lambda)$$

where h_i is the distance from facet i to a point O within the crystal (see Figure 2) resulting from the Wulff construction.[24]

When one of the facets (facet λ) constitutes the crystal−foreign particle interface while all the others lie within the liquid phase (see Figure 3), the shape of the crystal will differ from that in which all facets are in contact with the liquid. Modified Wulff's relations, taking into account the effect of the line tension on the equilibrium shape of the crystal, can be obtained by using a generalized version of the Gibbs−Curie theorem[33] (see also, e.g., chapter 17 of ref 24): the equilibrium shape of a crystal of given volume V^{γ} should minimize the function

$$\phi = \sum_{i=1}^{\lambda-1} \sigma_i A_i + (\sigma_{\lambda} - \sigma^{\alpha\beta}) A_{\lambda} + \sum_{k \in \{\kappa\}} \tau_{\lambda k} L_{\lambda k} \quad (3)$$

On the right-hand side of eq 3 the summation goes over the facets of the crystal in the first term and over the pieces of a three-phase contact line in the third term, where $\{\kappa\}$ is the set of facets adjacent to facet λ, and $\tau_{\lambda k}$ and $L_{\lambda k}$ are the line tension and length of the edge formed by adjacent facets λ and k (as already mentioned, the foreign particle is assumed to be much larger than the crystal clusters). The necessary and sufficient condition for the function to have an extremum subject to the constraint V^{γ} = constant is

$$\frac{\partial(\phi - mV^{\gamma})}{\partial h_i} = 0 \quad (4)$$

where m is a Lagrange multiplier. Thus one can obtain the following modified Wulff relations

$$\frac{1}{h_1}\left(\sigma_1^{\alpha\gamma} - \sum_{k \in \{\kappa\}} \tau_{\lambda k} \frac{\partial L_{\lambda k}}{\partial A_1}\right) = \frac{1}{h_2}\left(\sigma_2^{\alpha\gamma} - \sum_{k \in \{\kappa\}} \tau_{\lambda k} \frac{\partial L_{\lambda k}}{\partial A_2}\right) = \cdots = \frac{1}{h_{\lambda}}\left(\sigma_{\lambda}^{\gamma\delta} - \sigma^{\alpha\delta} - \sum_{k \in \{\kappa\}} \tau_{\lambda k} \frac{\partial L_{\lambda k}}{\partial A_{\lambda}}\right) = \frac{m}{2} \quad (5)$$

Equation 5 can be derived from eq 4 by taking into account that $\partial V^{\gamma}/\partial h_i = A_i$, $\partial A_i/\partial h_j = \partial A_j/\partial h_i$, and $A_i = {}^1/_2 \sum_j h_j \partial A_i/\partial h_j = {}^1/_2 \sum_j h_j \partial A_j/\partial h_i$.

In the above considerations, it is assumed that the mechanical effects within the crystal (e.g., stresses) reduce to an isotropic pressure P. In this case[24]

$$P^{\gamma} - P^{\alpha} = m \quad (6)$$

The relations implied in eq 6 for a crystal are equivalent to Laplace's equation applied to a liquid. Thus, just as for a droplet, one can expect to find a high pressure within a small crystal. It is this pressure that increases the chemical potential within the crystal.

Note that the line tension contributions to the free energy of crystal formation were omitted in the model for homogeneous crystal nucleation in the surface-stimulated mode[22,23] because they were assumed to be negligible compared to the volume and surface contributions. However, this assumption may no longer be valid for heterogeneous crystal nucleation because the nucleus is now much smaller (compared to the homogeneously formed one) and hence the contributions of three-phase contact lines can be more important.[34−36]

Equation 2 can be rewritten in the form

$$W^{\text{imm}} = \nu[\mu^{\gamma}(P^{\alpha}, T) - \mu^{\alpha}(P^{\alpha}, T)] + \sum_{i=1}^{\lambda-1} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_{\lambda}^{\gamma\delta} A_{\lambda}^{\gamma\delta} - \sigma^{\alpha\delta} A_{\lambda}^{\gamma\delta} + \tau^{\alpha\gamma\delta} L^{\alpha\gamma\delta} \quad (7)$$

In this equation, the first term represents the excess Gibbs free energy of the molecules in the crystal compared to their Gibbs free energy in the liquid state. This term is related to the enthalpy of fusion Δq by (see, e.g., ref 24)

$$\mu^{\gamma}(P^{\alpha}, T) - \mu^{\alpha}(P^{\alpha}, T) = -\int_{T_0}^{T} \Delta q \frac{\mathrm{d}T'}{T'} \quad (8)$$

where T_0 is the melting temperature of the bulk solid ($T < T_0$) and $\Delta q < 0$.

If the supercooling $T - T_0$ is not too large or, alternatively, if in the temperature range between T and T_0 the enthalpy of fusion does not change significantly, eq 8 takes the form

$$\mu^{\gamma}(P^{\alpha}, T) - \mu^{\alpha}(P^{\alpha}, T) = -\Delta q \ln \Theta \quad (9)$$

with $\Theta = T/T_0$. Thus, one can rewrite eq 7 in the following form

$$W^{\text{imm}} = -\nu \Delta q \ln \Theta + \sum_{i=1}^{\lambda-1} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_{\lambda}^{\gamma\delta} A_{\lambda}^{\gamma\delta} - \sigma^{\alpha\delta} A_{\lambda}^{\gamma\delta} + \tau^{\alpha\gamma\delta} L^{\alpha\gamma\delta} \quad (10)$$

By definition, the critical crystal (i.e., nucleus) is in unstable equilibrium with the surrounding melt. For such a crystal, the first term in eq 2 vanishes. On the other hand, for a crystal with one of its facets constituting a crystal−foreign particle interface, and the others interfaced with the liquid, one can show that

$$V^{\gamma}(P^{\gamma}-P^{\alpha})=\frac{2}{3}\left(\sum_{i=1}^{\lambda-1}\sigma_i^{\alpha\gamma}A_i^{\alpha\gamma}+\sigma_{\lambda}^{\gamma\delta}A_{\lambda}^{\gamma\delta}-\sigma^{\alpha\delta}A_{\lambda}^{\gamma\delta}\right)-\frac{2}{3}\sum_{k\in\{\kappa\}}\tau_{\lambda k}\frac{\partial L_{\lambda k}}{\partial A_k}A_k \quad (11)$$

This equality can be derived by representing V^{γ} as the sum $^1/_3\Sigma_{i=1}{}^{\lambda}h_iA_i$ of the volumes of λ pyramids with their bases at the crystal facets and their apexes at point O. The difference $P^{\gamma} - P^{\alpha}$ for every term in this sum is replaced by the right-hand side of the corresponding equality in eq 6. Substituting eq 11 into eq 2, one obtains the following expression for the reversible work $W_*{}^{\text{imm}}$ of formation of a critical crystal:

$$W_*{}^{\text{imm}}=\frac{1}{3}\left(\sum_{i=1}^{\lambda-1}\sigma_i^{\alpha\gamma}A_i^{\alpha\gamma}+\sigma_{\lambda}^{\gamma\delta}A_{\lambda}^{\gamma\delta}-\sigma^{\alpha\delta}A_{\lambda}^{\gamma\delta}\right)+\tau^{\alpha\gamma\delta}L^{\alpha\gamma\delta}+\frac{2}{3}\sum_{k\in\{\kappa\}}\tau_{\lambda k}\frac{\partial L_{\lambda k}}{\partial A_k}A_k \quad (12)$$

or, alternatively

$$W_*{}^{\text{imm}}=\frac{1}{2}V_*{}^{\gamma}(P_*{}^{\gamma}-P^{\alpha})+\tau^{\alpha\gamma\delta}L^{\alpha\gamma\delta}+\sum_{k\in\{\kappa\}}\tau_{\lambda k}\frac{\partial L_{\lambda k}}{\partial A_k}A_k \quad (13)$$

(Hereafter the asterisk subscript indicates the quantities for the nucleus; it is omitted on the right-hand side of expressions for $W_*{}^{\text{imm}}$ to avoid the overcrowding of indices.)

Clearly, in the atmosphere the crystal cluster forms not in the bulk liquid but within a liquid droplet (see Figure 1) which is itself surrounded by a vapor phase. The reasoning here is almost identical to the preceding if, again, we neglect the density difference between the liquid and crystal phases. One can easily show that all above equations, starting with eq 2 and including eqs 12 and 13 for the reversible work $W_*{}^{\text{imm}}$ of formation of the critical crystal, remain valid except that P^{α} and P^{β}, pressures in the liquid and vapor phases, are related by the Laplace equation $P^{\alpha} = P^{\beta} + 2\sigma^{\alpha\beta}/R$, with R being the radius of the droplet (assumed to remain constant during freezing).

