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Thermodynamic Conditions for the Surface-Stimulated Crystallization of Atmospheric Droplets

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Received: April 24, 2002; In Final Form: August 13, 2002

We attempt to explain the experimental and molecular dynamics simulation evidence that suggests that the freezing of atmospheric aerosols occurs beginning at the droplet surface. By using the capillarity approximation, we derive the reversible work of formation of a crystal nucleus in the cases where it forms homogeneously within a (supercooled) bulk liquid and where it forms “pseudoheterogeneously” at the surface. Comparing the works of formation in these two cases, one obtains a condition that must hold in order for pseudoheterogeneous (surface) crystallization to be thermodynamically more favorable than homogeneous (bulk) crystallization. This condition is satisfied when at least one crystal facet is only partially wettable by its own melt.

1. Surface versus Bulk Nucleation

This paper may be regarded as a sequel to the preceding paper,¹ in which the analysis of existing laboratory data on the freezing of droplets of aqueous HNO₃ into NAT and NAD particles suggests a nucleation process that is surface based. Here, we present a theoretical analysis to determine conditions under which the surface-stimulated mode of crystallization is thermodynamically favored over the volume-based mode.

The composition and phases of aerosol and cloud particles affect their radiative and chemical properties.² Although many phase transformations in aqueous and cloud droplets occur as a result of heterogeneous nucleation on preexisting solid particles,³ in a number of important cases atmospheric particles appear to freeze homogeneously.^{4–8} 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.^{4–6} Radiative properties of ice clouds and their subsequent effect on climate depend strongly on the size of the cloud particles,⁹ a quantity closely linked to the rate at which ice particles in the cloud nucleate and grow. Also, it has been suggested that aqueous nitric acid-containing cloud droplets in the polar stratosphere freeze into nitric acid hydrates via homogeneous nucleation.^{7,8} Understanding how nitric acid clouds form and grow in the stratosphere is a topic of current interest because such clouds participate in heterogeneous chemistry that leads to springtime ozone depletion over the polar regions.¹⁰

The first theoretical description on the freezing of supercooled water droplets into ice was presented in 1939 by Völmer.¹¹ In

this study, a classical volume-based nucleation rate theory was developed, i.e., an ice nucleus was assumed to form only inside the volume of a droplet. The current theory of homogeneous freezing still relies on Volmer's assumption. Under that assumption, the freezing rate of ice becomes proportional to the volume of the droplet. Similarly, with the exception of the preceding paper,¹ all of the data from laboratory studies on the freezing of aqueous nitric acid droplets into hydrates of nitric acid^{8,12–14} have been analyzed assuming that crystalline nuclei form inside the droplet volume.^{2,11} However, the analyses presented in the preceding paper¹ and in another paper on the freezing of water droplets¹⁵ have provided evidence that crystal nuclei appear to form on droplet surfaces for both systems. In addition to atmospheric examples, differential thermal analysis on the crystallization kinetics of molten tin droplets suggests that nucleation occurs at the droplet surface.¹⁶ Moreover, several molecular dynamics simulation studies¹⁷ show that for all kinds of supercooled liquid clusters (molecular, ionic, and metallic), crystal nuclei appear preferentially at, or very close to, the surface. As a result, because clusters have a high surface-to-volume ratio, nucleation rates in clusters tend to be higher than in the bulk.

The underlying physical reason for solid nucleus formation on the particle surface rather than within its volume has remained obscure, although both experimental work (see, e.g., ref 16 and the analysis in ref 15) and molecular dynamics simulations studies¹⁷ suggest that surface crystal nucleation is thermodynamically favored over crystallization in the bulk. This idea is in general agreement with the observed fact that the free energy barrier of heterogeneous nucleation is lower than that of homogeneous nucleation.

