Effect of the Surface-Stimulated Mode on the Kinetics of Homogeneous Crystal Nucleation in Droplets

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The thermodynamics of surface-stimulated crystal nucleation demonstrates that if at least one of the facets of the crystal is only partially wettable by its melt, then it is thermodynamically more favorable for the nucleus to form with that facet at the droplet surface rather than within the droplet. So far, however, the kinetic aspects of this phenomenon had not been studied at all. In the present paper, a kinetic theory of homogenous crystal nucleation in unary droplets is proposed by taking into account that a crystal nucleus can form not only in the volume-based mode (with all its facets within the droplet) but also in the surface-stimulated one (with one of its facets at the droplet surface). The theory advocates that even in the surface-stimulated mode crystal nuclei initially emerge (as subcritical clusters) homogeneously in the subsurface layer, not "pseudo-heterogeneously" at the surface. A homogeneously emerged subcritical crystal can become a surface-stimulated nucleus due to density and structure fluctuations. This effect contributes to the total rate of crystal nucleation (as the volume-based mode does). An explicit expression for the total per-particle rate of crystal nucleation is derived. Numerical evaluations for water droplets suggest that the surface-stimulated mode can significantly enhance the per-particle rate of crystal nucleation in droplets as large as 10 μm in radius. Possible experimental verification of the proposed theory is discussed.

1. Introduction

Crystallization in confined liquids constitutes one of the major problems of modern theory of first order phase transitions. This phenomenon is widely used (in controlled manner) in nanotechnology and is ubiquitous in atmosphere.

The composition, size, and phases of aerosols and cloud particles determine their radiative and chemical properties,[1,2] thus determining the extent to and manner in which the Earth's climate is affected. 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 participating in these atmospheric processes; hence great importance is attributed to studying aqueous aerosols and cloud droplets as well as their phase transformations.

Although many phase transitions in aqueous aerosols and cloud droplets occur via heterogeneous nucleation on preexisting solid particles, in a number of important cases atmospheric droplets appear to freeze homogeneously.[2,3,5] 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.[6,7]

Crystallization process in pure systems had long been assumed to initiate within the volume of the supercooled phase.[8,9] Under that assumption, the rate of crystallization of a droplet is proportional to its volume.[2,3,8,9] However, using the classical nucleation theory (CNT) based on the capillarity approximation,[10] we recently developed[11,12] a thermodynamic theory that prescribes the condition under which 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 over its formation with all the facets *within* the liquid phase. This condition has the form of an inequality which, when satisfied, predicts that crystal nucleation in the droplet occurs mostly in a "surface-stimulated" mode rather than in a "volume-based" one. For both unary[11] and multicomponent[12] droplets, the inequality coincides with the condition for the partial wettability of at least one of the facets of a crystal nucleus by its own melt.[13] This effect was experimentally observed for several systems,[14,15] including water−ice[16] at temperatures at or below 0 °C.

Although kinetic factors may play as important a role as thermodynamic ones in determining the mode of crystal nucleation, the partial wettability of a solid by its melt may help to explain why, in molecular dynamics simulations of various kinds of supercooled liquid clusters,[17] crystal nuclei appear preferentially very close to the surface. As a result, because smaller clusters have a higher surface-to-volume ratio, nucleation rates in smaller clusters tend to be higher than 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. The analysis[18,19] of laboratory data provided by various authors also suggests that the nucleation of both ice in supercooled water droplets and nitric acid hydrates in concentrated aqueous nitric acid droplets may initiate at the droplet surface layer. Recent experiments[20,21] on the heterogeneous freezing of water droplets in both immersion and contact modes 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.

It is well-known that under otherwise identical thermodynamic conditions the free energy barrier of heterogeneous nucleation is usually much lower than that of homogeneous

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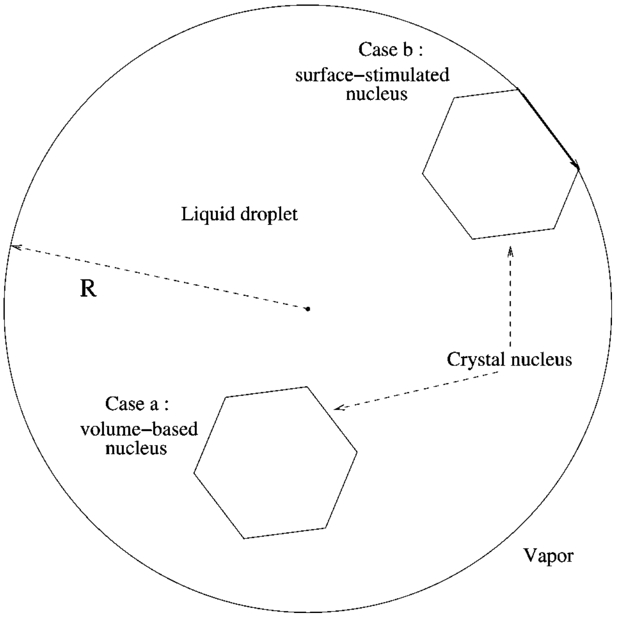