2.2. Foreign Particle in Contact with a Liquid−Vapor Interface.

Now let us consider a foreign particle which is not immersed in a bulk liquid but is in some kind of contact with the liquid−vapor interface (Figures 1 and 4), with the vapor phase being at constant pressure and temperature. (Clearly, the particle must be completely wettable by the liquid in order for the same particle to be able to be in mechanical and thermodynamic equilibrium in both immersion and contact modes.) Upon sufficient supercooling, a crystal nucleus may form heterogeneously with one of its facets (marked with the subscript "λ") on the foreign particle and another one at the vapor−liquid interface. The latter facet will be marked with the subscript $\lambda - 1$. All the other $\lambda - 2$ facets lie within the liquid phase.

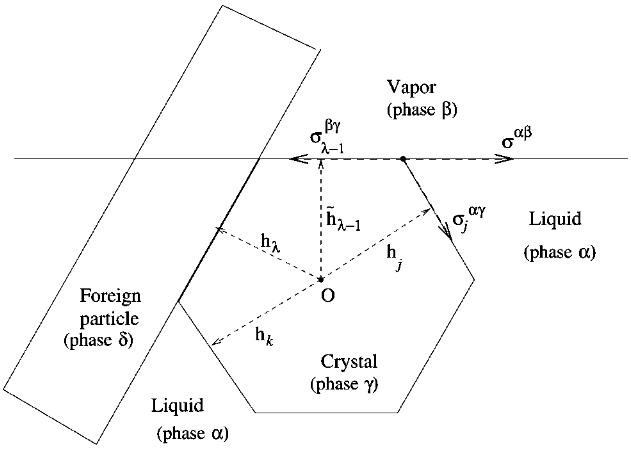

Figure 4. Heterogeneous formation of a crystal nucleus on a foreign particle in contact with the liquid−vapor interface.

Again, neglecting the density change upon freezing, the reversible work of heterogeneous formation of the crystal with its facet λ on the foreign particle, the facet $\lambda - 1$ interfacing vapor (i.e., in the contact mode), and all the others within the liquid phase will be given by the expression

$$W^{\text{con}}=\nu[\mu^{\gamma}(P^{\gamma},T)-\mu^{\alpha}(P^{\alpha},T)]-V'^{\gamma}(P^{\gamma}-P^{\alpha})+\sum_{i=1}^{\lambda-2}\sigma_i^{\alpha\gamma}A_i^{\alpha\gamma}+\sigma_{\lambda-1}^{\beta\gamma}A_{\lambda-1}^{\beta\gamma}-\sigma^{\alpha\beta}A_{\lambda-1}^{\beta\gamma}+\sigma_{\lambda}^{\gamma\delta}A_{\lambda}^{\gamma\delta}-\sigma^{\alpha\delta}A_{\lambda}^{\gamma\delta}+\tau^{\alpha\beta\gamma}L^{\alpha\beta\gamma}+(\tau^{\beta\gamma\delta}-\tau^{\alpha\beta\gamma})L^{\beta\gamma\delta}+\tau^{\alpha\gamma\delta}L'^{\alpha\lambda\delta} \quad (14)$$

Considering the contact mode, the prime will indicate quantities whereof the values may differ from those in the immersion mode. The equilibrium shape of the crystal (the Wulff form) will differ from that formed heterogeneously in the immersion mode (i.e., when all facets, except for facet λ, are in contact with the liquid). Corresponding Wulff's relations, taking into account the effect of line tensions on the equilibrium shape of the crystal, can be again derived by using an extended version of the Gibbs−Curie theorem,[33,24] leading to

$$\frac{1}{h'_1}\left(\sigma_1^{\alpha\gamma}-\sum_{j\in\{\omega\}}\tau_{\lambda-1,j}\frac{\partial L_{\lambda-1,j}}{\partial A_1}-\sum_{k\in\{\kappa\}}\tau_{\lambda k}\frac{\partial L_{\lambda k}}{\partial A_1}\right)=\frac{1}{h'_2}\left(\sigma_2^{\alpha\gamma}-\sum_{j\in\{\omega\}}\tau_{\lambda-1,j}\frac{\partial L_{\lambda-1,j}}{\partial A_2}-\sum_{k\in\{\kappa\}}\tau_{\lambda k}\frac{\partial L_{\lambda k}}{\partial A_2}\right)=\cdots=\frac{1}{h'_{\lambda-1}}\left(\sigma_{\lambda-1}^{\gamma\beta}-\sigma^{\alpha\beta}-\sum_{j\in\{\omega\}}\tau_{\lambda-1,j}\frac{\partial L_{\lambda-1,j}}{\partial A_{\lambda-1}}-\sum_{k\in\{\kappa\}}\tau_{\lambda k}\frac{\partial L_{\lambda k}}{\partial A_{\lambda-1}}\right)=\frac{1}{h'_{\lambda}}\left(\sigma_{\lambda}^{\gamma\delta}-\sigma^{\alpha\delta}-\sum_{j\in\{\omega\}}\tau_{\lambda-1,j}\frac{\partial L_{\lambda-1,j}}{\partial A_{\lambda}}-\sum_{k\in\{\kappa\}}\tau_{\lambda k}\frac{\partial L_{\lambda k}}{\partial A_{\lambda}}\right)=\frac{m'}{2} \quad (15)$$

where $\{\omega\}$ is the set of facets adjacent to facet $\lambda - 1$, $\tau_{\lambda-1,j}$ and $L_{\lambda-1,j}$ are the line tension and length of the edge formed by adjacent facets $\lambda - 1$ and j. Note that m' in eq 15 is the Lagrange multiplier analogous (but not identical) to m, both arising from the minimization of the free energy of formation of a crystal cluster subject to the constraint V^{γ} = constant. Consequently, eq 6 (the equivalent of Laplace's equation applied to crystals) becomes

$$P^{\gamma}-P^{\alpha}=m' \quad (16)$$

Equation 14 can be rewritten as

$$W^{\text{con}}=\nu[\mu^{\gamma}(P^{\alpha},T)-\mu^{\alpha}(P^{\alpha},T)]+\sum_{i=1}^{\lambda-2}\sigma_i^{\alpha\gamma}A_i^{\alpha\gamma}+\sigma_{\lambda}^{\beta\gamma}A_{\lambda-1}^{\beta\gamma}-\sigma^{\alpha\beta}A_{\lambda-1}^{\beta\gamma}+\sigma_{\lambda}^{\gamma\delta}A_{\lambda}^{\gamma\delta}-\sigma^{\alpha\delta}A_{\lambda}^{\gamma\delta}+\tau^{\alpha\beta\gamma}L^{\alpha\beta\gamma}+(\tau^{\beta\gamma\delta}-\tau^{\alpha\beta\delta})L^{\beta\gamma\delta}+\tau^{\alpha\gamma\delta}L'^{\alpha\gamma\delta} \quad (17)$$

Furthermore, using eq 9 one can rewrite eq 17 in the following form

$$W^{\mathrm{con}} = -\nu\Delta q \ln\Theta + \sum_{i=1}^{\lambda-2}\sigma_i{}^{\alpha\gamma}A_i{}^{\alpha\gamma} + \sigma_{\lambda-1}{}^{\beta\gamma}A_{\lambda-1}{}^{\beta\gamma} - \sigma^{\alpha\beta}A_{\lambda-1}{}^{\beta\gamma} + \sigma_\lambda{}^{\gamma\delta}A_\lambda{}^{\gamma\delta} - \sigma^{\alpha\delta}A_\lambda{}^{\gamma\delta} + \tau^{\alpha\beta\gamma}L^{\alpha\beta\gamma} + (\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta})L^{\beta\gamma\delta} + \tau^{\alpha\gamma\delta}L'^{\alpha\gamma\delta} \quad (18)$$

For a crystal with one of its facets constituting a solid−vapor interface, and the others interfaced with the liquid, one can obtain

$$V'^{\gamma}(P^\gamma - P^\alpha) = \frac{2}{3}\left(\sum_{i=1}^{\lambda-2}\sigma_i{}^{\alpha\gamma}A_i{}^{\alpha\gamma} + \sigma_{\lambda-1}{}^{\beta\gamma}A_\lambda{}^{\beta\gamma} - \sigma^{\alpha\beta}A_{\lambda-1}{}^{\beta\gamma} + \sigma_\lambda{}^{\gamma\delta}A_\lambda{}^{\gamma\delta} - \sigma^{\alpha\delta}A_\lambda{}^{\gamma\delta}\right) - \frac{2}{3}\sum_{j\in\{\omega\}}\tau_{\lambda-1,j}\frac{\partial L_{\lambda-1,j}}{\partial A_j}A_j - \frac{2}{3}\sum_{k\in\{\kappa\}}\tau_{\lambda k}\frac{\partial L_{\lambda k}}{\partial A_k}A_k \quad (19)$$