In the present paper, we develop a thermodynamic theory that prescribes the condition under which surface-stimulated crystallization would be favored over bulk crystallization. This condition has the form of an inequality, which, when satisfied, predicts that surface crystal nucleation will be favored over nucleation in the bulk. The inequality coincides with the

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condition for the partial wettability of at least one of the facets of the crystalline nucleus by its own melt.¹⁸ This effect was experimentally observed for several systems,^{11,19} including water–ice²⁰ at temperatures at or below 0 °C. When air was added to water vapor,²⁰ for *some* orientations (facets) of water crystals partial wetting transformed into complete wetting. However, as is well known, the wettability of solids by fluids usually decreases with decreasing temperature.^{21,22} Because 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,^{21a} perfect wetting of a solid surface by a liquid is not generally observed away from the critical point, and Dietrich^{21b} presented further examples of this phenomenon. In Cahn's theory, the general restrictions on the solid phase are that its surface is sharp on an atomic scale, and interactions between surface and fluid are sufficiently short-range. That theory can also be applied to the particular case where the temperature is far below the fluid critical point and the solid is of the same chemical nature as the fluid phases.

Thus, partial wettability of a solid by its melt may help to explain why, in computer simulation studies, crystallization begins at or near the surface, and also why it is easier, experimentally, to observe the crystallization of aerosols, having a large collective surface area, than those having a large volume. Moreover, our result is physically reasonable because,^{22,23} if the condition of partial wettability holds, the free energy per unit area required to form a *direct* interface between bulk vapor and solid (as in case of surface-stimulated crystallization) is less than the free energy required to form a uniform *intruding* layer of liquid phase, which involves creation of two interfaces “solid–liquid and “liquid–vapor”. Note that with changing (usually increasing) temperature, a wetting transition may occur^{21,22} such that partial wetting transforms into complete wetting. In this case, the inequality constituting the condition for surface-stimulated crystallization will not be satisfied and surface nucleation may no longer be favored over the volume-based mode of crystallization.

2. Free Energy of Crystal Formation using the Capillarity Approximation

In this section, we first present a classical derivation (within the framework of the capillarity approximation¹⁸) of the free energy of formation of a crystal nucleus within a melt as well as at its interface. Although, this will simplify the problem, it will be clear from the following that our result will be valid for multicomponent systems as well. Certainly, in addition to the effects discussed in the present paper, in multicomponent systems, there may be other effects (e.g., surface adsorption, dissociation, etc.) that may favor surface-stimulated crystallization over a bulk process. For example, the surface-stimulated crystallization of NAT/NAD in aqueous nitric acid aerosols may be enhanced due to the adsorption of neutral HNO₃ molecules at the “liquid–vapor” interface.^{24,25} These effects, however, are not considered in the present work but will be the subject of future investigation.

As a prelude to considering crystal nucleation at the liquid–vapor interface, it is convenient to first consider the case of a crystal nucleus forming within a bulk liquid or a liquid drop. Following this analysis, it is appropriate to consider the case of the crystal nucleus forming at the surfaces of a bulk liquid or a liquid drop.

The reversible work of crystal formation, W , is the difference between X_{fin} , the magnitude of the appropriate thermodynamic

potential of the system in its final state (liquid + crystal), and X_{in} , its magnitude in its initial state (liquid)

$$W = X_{\text{fin}} - X_{\text{in}} \quad (1)$$

Consider a single-component bulk liquid. Crystallization will take place in this liquid if it is in a metastable (supercooling) state. Because 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 because the volume work that the entire system exchanges with the environment should not be regarded as work involved in the formation of a local nucleus. As an approximation, the use of the Helmholtz free energy is still acceptable because in the thermodynamic limit, 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 (because the unconnected volume work exchanged with the environment is automatically removed from the Gibbs free energy). In this case, however, another problem might seem to arise because the pressure within the system is not, strictly speaking, uniform upon crystal formation: the pressure within the crystal differs from the pressure in the surrounding fluid. However,²⁶ this turns out not to be a problem, and the change in the Gibbs free energy of the system upon embryo formation will properly yield the reversible work of formation of the nucleus. Thus, in the thermodynamic limit, the use of either the Gibbs or Helmholtz free energy or grand thermodynamic potential is acceptable in the evaluation of W . Here, we will work with the Helmholtz free energy.

In the case of crystallization in a bulk liquid, the release of the latent heat of fusion is unlikely to be of significant importance since the bulk liquid will serve as a thermal reservoir for crystal nuclei and take away the latent heat from the nascent crystals. However, the effect of the latent heat release may play an important role in the crystallization of droplets, and it may significantly influence the rates of both crystal nucleation and growth. One can take these effects into account by developing a perturbation-like kinetic theory of crystal nucleation as is done for the vapor-to-liquid nucleation (see, e.g., ref 27 and citations therein). That approach allows one to use the thermodynamic theory developed for the case of isothermal nucleation (i.e., working in either PVT , NVT , or μVT , etc...ensemble).