Figure 1. Liquid droplet surrounded by vapor. Case a: homogeneous crystal nucleation *within* the droplet (volume-based mode). Case b: homogeneous crystal nucleation with one of crystal facets *at* the droplet surface (surfac-stimulated mode).

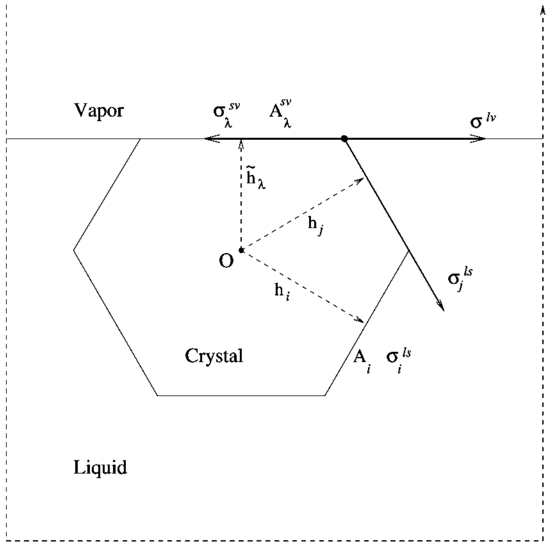

Figure 2. Illustration to Wulff's relations (4) and (9). The surface area and surface tension of the facet i are denoted by A_i and σ_i, respectively; h_i is the distance from the facet i to the reference point O (see the text for more detail).

nucleation,[13] so it might seem that the idea of surface-stimulated crystal nucleation does not significantly contribute to clarifying the underlying physics of the crystallization phenomenon. In this regard, it should be noted that the surface-stimulated crystallization is *not* a particular case of heterogeneous nucleation. On the contrary, it is a particular case of homogeneous crystal nucleation; hence its apparent thermodynamic similarities with heterogeneous nucleation should be interpreted with due caution. Our analysis in the present paper will show that the kinetics of this process cannot be treated by using the formalism of heterogeneous nucleation on foreign surfaces.

The paper is structured as follows. In section 2 we briefly outline main results[11,12] concerning the thermodynamics of surface-stimulated crystal nucleation occurring homogeneously. 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 in the same manner as the unary theory in ref 11 was extended to multicomponent systems in ref 12 A kinetic theory of such a process is presented in section 3. Numerical predictions and possible experimental verification of the model are discussed in Section 4. The results and conclusions are summarized in section 5.

2. Thermodynamics of Surface-Stimulated Crystal Nucleation

To determine the conditions under which the surface of a droplet can thermodynamically stimulate its crystallization, it is necessary to consider the formation of a crystal cluster a) within a liquid droplet and b) with one of the crystal facets at the liquid-vapor interface (Figure 1). The criterion for the surface-stimulated crystallization is obtained by comparing the reversible works of formation of a crystal nucleus (critical cluster) in these two cases. This was done in the framework of CNT for both unary[11] and multicomponent[12] droplets. The main results for unary droplets are outlined in this section.

Upon the formation of a crystal cluster in a liquid phase, the difference between liquid and solid causes a change in the volume determined by the external boundary of the liquid phase. One can consider the initial system to consist either of only a liquid phase[11] or of liquid phase in contact with vapor phase.[12] In the former case, the volume of the system is not constant upon crystal nucleation, but one can impose the condition of constant pressure or chemical potential on the system. In the latter case, one can assume that the initial system "liquid + vapor" maintains a constant volume upon crystal nucleation, but then the pressures or chemical potentials in the liquid and vapor phases become functions of the crystal cluster size during nucleation (additional complexity arises if crystallization occurs in a liquid droplet). Thus, the reversible work W of formation of a crystal cluster should be calculated in a thermodynamic ensemble corresponding to the actual physical system of interest. However, in the thermodynamic limit, the use of either the Gibbs or Helmholtz free energy or grand thermodynanmic potential is acceptable for the calculation of W.[13–22]