This equality makes it possible to represent the reversible work W of formation of a critical crystal by the expression

$$W_*{}^{\mathrm{con}} = \frac{1}{3}\left(\sum_{i=1}^{\lambda-2}\sigma_i{}^{\alpha\gamma}A_i{}^{\alpha\gamma} + \sigma_{\lambda-1}{}^{\beta\gamma}A_{\lambda-1}{}^{\beta\gamma} - \sigma^{\alpha\beta}A_{\lambda-1}{}^{\beta\gamma} + \sigma_\lambda{}^{\gamma\delta}A_\lambda{}^{\gamma\delta} - \sigma^{\alpha\delta}A_\lambda{}^{\gamma\delta}\right) + \tau^{\alpha\beta\gamma}L^{\alpha\beta\gamma} + (\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta})L^{\beta\gamma\delta} + \tau^{\alpha\gamma\delta}L'^{\alpha\gamma\delta} + \frac{2}{3}\sum_{j\in\{\omega\}}\tau_{\lambda-1,j}\frac{\partial L_{\lambda-1,j}}{\partial A_j}A_j + \frac{2}{3}\sum_{k\in\{\kappa\}}\tau_{\lambda k}\frac{\partial L_{\lambda k}}{\partial A_k}A_k \quad (20)$$

or, alternatively, as

$$W_*{}^{\mathrm{con}} = \frac{1}{2}V'_*{}^{\gamma}(P_*{}^\gamma - P^\alpha) + \tau^{\alpha\beta\gamma}L^{\alpha\beta\gamma} + (\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta})L^{\beta\gamma\delta} + \tau^{\alpha\gamma\delta}L'^{\alpha\gamma\delta} + \sum_{j\in\{\omega\}}\tau_{\lambda-1,j}\frac{\partial L_{\lambda-1,j}}{\partial A_j}A_j + \sum_{k\in\{\kappa\}}\tau_{\lambda k}\frac{\partial L_{\lambda k}}{\partial A_k}A_k \quad (21)$$

Equations 20 and 21 are similar to eqs 12 and 13 which apply to heterogeneous crystal nucleation in the immersion mode. Along with eq 13, eq 21 will be most useful in later discussions.

2.3. The Comparison of the Immersion and Contact Modes. Clearly, to calculate $W_*{}^{\mathrm{imm}}$ and $W_*{}^{\mathrm{con}}$ it is necessary to know not only the physicochemical characteristics of the forming crystals (such as Δq, σ's, and τ's, etc.) but also the shape and size of the crystal nuclei. The latter, however, can be accurately determined analytically if the former are known (see the Appendix).

The reversible works of heterogeneous formation of crystal nuclei in the immersion and contact modes can be also compared by using the above results. The difference between the internal pressure of the nucleus and the external pressure does not depend on whether the nucleus forms in the immersed mode (let us denote it by $(P_*{}^\gamma - P^\alpha)^{\mathrm{imm}}$) or in the contact mode (denoted by $(P_*{}^\gamma - P^\alpha)^{\mathrm{con}}$). Indeed, by using eq 9 and the equilibrium condition for the nucleus

$$\mu^\gamma(P^\gamma, T) - \mu^\alpha(P^\alpha, T) = 0 \quad (22)$$

and assuming the crystal to be incompressible, one can show that in both cases the difference $P_*{}^\gamma - P^\alpha$ for the nucleus is determined by the supercooling of the liquid, so that

$$(P_*{}^\gamma - P^\alpha)^{\mathrm{con}} = (P_*{}^\gamma - P^\alpha)^{\mathrm{imm}} = \frac{\Delta q}{v^\gamma}\ln\Theta \quad (23)$$

where v^γ is the volume per molecule in the crystal phase. According to eqs 13 and 21

$$W_*{}^{\mathrm{con}} - W_*{}^{\mathrm{imm}} = \frac{1}{2}(V'_*{}^{\gamma} - V_*{}^{\gamma})(P_*{}^\gamma - P^\alpha) + \tau^{\alpha\gamma\delta}(L'_\lambda{}^{\alpha\gamma\delta} - L_\lambda{}^{\alpha\gamma\delta}) + (\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta})L'^{\beta\gamma\delta} + \tau^{\alpha\beta\gamma}L'_{\lambda-1}{}^{\alpha\gamma\delta} + \sum_{j\in\{\omega\}}\tau'_{\lambda-1,j}\frac{\partial L'_{\lambda-1,j}}{\partial A'_j}A'_j + \sum_{k\in\{\kappa\}}\left(\tau'_{\lambda k}\frac{\partial L'_{\lambda k}}{\partial A'_k}A'_k - \tau_{\lambda k}\frac{\partial L_{\lambda k}}{\partial A_k}A_k\right) \quad (24)$$

(recall that primes are used to distinguish between the same quantities in the contact and immersion modes).

For homogeneous crystal nucleation the difference $W_*{}^{\mathrm{con}} - W_*{}^{\mathrm{imm}}$ (i.e., the right-hand side of eq 24) was obtained and analyzed without taking the line tension effects into account.[22,23] In such an approximation, the first equality in eq 23 is equivalent to

$$h'_{\lambda-1} = \frac{\sigma_{\lambda-1}{}^{\beta\gamma} - \sigma^{\sigma\beta}}{\sigma_{\lambda-1}{}^{\alpha\gamma}}h_{\lambda-1} \quad (25)$$

On the other hand, by virtue of eqs 5, 6, 15, 16, and 23, $h_i = h'_i$ for $i = 1,\ldots, \lambda - 2, \lambda$. This would mean that the Wulff shape of the crystal in the contact mode is obtained by simply changing the height of the $(\lambda - 1)$th pyramid of the Wulff crystal in the immersion mode. It would be hence clear that if $\sigma_{\lambda-1}{}^{\beta\gamma} - \sigma^{\alpha\beta} < \sigma_{\lambda-1}{}^{\beta\gamma}$, then

$$h'_{\lambda-1} < h_{\lambda-1} \Rightarrow V'_*{}^{\gamma} < V_*{}^{\gamma} \quad (26)$$

Because of eqs 25 and 26, if

$$\sigma_{\lambda-1}{}^{\beta\gamma} - \sigma^{\alpha\beta} < \sigma_{\lambda-1}{}^{\alpha\gamma} \quad (27)$$

then the first term on the right-hand side of eq 24 would be negative. Thus, one could conclude that if the condition in eq 27 is fulfilled, it is thermodynamically more favorable for the crystal nucleus to form with its facet $\lambda-1$ at the surface rather than within the liquid. Inequality 27 coincides with the condition of partial wettability of the $(\lambda - 1)$th facet of the crystal by its own liquid phase.[24]

However, the presence of the line tension contribution on the right-hand side of eq 27 makes it impossible to draw unambiguous conclusions concerning the difference $W_*{}^{\mathrm{con}} - W_*{}^{\mathrm{imm}}$ for heterogeneous crystal nucleation even when inequality 27 is fulfilled. Although the first term on the right-hand side of eq 24 is negative and gives rise to the thermodynamic propensity of the crystal nucleus to form with facet $\lambda - 1$ at the droplet surface, the line tension contributions can be both negative and positive because any of the line tensions involved can be either negative or positive.[34−36] Moreover, depending on the temperature at which the crystallization occurs, the sign of the line tension may change.

As clear from eqs 5 and 10 and from eqs 15 and 18, taking into account the effect of the line tension of three-phase contacts on both W^{imm} and W^{con} has a 2-fold result. On one hand, there appear explicit contributions to the free energy of formation of a crystal cluster due to the line tension. The corresponding terms on the right-hand sides of eqs 10 and 18 have the form "line tension × length of the line". On the other hand, the line tension has a more subtle effect on W^{imm} and W^{con} because, as clear from eqs 5 and 15, it affects the equilibrium shape of the crystal cluster. These two effects are jointly represented on the right-hand side of eqs 13 and 21: the former (hereafter referred to as "the primary" effect of line tension) gives rise to terms proportional to the lengths of three-phase contact lines, while the latter (hereafter referred to as "the secondary" effect of the line tension) results in terms proportional to the first derivatives of the contact line lengths with respect to the areas of facets.