For simplicity, neglecting the density difference between liquid and solid phases and assuming the crystallization process to be isothermal, one can say that V , T , and N , the total volume, the temperature, and the number of molecules in the system, respectively, will be constant. Thus, the reversible work of formation of a crystal embryo can be evaluated as the difference between F_{fin} , the Helmholtz free energy of the system in its final state (liquid + crystal), and F_{in} , in its initial state (liquid). Thus

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

2.1 Crystal Nucleation in a Bulk Liquid. Introduce superscripts v , l , and s to denote quantities in the vapor, liquid, and crystal embryo, respectively. Double superscripts will denote quantities at the corresponding interfaces.

Consider a bulk liquid in a container (Figure 1) whose upper surface is in contact with the vapor phase of constant pressure

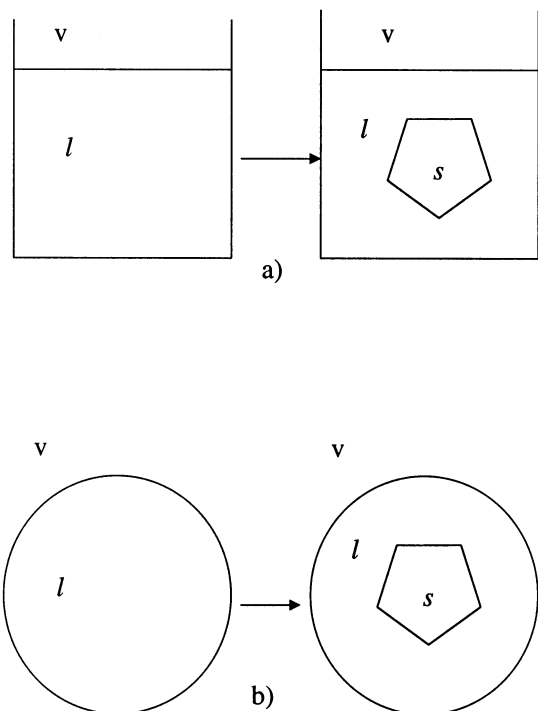


Figure 1. Scheme of homogeneous crystal formation (a) within a bulk liquid and (b) within a liquid drop.

and temperature. The Helmholtz free energy of the liquid in this initial state is

$$F_{\text{in}} = N_0^l \mu^l(P_0^l, T) + \sigma^{vl} a^{vl} + \sigma_0 A_0 - P_0^l V_0^l \quad (3)$$

where N_0^l and $\mu^l(P_0^l, T)$ are the number of molecules and chemical potential in the initial liquid of volume V_0^l and pressure P_0^l . The surface tensions of the interfaces “liquid–vapor” and “liquid–container” are denoted by σ^{vl} and σ_0 , respectively, whereas a^{vl} and A_0 are the corresponding interface areas.

Now, consider the same system but with a solid nucleus formed within the liquid (Figure 1). Hereafter, we adopt the definition of the surface tension of a solid, σ^{solid} , as given in chapter 17 of ref 18. 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 , respectively, 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.

The crystal is considered to be of arbitrary shape with λ facets (Figure 2). The surface area and surface tension of the facet i will be denoted by A_i and σ_i , respectively. (Anisotropic interfacial energies are believed to be particularly important in determining the character of the nucleation process.) The Helmholtz free energy of the system in this “final” state is

$$F_{\text{fin}} = N^l \mu^l(P^l, T) + \nu \mu^s(P^s, T) - P^l V^l - P^s V^s + \sum_{i=1}^{\lambda} \sigma_i^{\text{ls}} A_i^{\text{ls}} + \sigma^{vl} a^{vl} + \sigma_0 A \quad (4)$$

where N^l and $\mu^l(P^l, T)$ are the number of molecules and chemical potential in the remaining liquid of the system, and V^l , P^l are the liquid volume and pressure, respectively, whereas ν and

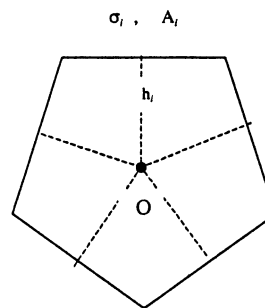


Figure 2. Equilibrium crystal with λ facets, the surface area and surface tension of the facet i being A_i and σ_i , respectively; h_i is the distance from the facet i to the central point O (see the text for more detail).