Assuming the crystallization process to be isothermal and neglecting the density difference between liquid and solid phases, one can say that the total volume V, temperature T, and number of molecules N in the system will be constant.[13,22] Then the reversible work of formation of a crystal cluster, W, can be found as a change in the Helmholtz free energy of the system upon its transition from the initial state (vapor + liquid) into the final one (vapor + liquid + crystal).[11,12]

Consider a crystal cluster (phase s) formed *within* a liquid droplet (phase l) that is surrounded by the vapor (phase v) (see Figure 1). The single superscripts l, s, and v will denote quantities in the corresponding phases, whereas double superscripts will denote quantities at the corresponding interfaces. The reversible work of formation of a crystal of arbitrary shape with n facets is

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

where ν and $\mu^{\mathrm{s}}(P^{\mathrm{s}}, T)$ 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. $\mu^{\mathrm{l}}(P^{\mathrm{l}}, T)$ is the chemical potential in the remaining liquid with pressure P^{l}, σ_i^{ls} and A_i^{ls} are the surface tension and surface area of facet i

(i = 1,..., n) of the crystal particle (anisotropic interfacial energies are crucial in determining the character of the nucleation process). By definition,[13] the surface tension of the solid is equal to the surface free energy per unit area if the adsorption at the solid-fluid interfaces is negligible, which usually is a reasonable assumption. The pressure in the droplet is related to the pressure P^{β} in the surrounding vapor via the Laplace equation $P^{\mathrm{l}} = P^{\mathrm{v}} + 2\sigma^{\mathrm{lv}}/R$, with σ^{lv} being the droplet surface tension and R the droplet radius (considered constant during crystallization).

The difference between the chemical potentials $\mu^{\mathrm{s}}(P^{\mathrm{s}}, T)$ and $\mu^{\mathrm{l}}(P^{\mathrm{l}}, T)$ is related to the enthalpy of melting (fusion) per molecule $\Delta h < 0$ by $\mu^{\gamma}(P^{\alpha}, T) - \mu^{\alpha}(P^{\alpha}, T) = -\int_{T_0}^{T} \Delta h \, \mathrm{d}T'/T'$, where T_0 is the melting temperature of the bulk crystal phase (see, e.g., the section treating the thermodynamics and kinetics of phase transitions in ref. 23). If in the temperature range between T and T_0 the enthalpy of fusion does not change significantly, one can rewrite (1) as

$$W = -\nu \Delta h \ln \Theta + \sum_{i=1}^{n} \sigma_i^{\mathrm{ls}} A_i^{\mathrm{ls}} \tag{2}$$

where $\Theta = T/T_0$. However, if the range $T \le T' \le T_0$ is so large that the temperature dependence of Δh is significant, it should be taken into account in calculating W. For instance, for the water−ice transition the absolute value of the enthalpy of melting was reported[24] to decrease by about 36% with decreasing temperature from 0 to −40 °C. In this case, assuming the temperature dependence of Δh to be roughly linear, i.e., $\Delta h \equiv \Delta h(T) = \Delta h_0 + d_h(T - T_0)$ with $\Delta h_0 = \Delta h(T_0)$ and $d_h = \mathrm{d}\Delta h(T)/\mathrm{d}T$, the product $\Delta h \ln \Theta$ in the first term on the RHS of (2) should be replaced by the sum $(\Delta h_0 - K_h T_0) \ln \Theta + d_h(T - T_0)$. A specific form of this term has no influence on the following arguments.

In (1) the mechanical effects within the crystal (e.g., stresses) are considered to reduce to an isotropic pressure P^{s}, so that[8,13]

$$P^{\mathrm{s}} - P^{\mathrm{l}} = \frac{2\sigma_i^{\mathrm{ls}}}{h_i} \qquad (i = 1, ..., n) \tag{3}$$

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

$$\frac{\sigma_1^{\mathrm{ls}}}{h_1} = \frac{\sigma_2^{\mathrm{ls}}}{h_2} = ... = \frac{\sigma_n^{\mathrm{ls}}}{h_n} \tag{4}$$

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 8 and 13).