On the right-hand side of eq 24 the second, third, and fourth terms represent the primary effect of the line tension on the difference $W_*^{\mathrm{con}} - W_*^{\mathrm{imm}}$, whereas the last two terms (the fifth and sixth ones) represent the secondary effect of line tension. To roughly evaluate the fifth term, consider facet $\lambda - 1$ such that $\tau^{\beta\gamma\delta} = \tau_{\lambda-1,j}$ for $j = \lambda$ and $\tau^{\alpha\beta\gamma} = \tau_{\lambda-1,j}$ for all other j values from the set $\{\omega\}$. Roughly assuming that $L_{\lambda-1,j}$ ($j \in \{\omega\}$) is proportional to $A_j^{1/2}$, we have $A_j \partial L_{\lambda-1,j}/\partial A_j \simeq {}^1/_2 L_{\lambda-1,j}$. Therefore, the fifth term (representing the secondary effect of line tension) on the right-hand side of eq 24 is smaller than the sum $\tau^{\beta\gamma\delta} L'^{\beta\gamma\delta} + \tau^{\alpha\beta\gamma} L_{\lambda-1}{}^{\beta\gamma\delta}$ (representing the primary effect of line tension) therein by a factor of 1/2. Thus, the former can be neglected compared to the latter in rough evaluations involving the uncertainty in the order of magnitude of τ values. Likewise, one can show that the sixth term (due to the secondary effect of line tension) on the right-hand side of eq 24 is negligible compared to the corresponding contributions in the second and third terms (due to the primary line tension effects) therein. Because all the following numerical evaluations will involve line tensions with large uncertainties in their orders of magnitude, the secondary effects of the line tension (e.g., the fifth and sixth terms on the right-hand side of eq 24) will be neglected hereafter.

3. Numerical Evaluations and Discussions

Whereas a detailed treatment is presented in the Appendix, the lack of information regarding the physical parameters required us to use an approximate evaluation in what follows.

To illustrate the above theory with numerical calculations, let us consider the formation of Ih crystals on foreign particles in water droplets in both immersion and contact modes at some themperature T K (specified below). By evaluating the difference $W_*^{\mathrm{con}} - W_*^{\mathrm{imm}}$ as a whole and the relative importance of the volume, surface, and contact line contributions thereto, one can shed some light on physical mechanisms underlying the enhancement of crystal nucleation in the contact mode compared to the immersion one.

To estimate the difference between W_*^{con} and W_*^{imm}, it is necessary to know the shape and the sizes of nuclei in both modes as well as the density of Ih, its enthalpy of melting, and all the surface and line tensions involved. This set of physicochemical characteristics also determines the shape and the size of the nuclei. Thus, information on ρ, Δq, $\sigma^{\alpha\beta}$, $\sigma^{\alpha\delta}$, $\sigma_{\mathrm{b}}^{\alpha\gamma}$, $\sigma_{\mathrm{p}}^{\alpha\gamma}$, $\sigma_{\mathrm{b}}^{\gamma\delta}$, $\sigma_{\mathrm{p}}^{\beta\gamma}$, $\tau^{\alpha\beta\gamma}$, $\tau^{\alpha\beta\delta}$, $\tau^{\alpha\gamma\delta}$, and $\tau^{\beta\gamma\delta}$ is needed to evaluate $W_*^{\mathrm{con}} - W_*^{\mathrm{imm}}$ and the relative importance of various terms on the right-hand side of eq 24. Subscripts b and p mark quantities for the basal and prismal facets, respectively.

Experimental data on $\rho^\gamma \equiv 1/v^\gamma$, Δq, and $\sigma^{\alpha\beta}$ are readily available (even as functions of temperature). For our evaluations they were taken to be $\rho^\gamma = (0.92N_{\mathrm{A}}/18)$ cm^{-3}, $\Delta q \simeq (333.55 \times 10^7 N_{\mathrm{A}}/18)$ erg (where N_{A} is the Avogadro number), and $\sigma^{\alpha\beta} = 83$ dyn/cm. Some data on the crystal−liquid and crystal−vapor surface tension have been also reported (see ref 2 for a short review). These data suffice to evaluate the size of the critical cluster for homogeneous crystal nucleation. Such estimates can serve as a reference point to evaluate the relative importance of the line tension contributions on the right-hand side of eq 24 for $W_*^{\mathrm{con}} - W_*^{\mathrm{imm}}$.

Indeed, consider the homogeneous freezing of water droplets at $T_{\mathrm{hm}} = 233$ K and assume that in the surface-stimulated mode one of the basal facets of the Ih crystal constitutes a part of the droplet surface. The height of the basal pyramid of the crystal cluster will be denoted by $\tilde{h}_{\mathrm{b}}$ when the basal facet is at the droplet surface and by h_{b} when the entire crystal is immersed in the droplet. According to ref 2 at this temperature $\sigma_{\mathrm{b}}^{\alpha\gamma} \simeq 19.2$ dyn/cm, $\sigma_{\mathrm{p}}^{\alpha\gamma} \simeq 20.5$ dyn/cm, and $\sigma_{\mathrm{b}}^{\beta\gamma} \simeq 102$ dyn/cm, $\sigma_{\mathrm{p}}^{\beta\gamma} \simeq 111$ dyn/cm. For the sake of rough evaluations neglecting the line tension contribution to W_*^{ss} (free energy of formation of a crystal nucleus in the surface-stimulated mode), by virtue of eq A2 of the Appendix (and equations thereafter) one can obtain for the crystal nuclei in the volume-based and surface-stimulated modes: $h_* \equiv 2h_{\mathrm{b}} \simeq 23 \times 10^{-8}$ cm, $\tilde{h}_* \equiv \tilde{h}_{\mathrm{b}} + h_{\mathrm{b}} \simeq 20 \times 10^{-8}$ cm, $W_*^{\mathrm{vb}} \simeq 47\ kT_{\mathrm{hm}}$, $W_*^{\mathrm{ss}} \simeq 40.5\ kT_{\mathrm{hm}}$, $\Delta W_* \equiv W_*^{\mathrm{ss}} - W_*^{\mathrm{vb}} \approx -6.5\ kT_{\mathrm{hm}}$ (W_*^{vb} is the free energy of formation of a crystal nucleus in the volume-based mode).

These evaluations are for homogeneous crystal nucleation in the volume-based versus surface-stimulated modes which correspond to the immersion and contact modes, respectively, of the heterogeneous crystal nucleation. At any particular temperature, the critical crystal of heterogeneous nucleation is much smaller than for homogeneous nucleation. On the other hand, the size of the nucleus increases with increasing temperature (i.e., decreasing supercooling). Thus, one can expect that for any foreign particle there exists a temperature 233 K $< T_{\mathrm{ht}} <$ 273 K such that the linear size of the crystal nucleus (hence the number of molecules therein, ν_{c}) for heterogeneous nucleation is comparable to that estimated above for homogeneous nucleation at $T_{\mathrm{hm}} = 233$ K.

Let us assume that for a selected foreign particle the temperature $T_{\mathrm{ht}} \simeq 253$ K with the thermal energy unit $k_{\mathrm{B}}T_{\mathrm{ht}} \simeq 3.5 \times 10^{-14}$ erg. At this temperature, the first term on the right-hand side of eq 24 (hereafter referred to as the "surface-stimulation term") can be roughly assumed to be equal to ΔW_* because both quantities represent the surface contribution to the difference between the free energy of nucleus formation in the surface-stimulated and volume-based modes (for heterogeneous and homogeneous nucleation, respectively). Thus, according to the above estimates

$$\frac{(1/2)(V'^{\gamma}_* - V^{\gamma}_*)(P^{\gamma}_* - P^{\alpha})}{k_{\mathrm{B}}T_{\mathrm{ht}}} \approx \frac{\Delta W_*}{k_{\mathrm{B}}T_{\mathrm{ht}}} \approx -6.5\frac{T_{\mathrm{hm}}}{T_{\mathrm{ht}}} \approx -6.0 \tag{28}$$

As mentioned above, this contribution is negative if facet $\lambda - 1$ (formed at the liquid−vapor interface) is only partially wettable by its melt (i.e., water), which is the case with the basal facet of the crystals of hexagonal ice. Consequently, the droplet surface always makes the contact mode of heterogeneous crystal nucleation in water droplets thermodynamically more favorable than the immersion mode, regardless of the nature of the foreign particle.

It is almost impossible to provide general unambiguous estimates for the line tension contributions to $W_*^{\mathrm{con}} - W_*^{\mathrm{imm}}$ in eq 24. Indeed, the line tension is notorious not only for the lack of reliable experimental data but (mostly) for its ability of being both negative and positive and take values in the range from 10^{-1} to 10^{-5} dyn (see, e.g., refs 34−36; according to ref 34, e.g., a positive line tension prevents a liquid droplet from spreading at the solid−vapor interface, while a negative line tension facilitates such spreading). Nevertheless, some estimates can provide useful insight into the problem of "contact mode vs immersion mode" of heterogeneous crystal nucleation.