$\mu^s(P^s, T)$ are the number of molecules and chemical potential in the solid particle formed within the liquid, P^s being the pressure within the crystal and V^s its volume, whereas A is the surface area of the liquid–container interface after the crystal has been formed.

Clearly, one can assume $P^l = P_0^l = P$, where P is the pressure of the vapor. If one neglects the density change upon freezing, $A = A_0$ and $V_0^l = V^l + V^s$. Because $N_0^l = N^l + \nu$, the reversible work of formation of the crystal will be given by the expression

$$W = \nu [\mu^s(P^s, T) - \mu^l(P^l, T)] - V^s (P^s - P^l) + \sum_{i=1}^{\lambda} \sigma_i^{\text{ls}} A_i^{\text{ls}} \quad (5)$$

In the above consideration, it is assumed that the mechanical effects within the crystal (e.g., stresses) reduce to an isotropic pressure P^s . In this case¹⁸

$$P^s - P^l = \frac{2\sigma_i^{\text{ls}}}{h_i} \quad (i = 1, \dots, \lambda) \quad (6)$$

where h_i is the distance from facet i to a point O within the crystal such that (see Figure 2)

$$\frac{\sigma_1^{\text{ls}}}{h_1} = \frac{\sigma_2^{\text{ls}}}{h_2} = \dots = \frac{\sigma_{\lambda}^{\text{ls}}}{h_{\lambda}} \quad (7)$$

These equalities represent the necessary and sufficient conditions for the equilibrium shape of the crystal. This is known as the Wulff form and the equalities themselves are Wulff's relations (see, e.g., refs 18 and 11).

Equation 6 applied to the crystal is the equivalent of Laplace's equation applied to liquid. Thus, just as for a droplet, one can expect to find a high pressure within a small crystal. It is this pressure that is the cause of the increase in the chemical potential within the crystal.

By using eqs 6 and 7, one can rewrite eq 5 as

$$W = \nu [\mu^s(P^l, T) - \mu^l(P^l, T)] + \sum_{i=1}^{\lambda} \sigma_i^{\text{ls}} A_i^{\text{ls}} \quad (8)$$

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 Δh by (see, e.g., ref 26)

$$\mu^s(P^l, T) - \mu^l(P^l, T) = - \int_{T_0}^T \Delta h \frac{dT}{T} \quad (9)$$

where T_0 is the melting temperature for the bulk solid, and $\Delta h < 0$. If the supercooling 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 9 takes the form

$$\mu^s(P^l, T) - \mu^l(P^l, T) = -\Delta h \ln \Theta \quad (10)$$

with $\Theta = T/T_0$. Thus

$$W = -\nu \Delta h \ln \Theta + \sum_{i=1}^{\lambda} \sigma_i^{ls} A_i^{ls} \quad (11)$$

Using eqs 6 and 7, one can show that, for a crystal surrounded by the liquid phase (melt)

$$V^s(P^s - P^l) = \frac{2}{3} \sum_{i=1}^{\lambda} \sigma_i^{ls} A_i^{ls} \quad (12)$$

By definition, the critical crystal (i.e., nucleus) is the one in equilibrium with the surrounding melt. For such a crystal the first term in eq 5 vanishes. Therefore, by virtue of eq 12, W_* , the reversible work of formation of the critical crystal (nucleus) can be written in the form

$$W_* = \frac{1}{3} \sum_{i=1}^{\lambda} \sigma_i^{ls} A_i^{ls} \quad (13)$$

or, alternatively, as

$$W_* = 2^{-1} V_*^s (P_*^s - P^l) \quad (14)$$

where the subscript “*” indicates quantities corresponding to the critical crystal (nucleus). In what follows, eq 14 will be very useful.