Equation 3 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. Using (3) and (4), one can show that, for a crystal surrounded by the liquid phase (melt),[11,12]

$$V^{s}(P^{\mathrm{s}} - P^{\mathrm{l}}) = \frac{2}{3}\sum_{i=1}^{n} \sigma_i^{\mathrm{ls}} A_i^{\mathrm{ls}} \tag{5}$$

By definition, the critical crystal (i.e., nucleus) is in equilibrium with the surrounding melt. For such a crystal the first term in (1) vanishes. Therefore, by virtue of (5), W_*, the reversible work of formation of the nucleus, can be written as

$$W_* = \frac{1}{2} V_*^{\mathrm{s}}(P_*^{\mathrm{s}} - P^{\mathrm{l}}) = \frac{1}{3}\sum_{i=1}^{n} \sigma_i^{\mathrm{ls}} A_{i*}^{\mathrm{ls}} \tag{6}$$

where the subscript "*" indicates quantities corresponding to the critical crystal (nucleus).

Now consider the case where a crystal cluster forms with one of its facets (e.g., facet λ) at a droplet surface. Assuming that $A_{\lambda}^{\mathrm{sv}}/\pi R^2 \ll 1$, the deformation of the droplet can be neglected[11] and the reversible work of formation of a crystal particle with its facet λ at the droplet surface is

$$\tilde{W} = \nu[\mu^{\mathrm{s}}(P^{\mathrm{s}}, T) - \mu^{\mathrm{l}}(P^{\mathrm{l}}, T)] - \tilde{V}(P^{\mathrm{s}} - P^{\mathrm{l}}) + \sum_{i=1}^{n}{}^{\lambda} \sigma_i^{\mathrm{ls}} A_i^{\mathrm{ls}} + \sigma_{\lambda}^{\mathrm{sv}} A_{\lambda}^{\mathrm{sv}} - \sigma^{\mathrm{lv}} A_{\lambda}^{\mathrm{sv}} \tag{7}$$

where $\tilde{V}$ is the volume of the crystal and where Σ^{λ} indicates that the term with $i = \lambda$ is excluded from the sum.

Wulff's relations in (4), 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 $\sigma_i^{\mathrm{ls}}/h_i = \sigma_{i+1}^{\mathrm{ls}}/h_{i+1}$. In the case where one of the facets (facet λ) is the crystal−vapor interface and all the others lie within the liquid phase (see Figure 2), the equilibrium conditions on the edges formed by this facet with the adjacent ones (hereafter marked by a subscript j) are given by

$$\frac{\sigma_j^{\mathrm{ls}}}{h_j} = \frac{\sigma_{\lambda}^{\mathrm{sv}} - \sigma^{\mathrm{lv}}}{\tilde{h}_{\lambda}} \tag{8}$$

Note that the height of the λth 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

$$\frac{\sigma_1^{\mathrm{ls}}}{h_1} = ... = \frac{\sigma_{\lambda-1}^{\mathrm{ls}}}{h_{\lambda-1}} = \frac{\sigma_{\lambda}^{\mathrm{ls}} - \sigma^{\mathrm{lv}}}{\tilde{h}_{\lambda}} = \frac{\sigma_{\lambda-1}^{\mathrm{ls}}}{h_{\lambda-1}} = ... = \frac{\sigma_n^{\mathrm{ls}}}{h_n} \tag{9}$$

and (3) becomes

$$P^{\mathrm{s}} - P^{\mathrm{l}} = \frac{2\sigma_i^{\mathrm{ls}}}{h_i} \qquad (i = 1, ... \lambda - 1, \lambda + 1, ..., n) \qquad P^{\mathrm{s}} - P^{\mathrm{l}} = \frac{2(\sigma_{\lambda}^{\mathrm{sv}} - \sigma^{\mathrm{lv}})}{\tilde{h}_{\lambda}} \tag{10}$$

Making use of (9) and (10), one can represent (7) as

$$\tilde{W} = -\nu \Delta h \ln \Theta + \sum_{i=1}^{n}{}^{\lambda} \sigma_i^{\mathrm{ls}} A_i^{\mathrm{ls}} + \sigma_{\lambda}^{\mathrm{sv}} A_{\lambda}^{\mathrm{sv}} - \sigma^{\mathrm{lv}} A_{\lambda}^{\mathrm{sv}} \tag{11}$$

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

$$\tilde{V}(P^{\mathrm{s}} - P^{\mathrm{l}}) = \frac{2}{3}\left(\sum_{i=1}^{n}{}^{\lambda} \sigma_i^{\mathrm{ls}} A_i^{\mathrm{ls}} + \sigma_{\lambda}^{\mathrm{sv}} A_{\lambda}^{\mathrm{sv}} - \sigma^{\mathrm{lv}} A_{\lambda}^{\mathrm{sv}}\right) \tag{12}$$