In the second term on the right-hand side of eq 24, $L'^{\alpha\gamma\delta} - L^{\alpha\gamma\delta}$ represents the difference between the lengths of the "liquid−crystal−foreign particle" contact line in the contact and immersion modes. It is negative because the length in the contact mode is smaller than the length in the immersion mode. Considering, as above, that it is the basal facet of the hexagonal ice crystal which forms at the liquid−vapor interface (with one of the six prismal facets formed on the foreign particle), one can conclude that $L'^{\alpha\gamma\delta} - L^{\alpha\gamma\delta} \approx -a = -12.2 \times 10^{-8}$ cm. As for the line tension $\tau^{\alpha\gamma\delta}$, its sign can be expected to be positive,[33−35] but we are not aware of any experimental or theoretical data reported for "foreign particle−crystal−vapor" three-phase contact regions. Assuming that $\tau^{\alpha\gamma\delta}$ can be anywhere in the range from 10^{-1} dyn to 10^{-5} dyn, it is still most likely to be closer to 10^{-5} than to 10^{-1} dyn because two out of three phases in contact are solid phases involving little inhomogeneities of density profiles in the contact region. Thus, one can cautiously suggest that (a) this three-phase contact line impedes the heterogeneous crystal nucleation in the immersion mode vs contact mode and (b) possible values of the term $\tau^{\alpha\gamma\delta}(L'^{\alpha\gamma\delta} - L^{\alpha\gamma\delta})/k_BT$ may be somewhere in the range from −100 to −10.

The third term on the right-hand side of eq 24 is due to the three-phase contact line "liquid−vapor−foreign particle. The length of this line, $L^{\beta\gamma\delta}$, is equal to $-(L'^{\alpha\gamma\delta} - L^{\alpha\gamma\delta})$, evaluated in the above paragraph, i.e., $L^{\beta\gamma\delta} \approx 12.2 \times 10^{-8}$ cm. Further, the density inhomogeneities in the "foreign particle−crystal−vapor" contact region can be expected to be negligible compared to those in the "foreign particle−crystal−liquid", "liquid−vapor−foreign particle", or "liquid−vapor−liquid". Therefore, one can consider that the line tension $\tau^{\beta\gamma\delta}$ is negligible when compared to $\tau^{\beta\gamma\delta}$, so that the third term becomes $(\tau^{\beta\gamma\delta} - \tau^{\alpha\gamma\delta})L^{\beta\gamma\delta} \simeq -\tau^{\alpha\beta\delta}L^{\beta\gamma\delta}$. Depending on the wettability of the foreign particle by liquid water in the water vapor, $\tau^{\alpha\beta\delta}$ can be positive as well as negative. It was noted, however, that for the same foreign particle to be able to serve as an equilibrium nucleating center in both immersion and contact modes it has to be completely wettable by water. Because of this, one can suggest[33−35] that the line tension $\tau^{\alpha\beta\delta} < 0$ with its absolute value closer to 10^{-5} dyn than to 10^{-1} dyn. Besides, the third term on the right-hand side of eq 24 can be expected to provide a contribution to $W_*^{\text{con}} - W_*^{\text{imm}}$ which is close to the contribution from the second term in absolute value and has the opposite sign. The approximate compensation of the second and third terms can thus be expected (if such compensation does not occur, the effect of the line tension on $W_*^{\text{con}} - W_*^{\text{imm}}$ will be even bigger).

The fifth term on the right-hand side of eq 24 is due to the three-phase contact line "liquid−vapor−crystal". Considering again the basal facet of the hexagonal ice crystal forms at the liquid−vapor interface (with one of the six prismal facets on the foreign particle), the length of this contact line is approximately $L^{\alpha\beta\gamma} \approx 5a$, that is, $L^{\alpha\beta\gamma} \approx 63.0 \times 10^{-8}$ cm. As the basal facet of an Ih crystal is partially wettable by liquid water with the contact angle (measured inside the liquid phase) less than $\pi/2$, one can consider $\tau^{\alpha\beta\gamma}$ to be negative.[31,32] Even assuming for the value of $\tau^{\alpha\beta\gamma}$ the smallest experimentally reported order of magnitude, 10^{-5} erg, one can conclude that (a) this contact line significantly enhances the contact mode of heterogeneous crystal nucleation compared to the immersion mode and (b) the absolute value of the line tension contribution to $W_*^{\text{con}} - W_*^{\text{imm}}$ from the "vapor−liquid−ice" contact line can be greater than that of the surface-stimulation term (first term on the right-hand side of eq 24) by 1 order of magnitude. Thus, this line tension contribution to $W_*^{\text{con}} - W_*^{\text{imm}}$ can dominate the surface-stimulation term.

Evaluations for the case where the nucleus of an Ih crystal is formed (a) in the immersion mode with the basal facet on the foreign particle and (b) in the contact mode with the basal facet on the particle and one of its prismal facet at the droplet−vapor interface can be carried out in a similar fashion. Besides one can consider the case where in the contact mode one prismal facet forms on the foreign particle and another at the droplet surface. Curiously, in this situation the foreign particle does not even have to be in contact with the droplet surface. Moreover, the crystal nucleus may form with one of its basal facets on the foreign particle and the other at the droplet surface, and in this case, the foreign particle cannot be in contact with the droplet surface at all (unless it has a very irregular, noncompact shape). In the latter case, the term " contact mode" is not even appropriate. Two common features of all these "contact mode" situations are that (a) one of the crystal facets always forms at the droplet surface and (b) there always exists a contact "vapor−liquid−crystal" of three water phases. Both of these factors (the latter even significantly stronger than the former) thermodynamically favor the formation of a crystal nucleus in the contact mode compared to the immersion one. The correctness of the term "contact mode" becomes, however, questionable, at least from a thermodynamic standpoint. One trivial exception from the above consideration is the case where the surface of the foreign particle touches the liquid−vapor interface from outside in parallel orientation (see Figure 1, case 4). In this situation the same facet of the crystal nucleus forms at the droplet surface and on the foreign particle, and there is no thermodynamic advantage for this mode compared to the immersion mode (when the crystal nucleus forms with the same facet on the same surface of the foreign particle).

As outlined above and in the Appendix, one can carry out accurate numerical evaluations (of a_* and h_* as well as $W_*^{\text{con}} - W_*^{\text{imm}}$) if information on ρ, Δq, $\sigma^{\alpha\beta}$, $\sigma^{\alpha\delta}$, $\sigma_b^{\alpha\gamma}$, $\sigma_p^{\alpha\gamma}$, $\sigma_b^{\gamma\delta}$, $\sigma_p^{\beta\delta}$, $\tau^{\alpha\beta\gamma}$, $\tau^{\alpha\beta\delta}$, $\tau^{\alpha\gamma\delta}$, and $\tau^{\beta\gamma\delta}$ were available. However, virtually no reliable data are currently available for any solid−ice and solid−water interfacial tensions and line tensions in "solid substrate−ice−liquid water−water vapor" systems. One can choose them somewhat arbitrarily, the main criterion being a reasonable agreement of the estimates extracted from eq A1 in the Appendix with those obtained in this section on the basis of a_*, h_*, and ΔW_* for homogeneous ice nucleation. Considering the nucleation of ice crystals on a foreign particle such that at a given temperature $\sigma^{\alpha\delta} = 40$ dyn/cm, $\sigma_b^{\alpha\gamma} = 23$ dyn/cm, $\sigma_p^{\alpha\gamma} = 24$ dyn/cm, $\sigma_b^{\gamma\delta} = 50$ dyn/cm, $\sigma_p^{\beta\gamma} = 102$ dyn/cm, $\tau^{\alpha\beta\gamma} = -10^{-4}$ dyn, $\tau^{\alpha\beta\delta} = 7 \times 10^{-5}$ dyn, $\tau^{\alpha\gamma\delta} = 10^{-5}$ dyn, and $\tau^{\beta\gamma\delta} = 5 \times 10^{-6}$ dyn (reasonable choice according to scarce data available in literature), equations for a_* and h_* would provide $a_* \simeq 29 \times 10^{-8}$ cm, $h_* \simeq 34.5 \times 10^{-8}$ cm, and $W_*^{\text{con}} - W_*^{\text{imm}} \simeq -12k_BT_{\text{ht}}$, which are consistent with expectations.

4. Concluding Remarks

Previously, in the framework of CNT a criterion was found for when the surface of a droplet can stimulate crystal nucleation therein so that the formation of a crystal nucleus with one of its facets at the droplet surface is thermodynamically favored (i.e., occurs in a surface stimulated mode) over its formation with all the facets within the liquid phase (i.e., in a volume-based mode). For both unary[22] and multicomponent[23] droplets, this criterion coincides with the condition of partial wettability of at least one of the crystal facets by the melt (the contact angle, measured inside the liquid phase, must be greater than zero).