Next, consider the case of a crystal forming not in the bulk liquid, but within a liquid drop (see Figure 1) which is itself surrounded by the vapor phase. The reasoning here is almost identical to the preceding if, again, we neglect the density difference between the liquid and crystal phases. Actually, eqs 2, 3 transform, respectively, into

$$F_{in} = N_0^l \mu_i^l(P_0^l, T) + \sigma^{vl} a_R^{vl} - P_0^l V_0^l \quad (15)$$

$$F_{fin} = N^l \mu_i^l(P^l, T) + \nu \mu^s(P^s, T) - P^l V^l - P^s V^s + \sum_{i=1}^{\lambda} \sigma_i^{ls} A_i^{ls} + \sigma^{vl} a_R^{vl} \quad (16)$$

where now $P^l = P_0^l = P + 2\sigma^{vl}/R$, with R being the radius of the drop (assumed to remain constant during freezing), and a_R^{vl} is its surface area. Keeping this in mind, one can easily show that all above equations (starting with eq 4), including eqs 13 and 14 for the reversible work W_* of formation of the critical crystal, remain valid.

2.2 Crystal Formation at the Liquid–Vapor Interface: Pseudoheterogeneous “Surface” Nucleation. Even if there are no foreign particles either in the bulk liquid or the liquid drop, there exists a possibility that crystallization will occur heterogeneously at the liquid–container interface or pseudoheterogeneously at the liquid–vapor interface in the case of bulk liquid, or only at the liquid–vapor interface in the case of a drop. We will consider crystallization at the liquid–vapor interface, which is of greatest interest for the freezing of cloud drops in the atmosphere.

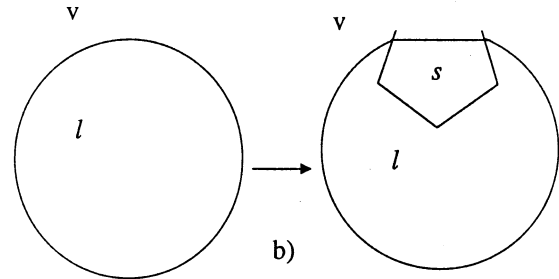
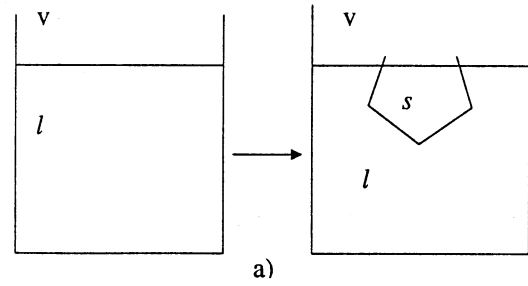


Figure 3. Scheme of pseudoheterogeneous crystal formation (a) at the surface of a bulk liquid and (b) at the surface of a liquid drop.

It is convenient to begin by considering bulk liquid in a container (Figure 3) whose upper surface is in contact with the vapor phase of constant pressure and temperature. In the “final state” of the system there is a crystal embryo. One of the facets of the crystal has been formed at the liquid–vapor interface. We will assign the subscript “ λ ” to this particular facet. The Helmholtz free energy of the system in the “initial state” (absence of crystal) is given by eq 3, whereas the free energy of the system in the “final state” is

$$F_{fin} = N^l \mu_i^l(P^l, T) + \nu \mu^s(P^s, T) - P^l V^l - P^s V^s + \sum_{i=1}^{\lambda-1} \sigma_i^{ls} A_i^{ls} + \sigma_{\lambda}^{vs} A_{\lambda}^{vs} + \sigma^{vl} (a^{vl} - A_{\lambda}^{vs}) + \sigma_0 A \quad (17)$$

where V^s is the volume of the crystal.

Because $P^l = P_0^l = P$, $A = A_0$, $V_0^l = V^l + V^s$, and $N_0^l = N^l + \nu$, the reversible work, W^* , of pseudoheterogeneous formation of the crystal at constant pressure is given by the expression

$$W^* = \nu [\mu^s(P^s, T) - \mu^l(P^l, T)] - V^s (P^s - P^l) + \sum_{i=1}^{\lambda-1} \sigma_i^{ls} A_i^{ls} + \sigma_{\lambda}^{vs} A_{\lambda}^{vs} - \sigma^{vl} A_{\lambda}^{vs} \quad (18)$$

which is the analogue of eq 5.