The reversible work $\tilde{W}_*$ of formation of a *critical* crystal can be thus represented as

$$\tilde{W}_* = \frac{1}{2}\tilde{V}_*(P^{\mathrm{s}}_* - P^{\mathrm{l}}) = \frac{1}{3}\left(\sum_{i=1}^{n}{}^{\lambda}\sigma_i^{\mathrm{ls}}A_i^{\mathrm{ls}} + \sigma_\lambda^{\mathrm{vs}}A_\lambda^{\mathrm{vs}} - \sigma^{\mathrm{vl}}A_\lambda^{\mathrm{vs}}\right) \qquad (13)$$

The similarity of (13) and (6) allows one to meaningfully compare them. One can show[11,12] that the difference $P^{\mathrm{s}}_* - P^{\mathrm{l}}$ for the nucleus is determined exclusively by the degree of supercooling of the liquid. Neglecting the temperature dependence of Δh in the range from T to T_0, in both (6) and (13)

$$(P^{\mathrm{s}}_* - P^{\mathrm{l}}) = \frac{\Delta h}{v}\ln\Theta \qquad (14)$$

where v is the volume per molecule in a solid phase. If the temperature dependence of Δh in the range from T to T_0 is significant, the RHS of (14) should be modified as indicated after (2). As already mentioned, a specific form of the RHS of (14) has no influence on what follows.

Using (3) and (10), one obtains

$$\tilde{h}_\lambda = \frac{\sigma_\lambda^{\mathrm{vs}} - \sigma^{\mathrm{lv}}}{\sigma_\lambda^{\mathrm{ls}}}h_\lambda \qquad (15)$$

On the other hand, $h_i = \tilde{h}_i$ for $i = 1,..., \lambda - 1, \lambda + 1,..., n$, by virtue of (3), (10), and (14). Therefore, the Wulff shape of the surface-stimulated crystal is obtained by simply changing the height of the λth pyramid of the volume-based Wulff crystal. It is thus clear that if $\sigma_\lambda^{\mathrm{sv}} - \sigma^{\mathrm{lv}} < \sigma_\lambda^{\mathrm{ls}}$, then $\tilde{h}_\lambda < h_\lambda$ and hence $\tilde{V}_* < V_*$. Because

$$\frac{\tilde{W}_*}{W_*} = \frac{\tilde{V}_*}{V_*} \qquad (16)$$

(according to (6), (13) and (14)), we can conclude that if

$$\sigma_\lambda^{\mathrm{sv}} - \sigma^{\mathrm{lv}} < \sigma_\lambda^{\mathrm{ls}} \qquad (17)$$

then $\tilde{W}_* < W_*$. In other words, if condition (17) is fulfilled, it is thermodynamically more favorable for the crystal nucleus to form with facet λ *at* the droplet surface rather than *within* the droplet.

Inequality (17) coincides with the condition of partial wettability of the λth facet of the crystal by its own liquid phase[13] (note that it has exactly the same form in multicomponent droplets[12]). This result is physically reasonable, because,[24] 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". This intuitive argument alone, however, is *not sufficient* to claim that the droplet surface stimulates crystal nucleation, because (as shown in refs 11 and 12) the volume-located and surface-faced nuclei *differ* from each other in shape and size (and, possibly, composition). It is necessary to compare the total surface contributions to the free energy of nucleus formation rather than the free energies per unit area of one particular facet of the nucleus, i.e., it is necessary to compare the quantity $^1/_3(\Sigma_{i=1}^{n}{}^{\lambda}\sigma_i^{\mathrm{ls}}A_i^{\mathrm{ls}} + \sigma_\lambda^{\mathrm{sv}}A_\lambda^{\mathrm{sv}} - \sigma^{\mathrm{lv}}A_\lambda^{\mathrm{sv}})$ to $^1/_3\Sigma_{i=1}^{n}\sigma_i^{\mathrm{ls}}A_i^{\mathrm{ls}}$ rather than quantity $\sigma_\lambda^{\mathrm{sv}}A_\lambda^{\mathrm{sv}} - \sigma_\lambda^{\mathrm{lv}}A_\lambda^{\mathrm{sv}}$ to $\sigma_\lambda^{\mathrm{ls}}A_\lambda^{\mathrm{ls}}$. It is a mere coincidence that the first comparison reduces to the second one.