A theory of crystal nucleation in droplets is very complex even for the homogeneous case. Not surprisingly, the presence of foreign particles, serving as nucleating centers, makes the crystal nucleation phenomenon (and hence its theory) significantly more involved. Numerous aspects of heterogeneous crystal nucleation still remain obscure. One of most intriguing problems in this field remains the strong enhancement of heterogeneous crystallization in the contact mode compared to the immersion one. It has been observed that the same nucleating center initiates the crystallization of a supercooled droplet at a higher temperature in the contact mode (with the foreign particle just *in contact* with the droplet surface) compared to the immersion mode (particle *immersed* in the droplet).[2] Many heterogeneous centers have different nucleation thresholds when they act in contact or immersion modes, indicating that the mechanisms may be actually different for the different modes. Underlying physical reasons for this enhancement have remained largely unclear, but the phenomenon of surface-stimulated (homogeneous) crystal nucleation had strongly suggested that the droplet surface could enhance heterogeneous nucleation in a way similar to the enhancement of the homogeneous process.

In this paper we have treated heterogeneous crystal nucleation on a solid particle (in both immersion and contact modes) and have presented a thermodynamic model shedding some light on the mechanism of the enhancement of this process in the contact mode. We have shown that the line tension has a 2-fold effect on the free energy of formation of a crystal cluster. A set of modified Wulff's relations determining the equilibrium shape of a crystal cluster is derived by using a generalized Gibbs−Curie theorem[24,33] taking into account the effect of line tensions involved. Our thermodynamic analysis suggests that the droplet surface can indeed thermodynamically enhance crystal nucleation in the contact mode compared to the immersion mode. Whether this occurs or not for a particular foreign particle is determined, however, by the interplay between various surface tensions and four line tensions involved in this process. For example, the effect can be expected to strongly depend on the degree of wettability of the foreign particle by water (the quantitative measure of wettability (or hydrophobicity or hydrophilicity) being the contact angle[2,3,31,32]). As clear from our model, the droplet surface may stimulate the heterogeneous crystal nucleation even in the case where the foreign particle is actually completely immersed therein but is situated closely enough to the surface. This suggests that the term "contact mode enhancement" is probably not very appropriate for this phenomenon.

As a numerical illustration of the proposed model, we have considered heterogeneous nucleation of Ih crystals on generic macroscopic foreign particles in water droplets at $T = 253$ K. Our results suggest that while the droplet surface always stimulates crystal nucleation on foreign particles in the "contact mode", the line tension contribution to this phenomenon (due to the contact of three water phases, "vapor−liquid−crystal") may be as important as the surface tension contribution.

Clearly, there is a great variety of factors affecting real atmospheric phenomena. The model presented above is an attempt to elucidate the effect of some of these factors on heterogeneous crystal nucleation in droplets. The more details that are included in the model, the more complex the model becomes. However, there is probably no alternative way to develop an increasingly adequate model of freezing of atmospheric droplets.

Acknowledgment. The authors thank F. M. Kuni and R. S. Kabisov for helpful discussions.

Appendix

A. Crystal Nuclei and Their Works of Formation. The shape of the crystal nucleus is determined by Wulff's relations 5 and 15. For example, since the shape of an ice crystal cluster is known (assumed to be a hexagonal prism), its state is completely determined by two geometric variables (provided that its density and temperature are given), e.g., the height of the prism and the length of a side of a (regular) hexagon (the base of the prism). However, owing to Wulff's relations, eqs 5 and 15, only one of these two variables is independent. Therefore, both works W^{imm} and W^{con} are functions of only one independent variable, say, variable a, the length of a side of the hexagon. The concrete form of the functions $W^{\mathrm{imm}} = W^{\mathrm{imm}}(a)$ and $W^{\mathrm{con}} = W^{\mathrm{con}}(a)$ depends on the mutual orientation and location of the crystal cluster and foreign particle (and droplet surface in the case of W^{con}).

For instance, consider a crystal cluster formed with one of its basal facets on a foreign particle in the immersion mode. For the contact mode, let us consider the same basal facet on the foreign particle and a prismal facet (assumed to be only partially wettable by water) at the droplet surface. Mark the basal facets with subscripts 1 and 8 and the prismal facets with subscripts 2, ..., 7 (Figure 5).

As agreed upon above, facet 8 forms on the foreign particle. Clearly, in the immersion mode $\sigma_{\mathrm{p}}^{\alpha\gamma} \equiv \sigma_2^{\alpha\gamma} = \cdot\cdot\cdot = \sigma_7^{\alpha\gamma}$, $A_{\mathrm{p}}^{\alpha\gamma} \equiv A_2^{\alpha\gamma} = \cdot\cdot\cdot\ A_7^{\alpha\gamma}$, $A_{\mathrm{b}}^{\alpha\gamma} \equiv A_1^{\alpha\gamma} = A_8^{\alpha\gamma}$. In the contact mode the prismal facet 7 (assumed to be only partially wettable by liquid water) represents the crystal−vapor interface; hence $\sigma_{\mathrm{p}}^{\alpha\gamma} \equiv \sigma_2^{\alpha\gamma} = \cdot\cdot\cdot = \sigma_6^{\alpha\gamma}$, $\sigma_{\mathrm{p}}^{\beta\gamma} = \sigma_7^{\beta\gamma}$. Unlike the crystal cluster in the immersion mode, the basal facet in the contact mode is not a regular hexagon, $A'{}_7^{\alpha\gamma} \equiv A'{}_1^{\alpha\gamma} = A'{}_8^{\alpha\gamma}$ and $A'{}_{\mathrm{b}}^{\alpha\gamma} < A_{\mathrm{b}}^{\alpha\gamma}$, i.e., the surface area of the basal facets in the contact mode is smaller than that in immersion mode, according to eq 25. Let us mark two prismal facets adjacent to facet 7 by subscripts 2 and 6. Clearly, $A_{\mathrm{p}}^{\alpha\gamma} = A_3^{\alpha\gamma} = A_4^{\alpha\gamma} = A_5^{\alpha\gamma}$, $A'{}_{\mathrm{p}}^{\alpha\gamma} \equiv A_2^{\alpha\gamma} = A_6^{\alpha\gamma} < A_{\mathrm{p}}^{\alpha\gamma}$, $A_{\mathrm{p}}^{\beta\gamma} \equiv A_7^{\beta\gamma} > A_7^{\alpha\gamma}$ (both inequalities are again due to eq 25).

Let us use $a_i$and a_i' $(i = 2, ..., 7)$ to denote the length of the edge formed by the basal facet with prismal facet i in the immersion and contact modes, respectively. In the immersion mode the base is a regular hexagon, i.e., $a \equiv a_2 = \cdot\cdot\cdot = a_7$. As clear from eq 25 and Figure 5b, in the contact mode $a_2' = a_6' < a$, $a_7' > a$, whereas $a_3' = a_4' = a_5' = a$ with

$$a_2{}' = a_6{}' = C_{\mathrm{p}}a, \qquad a_7{}' = (2 - C_{\mathrm{p}})a$$

and positive $C_{\mathrm{p}} = (\sigma_{\mathrm{p}}^{\beta\gamma} - \sigma^{\alpha\beta})/\sigma_{\mathrm{p}}^{\alpha\gamma} < 1$ (the vapor−crystal interfacial tension is greater than the liquid−crystal one).

In the first term on the right-hand sides of eqs 10 and 18 the number of molecules in the crystal cluster can be represented as $\nu = \rho^{\gamma}V^{\gamma}$ or $\nu = \rho^{\gamma}V'^{\gamma}$, respectively, where ρ^{γ} is the number density of molecules in phase γ (ice). The volume of an Ih crystal (shaped as a hexagonal prism) is equal to the product "height of the prism" × "surface area of the base". In both the immersion and contact modes the surface area of the base (regular hexagon in the former and irregular in the latter) is proportional to a^2, although the coefficients of proportionality are different. In both cases, the height of the prism, h, is linearly related to a according to Wulff's relations 5 and 15, respectively

$$h = a\frac{\sqrt{3}}{2}\frac{\sigma_{\mathrm{b}}{}^{\alpha\gamma} + \sigma_{\mathrm{b}}{}^{\gamma\delta} - \sigma^{\alpha\delta}}{\sigma_{\mathrm{p}}{}^{\alpha\gamma}}$$