Wulff’s relations in eq 7, which determine the equilibrium shape of a crystal, can be regarded as a series of equilibrium conditions on the crystal “edges” formed by adjacent facets. For example, on the edge between facets i and $i + 1$ the equilibrium condition is

$$\frac{\sigma_i^{ls}}{h_i} = \frac{\sigma_{i+1}^{ls}}{h_{i+1}} \quad (i = 1, \dots, \lambda) \quad (19)$$

In the case when one of the facets (facet λ) is the crystal–vapor interface while all the others lie within the liquid phase

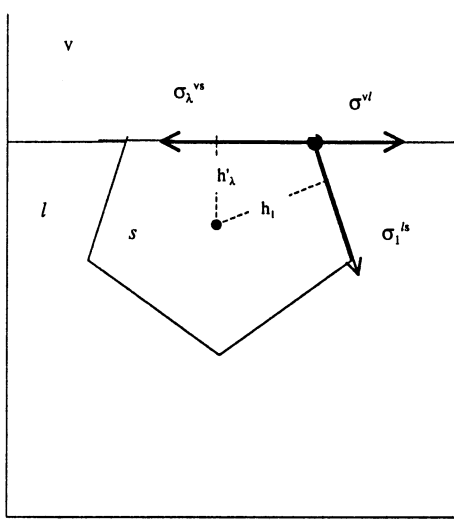


Figure 4. Illustration to Wulff's relations (21) (for more detail see the text).

(see Figure 4), the equilibrium conditions on the edges formed by this facet with the adjacent ones (hereafter marked by a subscript j) are given by

$$\frac{\sigma_j^{\text{ls}}}{h_j} = \frac{\sigma_\lambda^{\text{vs}} - \sigma^{\text{vl}}}{h'_\lambda} \quad (20)$$

Note that the height of the λ -th pyramid (constructed with base on facet λ and with apex at point O of the Wulff crystal) will differ from that with all of the facets in the liquid. Thus, the shape of the crystal will differ from that in which all facets are in contact with the liquid. For this case, Wulff's relations take the form

$$\frac{\sigma_1^{\text{ls}}}{h_1} = \frac{\sigma_2^{\text{ls}}}{h_2} = \dots = \frac{\sigma_\lambda^{\text{ls}} - \sigma^{\text{vl}}}{h'_\lambda} \quad (21)$$

and eq 6 becomes

$$P^s - P^l = \frac{2\sigma_1^{\text{ls}}}{h_1} \quad (i = 1, \dots, \lambda - 1), \quad P^s - P^l = \frac{2(\sigma_\lambda^{\text{vs}} - \sigma^{\text{vl}})}{h'_\lambda} \quad (22)$$

Making use of eqs 21 and 22, one can represent eq 18 as

$$W = v[\mu^s(P^l, T) - \mu^l(P^l, T)] + \sum_{i=1}^{\lambda-1} \sigma_i^{\text{ls}} A_i^{\text{ls}} + \sigma_\lambda^{\text{vs}} A_\lambda^{\text{vs}} - \sigma^{\text{vl}} A_\lambda^{\text{vs}} \quad (23)$$

(the analogue of eq 8). This expression is similar (but not identical, of course) to the expression for the reversible work of heterogeneous nucleation in fluid–fluid first-order phase transitions.¹⁸ Furthermore, using eq 10 we can rewrite eq 23 in the following form

$$W = -v\Delta h \ln \Theta + \sum_{i=1}^{\lambda-1} \sigma_i^{\text{ls}} A_i^{\text{ls}} + \sigma_\lambda^{\text{vs}} A_\lambda^{\text{vs}} - \sigma^{\text{vl}} A_\lambda^{\text{vs}} \quad (24)$$