3. Kinetics of Surface-Stimulated Crystal Nucleation

Inequality (17) allows one to predict whether crystallization in a supercooled droplet will or will not be thermodynamically stimulated by the surface. To apply this in practice, however, one needs accurate and detailed information about the surface tension of the liquid−vapor interface and the surface tensions of crystal facets both in the liquid and in the vapor. Data on σ^{lv} are available for most liquids of interest or can be easily obtained. The availability of data on σ^{ls} and σ^{sv} is more problematic. Data on σ^{ls} are often obtained by matching experimental crystal nucleation rates with the predictions of CNT, treating the surface tension of the crystal nucleus as an adjustable parameter.[9,25] However, such data are not suitable for using in (17) for several reasons (see refs 11 and 12 for more details), one of which is the unsatisfactory state of the kinetic theory of crystal nucleation in light of the results outlined in the previous section.

Indeed, the classical expression for the rate of crystal nucleation conventionally used in atmospheric models as well as for treating experimental data, is derived by assuming that crystal nuclei form *within* the liquid.[8,9,2,3] However, under conditions of partial wettability of at least one crystal facet by its melt, the formation of a crystal nucleus with that facet at the droplet surface is thermodynamically favored over its formation with all the facets *within* the droplet. This effect can become important when the crystallizing liquid is in a dispersed state, which is the case with the freezing of atmospheric droplets[2,3] and many experiments.[26]

Assuming a monodisperse (or sharp enough Gaussian) distribution of liquid droplets, the average crystallization time of the ensemble equals that of a single droplet (for simplicity, hereafter we will discuss only the monodisperse distribution, although results will be also applicable to a narrow enough Gaussian-like distribution). Let us denote that time by t_1. Typical sizes of atmospherically relevant droplets allow one to assume that the formation of a single crystal nucleus in a droplet immediately leads to the crystallization of the latter, i.e., the time of growth of a crystal nucleus to the size of the whole droplet is negligible compared to the time necessary for the first nucleation event in the droplet to occur (in experiments this can be achieved by using special techniques[26]). Consequently,

$$t_1 = 1/I \qquad (18)$$

where I is the per-particle (pp) nucleation rate, i.e., the total number of crystal nuclei appearing in the whole volume of the liquid droplet per unit time. Until recently, atmospheric models had considered homogeneous crystal nucleation in droplets to be exclusively volume-based, with

$$I = I^{\mathrm{vb}} \equiv J_{\mathrm{v}}V_1 \qquad (19)$$

where V_1 is the volume of a single droplet and J_v is the the rate of volume-base crystal nucleation given, e.g., by refs 9, 2, and 3

$$J_{\mathrm{v}} = \frac{kT}{h}\rho_{\mathrm{l}}\mathrm{e}^{-W_*/kT} \qquad (20)$$

with k and h being the Boltzmann and Planck constants and ρ_{l} the number density of molecules in the liquid phase. However, because the surface-to-volume ratio of a droplet increases with decreasing droplet size, (19) may become inadequate for small enough droplets in which the surface-stimulated crystal nucleation can compete with (or even dominate) the volume-based process. To take this possibility into account, it was recently[18,19] suggested that instead of (19) the pp-rate of crystal nucleation should consist of two contributions,

$$I = J_{\mathrm{s}}S_1 + J_{\mathrm{v}}V_1 \qquad (21)$$

where S_1 is the area of the droplet surface and J_{s} is the number of crystal nuclei forming per unit time on unit surface area of the droplet (i.e., in a surface stimulated mode). The rate J_s was conjectured[18,19] to have the following form (reminiscent of that for the rate of crystal nucleation on heterogeneous surfaces[2,3])

$$J_s = \frac{kT}{h}\rho_l^s e^{-\tilde{W}_*/kT} \qquad (22)$$

with ρ_l^s being the number of (liquid phase) molecules per unit area of the droplet surface.

As is clear, using (22) for J_s on the RHS of (21) amounts to implicitly assuming that in the surface-stimulated mode the crystal nucleus forms in a heterogeneous fashion on a molecule m_s located in the droplet surface monolayer. As a first step, the first nearest neighbors (both in the bulk and in the droplet surface layer) of molecule m_s would acquire a stable crystalline configuration (this would be due to fluctuations and hence might be temporary). At the second step, the second nearest neighbors (including those in the droplet surface layer) of molecule m_s would acquire a stable crystalline order (this would be again due to fluctuations and hence temporary). These steps would continue until the crystalline cluster formed around m_s attained a critical size (i.e., became a crystal nucleus with one of its facets at the droplet-vapor interface), which would be followed by a quick crystallization of the whole droplet (this process is schematically shown in Figure 3a). The number of nuclei forming per unit time per unit area of the droplet surface (i.e., the surface nucleation rate J_s) would be then given by (22).