Thus, in both eqs 10 and 18 $v \propto \rho^{\gamma}a^3$. Likewise, one can show that all the surface tension and line tension terms on the right-hand sides of eqs 10 and 19 are proportional to a^2 and a, respectively. Therefore, the reversible works of formation of a crystal cluster in these modes can be written (tedious but simple algebra is omitted) as

$$W^{\mathrm{imm}}(a) = -I_3a^3 + I_2a^2 + I_1a \tag{A1}$$

$$W^{\mathrm{con}}(a) = -C_3a^3 + C_2a^2 + C_1a$$

where I_3, I_2, I_1 and C_3, C_2, C_1 are positive coefficients

$$I_3 = \frac{9}{4}\rho^{\gamma}\Delta q \ln(\Theta)(\sigma_{\mathrm{b}}{}^{\alpha\gamma} + \sigma_{\mathrm{b}}{}^{\gamma\delta} - \sigma^{\alpha\delta})/\sigma_{\mathrm{p}}{}^{\alpha\gamma}$$

$$I_2 = \frac{3\sqrt{3}}{2}[2\sigma_{\mathrm{b}}{}^{\alpha\gamma} + 3(\sigma_{\mathrm{b}}{}^{\gamma\delta} - \sigma^{\alpha\delta})]$$

$$I_1 = 6\tau^{\alpha\gamma\delta}$$

and

$$C_3 = \rho^{\gamma}\Delta q \ln(\Theta)\frac{\sqrt{3}}{2}2\left(3 - \frac{2}{\sqrt{3}}C_{\mathrm{h}} + \frac{2C_{\mathrm{h}}{}^2}{3}\right)C_{\mathrm{h}}$$

$$C_2 = \left(3 - \frac{2}{\sqrt{3}}C_{\mathrm{h}} + \frac{2C_{\mathrm{h}}{}^2}{3}\right)C_{\mathrm{h}} + [\sigma_{\mathrm{p}}{}^{\alpha\gamma}(3 + 2C_{\mathrm{p}}) + (\sigma_{\mathrm{p}}{}^{\beta\gamma} - \sigma^{\alpha\beta})(2 - C_{\mathrm{p}})C_{\mathrm{h}}$$

$$C_1 = 2(\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta}) + 3\tau^{\alpha\gamma\delta} + 2\tau^{\alpha\beta\gamma} + (-(\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta}) + 2\tau^{\alpha\gamma\delta} - \tau^{\alpha\beta\gamma})C_{\mathrm{p}} + \tau^{\alpha\beta\gamma}2C_{\mathrm{h}}$$

with $C_{\mathrm{h}} = (3^{1/2}/2)(\sigma_{\mathrm{b}}{}^{\alpha\gamma} + \sigma_{\mathrm{b}}{}^{\gamma\delta} - \sigma^{\alpha\beta})/\sigma_{\mathrm{p}}{}^{\alpha\gamma}$. Note that, although the linear (in a) contribution to $W^{\mathrm{con}}(a)$ is due to the line tensions, the coefficient, C_1, depends not only on the line tensions but also on the surface tensions of both prismal and basal facets of the crystal cluster because the lengths of the three-phase contact lines, as functions of a, depend on those surface tensions (see Figures 4 and 5).

Using eq A1, one can find the length a_* of a side of the hexagonal base of the crystal nucleus. According to CNT (whereof the framework has been adopted for our treatment), the free energy of formation of a cluster as a function of a single variable of state of the cluster attains a maximum for the critical cluster, i.e., nucleus. Therefore, a_* can be found as the positive solution of the equation $\mathrm{d}W^{\mathrm{imm}}(a)/\mathrm{d}a|_{a_*} = -3I_3a_*^2 + 2I_2a_* + I_1 = 0$, or alternatively, $\mathrm{d}W^{\mathrm{con}}(a)/\mathrm{d}a|_{a_*} = -3C_3a_*^2 + 2C_2a_* + C_1 = 0$, which lead to $a_* = (2I_2 + (4I_2^2 + 12I_1I_3)^{1/2})/6I_3$ or $a_* = (2C_2 + (4C_2^2 + 12C_1C_3)^{1/2})/6C_3$ (see two paragraphs above eq A1). The height of the crystal nucleus (shaped as a hexagonal prism) is the same in both immersion and contact modes, $h_* = a_*(3^{1/2}/2)(\sigma_{\mathrm{b}}{}^{\alpha\gamma} + \sigma_{\mathrm{b}}{}^{\gamma\delta} - \sigma^{\alpha\delta})/\sigma_{\mathrm{p}}{}^{\alpha\gamma}$.

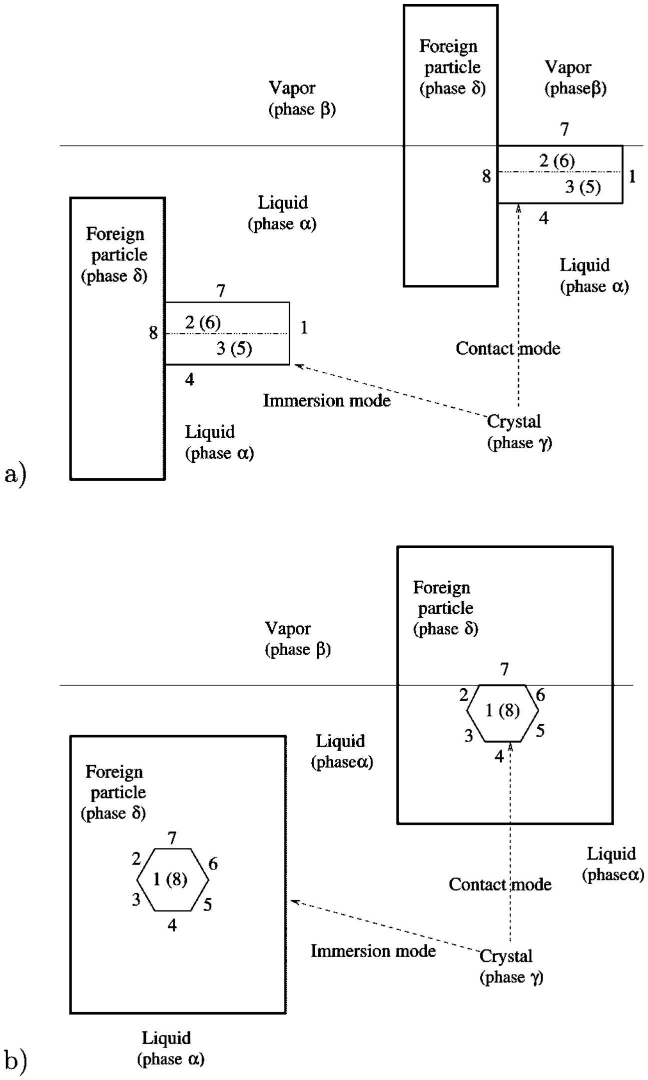

Figure 5. Heterogeneous formation of an Ih cluster on a foreign particle in the immersion and contact modes. The crystal cluster has a shape of a hexagonal prism. One of the basal facets (facet 8) is formed on the foreign particle, the other (facet 1) interfaces the liquid. Two of the prismal facets (with numbers 4 and 7) lie in the plane perpendicular to the figure. (a) A section along the axis of the prism and perpendicular to prismal facets 4 and 7. Prismal facets 5 and 6 cannot be seen by the reader, so their numbers are shown in the parentheses. (b) A view of basal facet 1 perpendicular thereto (basal facet 8, facing the foreign particle, cannot be seen hence its number is shown in the parentheses).

The immersion and contact modes of the heterogeneous crystal nucleation are heterogeneous versions of the volume-based and surface-stimulated modes,[22,23] respectively, of homogeneous crystal nucleation. The difference is that no foreign particles are involved in the homogeneous process. Let us denote the corresponding works of formation as $W^{\mathrm{vb}} \equiv W^{\mathrm{vb}}(a)$ (for the volume-based mode) and $W^{\mathrm{ss}} \equiv W^{\mathrm{ss}}(a)$ (for the surface-stimulated mode).

Clearly, homogeneous crystal nucleation in the surface-stimulated mode differs from the heterogeneous crystal nucleation in the immersion mode only in that one of the crystal facets (a basal one in our particular example) forms at the droplet surface (in the former case) rather than on an immersed foreign particle (in the latter case). Therefore, the function $W^{\mathrm{ss}}(a)$ can be formally obtained from $W^{\mathrm{imm}}(a)$ by replacing all the superscripts with the superscript β. On the other hand, in the volume-based mode of the homogeneous process all the crystel facets represent the liquid−crystal interface and the height (h) of the crystal cluster (shaped as a right prism with a regular hexagon at its base) is related to the radius of a regular hexagon (a) as $h = a(3^{1/2})(\sigma_{\mathrm{b}}{}^{\alpha\gamma}/\sigma_{\mathrm{p}}{}^{\alpha\gamma})$.