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

$$V^s(P^s - P^l) = \frac{2}{3} \left(\sum_{i=1}^{\lambda-1} \sigma_i^{\text{ls}} A_i^{\text{ls}} + \sigma_\lambda^{\text{vs}} A_\lambda^{\text{vs}} - \sigma^{\text{vl}} A_\lambda^{\text{vs}} \right) \quad (25)$$

which makes it possible to represent the reversible work W^* of formation of a critical crystal by the expression

$$W^* = \frac{1}{3} \left(\sum_{i=1}^{\lambda-1} \sigma_i^{\text{ls}} A_i^{\text{ls}} + \sigma_\lambda^{\text{vs}} A_\lambda^{\text{vs}} - \sigma^{\text{vl}} A_\lambda^{\text{vs}} \right) \quad (26)$$

or, alternatively, as

$$W^* = \frac{1}{2} V^s (P^s - P^l) \quad (27)$$

Equations 26 and 27 are similar to eqs 13 and 14 which apply to homogeneous crystallization within the liquid. Along with eq 14, eq 27 will also be important in later discussions.

The analysis of the case where the crystallization begins at a drop surface can be considerably more complicated as compared to the case where it forms at the bulk liquid surface. This results from the deformation of the drop if freezing is initiated at its surface (Figure 3). However, we can show that under the following condition

$$\frac{A_\lambda^{\text{vs}}}{\pi R^2} \ll 1 \quad (28)$$

the formation of a crystal at a drop surface can be considered as crystallization at the surface of a *bulk* liquid. Under conditions relevant to the freezing of PSC drops, crystal nuclei are usually of nanometer size, whereas the drops themselves are in submicron to micrometer size range, i.e., condition (28) is well satisfied. Because the analysis of the freezing of PSC drops is our ultimate goal, we can use the preceding equations in the analysis of crystallization at a drop surface and therefore avoid the complexity of developing new equations for a drop.

The reversible works of formation of nuclei for homogeneous and heterogeneous crystallization can now be compared. For this purpose, eqs 14 and 27 are most convenient, and it is best to rewrite them as

$$W_* = \frac{1}{2} V_*^s (P_*^s - P^l)_{\text{hom}}, \quad W_* = \frac{1}{2} V_*^s (P_*^s - P^l)_{\text{het}} \quad (29)$$

respectively. Here, the subscripts indicate that the difference between the internal pressure of the nucleus and the external pressure might be different, depending on whether the nucleus forms homogeneously or heterogeneously. However, by using eq 10 and the equilibrium condition for the nucleus, namely

$$\mu^s(P^s, T) - \mu^l(P^l, T) = 0$$

while assuming the crystal to be incompressible, one can show that the difference $P_*^s - P^l$ for the nucleus, in both cases, is determined by the degree of supercooling of the liquid, so that

$$(P_*^s - P^l)_{\text{het}} = (P_*^s - P^l)_{\text{hom}} = \frac{\Delta h}{v} \ln \Theta \quad (30)$$

where v is the volume per molecule in a solid phase. The first equality in eq 30 is equivalent to

$$\frac{\sigma_\lambda^{\text{vs}} - \sigma^{\text{vl}}}{h'_\lambda} = \frac{\sigma_\lambda^{\text{ls}}}{h_\lambda}$$

from which it follows that

$$h'_\lambda = \frac{\sigma_\lambda^{\text{vs}} - \sigma^{\text{vl}}}{\sigma_\lambda^{\text{ls}}} h_\lambda. \quad (31)$$

On the other hand, $h_i = h'_i$ for $i = 1, \dots, \lambda - 1$, by virtue of eqs 6, 22, and 30. This means that the Wulff shape of the crystal, in the case of heterogeneous crystallization, is obtained by simply changing the height of the λ -th pyramid of the Wulff crystal that corresponded to the case of homogeneous crystallization. It is clear that if $\sigma_\lambda^{\text{vs}} - \sigma^{\text{vl}} < \sigma_\lambda^{\text{ls}}$, then $h'_\lambda < h_\lambda$ and hence $V_*^{\text{rs}} < V_*$. Because, according to eqs 29 and 30

$$\frac{W'_*}{W_*} = \frac{V_*^{\text{rs}}}{V_*} \quad (32)$$

we can conclude that if

$$\sigma_\lambda^{\text{vs}} - \sigma^{\text{vl}} < \sigma_\lambda^{\text{ls}} \quad (33)$$

then $W'_* < W_*$. In other words, if the condition in eq 33 is fulfilled, it is thermodynamically more favorable for the crystal nucleus to form at the surface rather than within the liquid.