However, there is a weak point in the above reasoning. Indeed, the heterogeneous mechanism of nucleation implies that the *initial* stage of the formation of a new phase fragment around a heterogeneous center is thermodynamically favorable; i.e., it is accompanied by a decrease in the appropriate free energy of the system. This was clearly demonstrated for heterogeneous condensation on ions[27,28] as well as on insoluble,[29,30] mixed,[31] and various soluble[32] macroscopic particles. For all these phenomena a specific physical effect, causing the initial decrease in the free energy of the system upon the formation of a new phase particle around a heterogeneous center, can be unambiguously identified. This is not the case with surface-stimulated crystal nucleation in droplets. The formation of a crystal nucleus with one of its facets at the droplet surface cannot *start* preferentially *at* the surface, because the latter does not have any sites which would make the ordering of the surrounding *surface located* molecules thermodynamically more favorable than the ordering of interior molecules. On the contrary, the surface layer of a crystalline structure remains disordered far below the freezing/melting temperature. This phenomenon is often referred to as premelting[33] and was observed both experimentally[34–36,15] and by simulations.[37–40]

According to the empirical criterion proposed by Lindemann,[41] melting in the bulk can occur when the root mean amplitude of thermal vibrations of an atom exceeds a certain threshold value of more or about 10% of the distance to the nearest neighbor in the crystalline structure. Developing this criterion, Tammann suggested[33] that the outermost layer of the crystal should become disordered far below the bulk melting point due to the higher freedom of motion for surface-located molecules which have a reduced number of neighbors and hence have a higher vibrational amplitude compared to those in the bulk. Thus, one can expect the Lindemann criterion for surface atoms to be satisfied at a temperature lower than that for atoms located within the crystalline structure. The surface melting (often referred to as premelting) involves the formation of a thin disordered layer at a temperature significantly below the melting one.

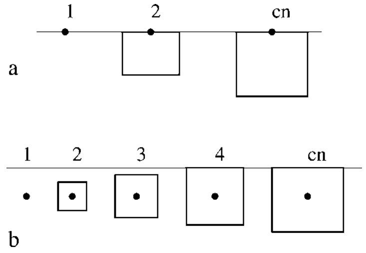

Figure 3. Schematic representation of the "pseudo-heterogeneous" and homogeneous formation of a surface stimulated crystal nucleus (Figures 3a and 3b, respectively). In both cases the crystal nucleus is exactly the same, shown by the symbols "cn" above the droplet-vapor interface shown as a thin straight line.

Experimentally, the premelting phenomenon was apparently first detected by Lyon and Somorjai[34] who studied the structures of clean (111), (110), and (100) crystal faces of platinum as a function of temperature by means of low-energy electron diffraction and observed the formation of disordered surface structures at temperatures far below the melting temperature T_m = 2043 K. Direct experiments on the surface-initiated melting were also carried out by Frenken et al.[35] using Rutherford backscattering in conjunction with ion-shadowing and blocking. That experiment revealed a reversible order–disorder transition on the (110) surface of a lead crystal well below its melting point T_m = 600.7 K. Other techniques have been employed such as calorimetry, electron, neutron, and X-ray diffraction, microscopy, ellipsometry, and helium scattering. Although most experiments were carried out under equilibrium conditions, melting tended to be initiated at the surface even when the crystalline solid was heated very quickly so that equilibrium conditions were not established.[36] Lately, molecular dynamics simulations have been also widely used to study premelting (see, e.g., ref 37 and recent simulations of premelting in AgBr (ref 38), in Cr_2O_3 (ref 39), and the premelting of a clean Al (110) surface [40]).

Of utmost atmospheric relevance, there has been accumulated undeniable evidence[16,42–44] for the premelting of ice (first apparently discussed by Faraday[45]). Relatively recently, Wei et al.[46] experimentally observed that the premelting of the (0001) face of hexagonal ice occurs at the temperature of about 200 K, i.e., much below the lowest temperature reported for homogeneous freezing of atmospheric droplets.

Thus, on the basis of the experimental and simulational evidence on premelting,[34–40] one can conclude that a crystal nucleus with one facet as a droplet-vapor interface *cannot begin* its formation (as a subcritical crystal) at the droplet surface. This conclusion is enhanced by the theory of heterogeneous nucleation.[27–32] A question arises then: How can the droplet surface stimulate crystal nucleation (under condition (17)) therein? For this enhancement to take place, a crystal nucleus has to start its formation somewhere. Because it cannot do it at the surface, a crystal cluster has to begin its initial evolution homogeneously in a spherical layer adjacent to the droplet surface ("subsurface layer"). When this crystal becomes large enough (due to fluctuational growth usual for the nucleation stage), one of its facets hits the droplet surface and at this moment or shortly thereafter it becomes a nucleus owing to a drastic change in its thermodynamic state (this mechanism is schematically shown in Figure 3b).