Thus, the functions $W^{\mathrm{ss}}(a)$ and $W^{\mathrm{vb}}(a)$ can be written in the form

$$W^{\mathrm{ss}}(a) = -S_3a^3 + S_2a^2 + S_1a \tag{A2}$$

$$W^{\mathrm{vb}}(a) = -B_3a^3 + B_2a^2 + B_1a$$

with

$$S_3 = \frac{9}{4}\rho^{\gamma}\Delta q \ln(\Theta)(\sigma_{\mathrm{b}}{}^{\alpha\gamma} + \sigma_{\mathrm{b}}{}^{\alpha\beta} - \sigma^{\alpha\beta})/\sigma_{\mathrm{p}}{}^{\alpha\gamma}$$

$$S_2 = \frac{3\sqrt{3}}{2}[2\sigma_{\mathrm{b}}{}^{\alpha\gamma} + 3(\sigma_{\mathrm{b}}{}^{\gamma\beta} - \sigma^{\alpha\beta})]$$

$$S_1 = 6\tau^{\alpha\gamma\beta}$$

and

$$B_3 = \frac{9}{2}\rho^{\gamma}\Delta q \ln(\Theta)(\sigma_{\mathrm{b}}{}^{\alpha\gamma}/\sigma_{\mathrm{p}}{}^{\alpha\gamma})$$

$$B_2 = 9\sqrt{3}\sigma_{\mathrm{b}}{}^{\alpha\gamma}$$

$$B_1 = 0$$

(there is no three-phase contact line in the volume-based mode of homogeneous crystal nucleation, hence $B_1 = 0$). Again, one can find the radius a_* of the hexagonal base of the crystal nucleus as the positive solution of the equation $\mathrm{d}W^{\mathrm{ss}}(a)/\mathrm{d}a|_{a_*} = -3S_3a_*^2 + 2S_2a_* + S_1 = 0$, or alternatively, $\mathrm{d}W^{\mathrm{vb}}(a)/\mathrm{d}a|_{a_*} = -3B_3a_*^2 + 2B_2a_* + B_1 = 0$, which leads to $a_* = (2S_2 + (4S_2^2 + 12S_1S_3)^{1/2})/6S_3$ or $a_* = (2B_2 + (4B_2^2 + 12B_1B_3)^{1/2})/6B_3$. The heights of the crystal nucleus (a hexagonal prism) are now different in the surface-stimulated and volume-based modes, namely, $h_*{}^{\mathrm{ss}} = a_*(3^{1/2}/2)\ (\sigma_{\mathrm{b}}{}^{\alpha\gamma} + \sigma_{\mathrm{b}}{}^{\alpha\beta} - \sigma^{\alpha\beta})/\sigma_{\mathrm{p}}{}^{\alpha\gamma}$ and $h_*{}^{\mathrm{vb}} = a_*(3^{1/2})(\sigma_{\mathrm{b}}{}^{\alpha\gamma}/\sigma_{\mathrm{p}}{}^{\alpha\gamma})$, respectively.

References and Notes

(1) *IPCC, Climate Change 2001: The scientific bases. Inter government Panel on Climate Change*; Cambridge University Press: Cambridge, UK, 2001.

(2) Pruppazrefscher, H. R.; Klett., J. D, *Microphysics of clouds and precipitation*; Kluwer Academic Publishers: Dordrecht and Boston, 1997.

(3) Fletcher, N. H., *The physics of rainclouds*; Cambridge University Press: Cambridge, 1962.

(4) Cox, S. K. *J. Atmos. Sci.* **1971**, *28*, 1513.

(5) Jensen, E. J.; Toon, O. B.; Tabazadeh, A.; Sachse, G. W.; Andersen, B. E.; Chan, K. R.; Twohy, C. W.; Gandrud, B.; Aulenbach, S. M.; Heymsfield, A.; Hallett, J.; Gary, B. *Geophys. Res. Lett.* **1998**, *25*, 1363.

(6) Heymsfield, A. J.; Miloshevich, L. M. *J. Atmos. Sci.* **1993**, *50*, 2335.

(7) Ruckenstein, E. *J. Colloid Interface Sci.* **1973**, *45*, 115.

(8) DeMott, P. J.; Cziczo, D.; Prenni, A.; Murphy, D.; Kreidenweis, S.; Thomson, D.; Borys, R.; Rogers, D. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 14655–14660.

(9) DeMott, P. J.; Sassen, K.; Poellot, M.; Baumgardner, D.; Rogers, D.; Brooks, S.; Prenni, A.; Kreidenweis, S. *Geophys. Res. Lett.* **2003**, *30*, 1732. doi:10.1029/2003GL017410.

(10) Sassen, K.; DeMott, P. J.; Prospero, J.; Poellot, M. *Geophys. Res. Lett.* **2003**, *30*, 1633. doi:10.1029/2003GL017371.

(11) Zuberi, B.; Bertram, A.; Koop, T.; Molina, L.; Molina, M. *J. Phys. Chem. A* **2001**, *105*, 6458–6464.

(12) Hung, H.-M.; Malinkowski, A; Martin, S. *J. Phys. Chem. A* **2003**, *107*, 1296–1306.

(13) Elias, V.; Simoneit, B.; Pereira, A.; Cabral, J.; Cardoso, J. *Environ. Sci. Technol.* **1999**, *33*, 2369–2376.

(14) Popovitz-Biro, R.; Wang, J.; Majewski, J.; Shavit, E.; Leiserowitz, L.; Lahav, M. *J. Am. Chem. Soc.* **1994**, *116*, 1179–1191.

(15) Fukuta, NExperimental studies of organic ice nuclei. *J. Atmos. Sci.* **1966**, *23*, 191–3196.

(16) Vali, G. In *Nucleation and Atmospheric Aerosols*; Kulmala, M., Wagner, P., Eds.; Pergamon: New York, 1996.

(17) Shaw, R. A.; Durant, A. J.; Mi, Y. *J. Phys. Chem. B* **2005**, *109*, 9865.

(18) Fletcher, N. H., *J. Atmos. Sci* **1970**, *27*, 1098.

(19) Guenadiev, N. *J. Rech. Atmos.* **1970**, *4*, 81.

(20) Evans, L. F. *Preprints Conference on Cloud Physics (1970, Fort Collins, CO)*; American Meteorological Society: Boston, MA, 1970; p 14.

(21) Fukuta, N. *J. Atmos. Sci.* **1975**, *32*, 1597–2371.

(22) Djikaev, Y. S.; Tabazadeh, A.; Hamill, P.; Reiss, H. *J. Phys. Chem. A* **2002**, *106*, 10247.

(23) Djikaev, Y. S.; Tabazadeh, A.; Reiss, H. *J. Chem. Phys.* **2003**, *118*, 6572–6581.

(24) Defay, R, Prigogine, I, Bellemans, A., and Everett, D. H. *Surface Tension and Adsorption*; John Wiley: New York, 1966.

(25) (a) Zell, J.; Mutaftshiev, B. *Surf. Sci.* **1968**, *12*, 317. (b) Grange, G.; Mutaftshiev, B. *Surf. Sci.* **1975**, *47*, 723. (c) Grange, G.; Landers, R.; Mutaftshiev, B. *Surf. Sci.* **1976**, *54*, 445.

(26) Chatain, D.; Wynblatt, P. In *Dynamics of Crystal Surfaces and Interfaces*; Duxbury, P. M., Pence, T. J., Eds.; Springer: New York, 2002; pp 53−58.

(27) Elbaum, M.; Lipson, S. G.; Dash, J. G. *J. Cryst. Growth* **1993**, *129*, 491.

(28) Chushak, Y. G.; Bartell, L. S. *J. Phys. Chem. B* **1999**, *103*, 11196.

(29) Zasetsky, A. Y.; Remorov, R.; Svishchev, I. M. *Chem. Phys. Lett.* **2007**, *435*, 50–53.

(30) Rusanov, A. I. *Phasengleichgewichte und Grenzflachenerscheinungen*; Akademie Verlag: Berlin, 1978.

(31) Rowlinson, J. S.; Widom, B. *Molecular Theory of Capillarity*; Clarendon Press,: Oxford, 1982.

(32) Boruvka, L.; Neumann, A. W. *J. Phys. Chem.* **1977**, *66*, 5464.

(33) (a) Gibbs, J. W. *The Collected Works of J. Willard Gibbs*; Longmans, Green and Co.: New York, 1928. (b) Curie, P. *Bull. Soc. Minér. Fr.* **1885**, *8*, 195.

(34) Widom, B. *J. Phys. Chem.* **1995**, *99*, 2803.

(35) Aveyard, R.; Clint, J. H. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 85–89.

(36) Amirfazli, A.; Neumann, A. W. *Adv. Colloid Interface Sci.* **2004**, *110*, 121–141.

JP803155F