The inequality in eq 33 coincides with the condition of partial wettability of the λ -th facet of the crystal by its own liquid phase.¹⁸ This effect has been experimentally observed for several systems^{11,19} including water–ice²⁰ at temperatures at or below 0 °C. In those experiments,²⁰ 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 decreasing temperature.^{21,22} Because 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,^{21a} perfect wetting of a solid by a liquid away from the critical point is not generally observed, i.e., the condition in eq 33 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 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, then 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 33 help to explain why, in molecular dynamics simulation studies, crystallization begins at or near a surface, and why it is easier, experimentally, to observe the crystallization of aerosols than that of the corresponding bulk liquid.

The inequality in eq 33 allows one to predict whether the crystallization in a particular supercooled liquid will, or will not, be thermodynamically more favorable at the surface. To implement this, 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 and in the vapor. There are a number of well-developed experimental methods for measuring σ^{vl} , so that these data are usually available for most substances of interest (or can be easily obtained). The situation is worse concerning the availability of data on σ^{ls} and σ^{vs} . Data on σ^{ls} are often obtained by matching experimental data on the crystal nucleation rate with the predictions of classical nucleation theory, treating the

surface tension of the crystal nucleus as an adjustable parameter.^{29a} However, such data on σ^{ls} cannot be used in eq 33 for at least three reasons. First, the surface tension obtained in this way will be an *average* (over all facets) of the crystal nucleus, while, in order for surface crystallization to be thermodynamically more favorable, it is necessary and sufficient that the inequality in eq 33 hold for at least *one* of the crystal facets so that even if the average surface tension of the crystal does not satisfy condition (33), there may be a facet whose surface tension does. (Clearly, if this condition is fulfilled for the average surface tension, it is fulfilled for at least one of the facets). Second, the classical theoretical expression for the rate of crystallization is derived by assuming that the crystal formation occurs within the bulk liquid.^{29–31} Therefore, that expression is not applicable to the process of surface crystallization. Third, data on the surface tension σ^{vs} are often (but not always³¹) obtained by using Young's relation¹⁸ with data on σ^{ls} and σ^{vl} , while assuming complete wettability of the solid by its own melt in its own vapor. This is another reason such data cannot be used in eq 33.

Overall, more accurate and detailed data on surface tensions are needed in order to apply the condition for surface crystallization (i.e., the inequality in eq 33). In particular, the surface tensions of the different facets of the Wulff crystal need to be known. For these purposes, in addition to few sophisticated experimental methods^{19,32–34} and computer simulation methods,^{35,36} a promising theoretical means for the calculation of the surface free energy is provided by density functional theory (DFT).³⁷

3. Concluding Remarks

There is experimental evidence suggesting that the freezing of atmospheric liquid aerosols is initiated at the aerosol droplet surface. Molecular dynamics simulation of crystallization has also shown, in all systems studied, that the process begins at the surface of the simulation cell. Both of the above contradict the existing kinetic theory of crystallization.

In the present work, we have attempted to arrive at a thermodynamic explanation of such preferential “surface” crystallization. By using the capillarity approximation we have been able to derive the reversible work of formation of a crystal nucleus in two cases, namely, 1) when it forms homogeneously within the (supercooled) bulk liquid, and 2) when it forms “pseudoheterogeneously” at the liquid–vapor interface. Comparison of the works of formation in these two cases leads to an inequality which must hold in order for pseudoheterogeneous (surface) crystallization to be thermodynamically favored over homogeneous (bulk) crystallization. This inequality is identical to the condition of partial wettability of at least one crystal facet by its own melt, and should be satisfied for most substances.

Although in the present work we have considered crystallization in single component systems, our result is probably valid for multicomponent systems as well. Clearly, in multicomponent systems there may be other effects that may favor surface crystallization over bulk crystallization. Such effects may be surface adsorption of some species, dissociation of neutral molecules into ions, etc. We plan to address these questions in future research.

Acknowledgment. Y.S.D. thanks Profs. F. M. Kuni and A. P. Grinin and Dr. R. Bowles for helpful discussions. The work was supported by NSF Grant No. CHE0076384 and by NASA's Atmospheric Chemistry Modeling and Analysis Program. A.T. also acknowledges support from a Presidential Early Career Award for Scientists and Engineers.

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