Let us consider the "subsurface" layer of the droplet hereafter referred to as an SSN layer (SSN can stand for both "subsurface nucleation" and "surface-stimulated nucleation"). Its thickness will be denoted by η (more detailed discussion of η is given in the following subsection). By definition (albeit somewhat loose for now), any crystalline cluster that starts its evolution with its center in the SSN layer has a potential to become a nucleus (by means of structural and density fluctuations) once one of its facets that satisfies the condition of partial wettability, (17), meets the droplet surface. Clearly, to become a surface-stimulated nucleus, the subcritical cluster must evolve in such a way that its facet λ (satisfying condition (17)) is parallel to the droplet surface at the time they meet. The orientation adjustment cannot be mechanical because this would require relatively long time scales, but may, or may not, occur by means of appropriate spatial distribution of density and structure fluctuations around the cluster.

In the framework of the SSN layer model, the pp-rate of crystal nucleation is given by the sum

$$I = J_{\mathrm{v}}^{\mathrm{s}} V_{\mathrm{l}}^{\mathrm{s}} + J_{\mathrm{v}}\left(V_{\mathrm{l}} - V_{\mathrm{l}}^{\mathrm{s}}\right) \tag{23}$$

(rather than by (19) or (21)), where $J_{\mathrm{v}}^{\mathrm{s}}$ is the number of crystal nuclei forming in a surface stimulated mode per unit time in unit volume of the SSN layer whereof the total volume is $V_{\mathrm{l}}^{\mathrm{s}}$. Equivalently,

$$I = I^{\mathrm{ss}} + I^{\mathrm{vb}} \tag{24}$$

where

$$I^{\mathrm{ss}} = \left(J_{\mathrm{v}}^{\mathrm{s}} - J_{v}\right) V_{1}^{\mathrm{s}} \tag{25}$$

and I^{vb} (defined by (19)) are the contributions to the total pp-rate of crystal nucleation arising from the surface-stimulated and volume-based modes, respectively. As clear from the above discussion,

$$J_{\mathrm{v}}^{\mathrm{s}} = \frac{kT}{h}\rho_{\mathrm{l}} \mathrm{e}^{-\tilde{W}_{*}/kT} \tag{26}$$

where the number density of molecules in the droplet is assumed to be uniform up to the dividing surface,[13] in consistency with the capillarity approximation.[10] In this approximation, the pre-exponential factors in (20) and (26) are the same, which reflects the *homogeneous* nature of the nascency of a subcritical cluster in both volume-based and surface-stimulated modes of crystal nucleation. On the other hand, the nuclei in these two modes are different hence have different free energies of formation, which results in different exponents: $-W^{*}/kT$ for the volume-based process and $-\tilde{W}_{*}/kT$ for the surface-stimulated mode (see section 2).

By virtue of (19), (20), and (26), one can rewrite equation (25) as

$$I^{\mathrm{ss}} = \alpha I^{\mathrm{vb}} \tag{27}$$

where

$$\alpha \equiv \alpha(\varepsilon) \equiv \alpha(\varepsilon, \Delta W_{*}(\eta(\mathrm{ep}))) = [1 - (1 - \varepsilon)^{3}](-1 + \mathrm{e}^{-\Delta W_{*}/kT}) \tag{28}$$

with $\varepsilon = \eta/R$ $(0 \le \varepsilon \le 1)$. As clear from (27), the ratio $\alpha = I^{\mathrm{ss}}/I^{\mathrm{vb}}$ characterizes the relative intensity of surface-stimulated and volume based modes of crystal nucleation in the droplet. If the volume-based process predominates over the surface-stimulated nucleation (i.e., $I^{\mathrm{ss}} \ll I^{\mathrm{vb}}$), then $\alpha \ll 1$. If the surface-stimulated mode prevails over the volume-based one (i.e., $I^{\mathrm{ss}} \gg I^{\mathrm{vb}}$), then $\alpha \gg 1$. In the crossover regime, when the nucleation mode factor is roughly in the range $0.33 \lesssim \alpha \lesssim 3$, the contributions from both modes to the total pp-rate of crystal nucleation are comparable to each other. The exact crossover point is given by the equality $I^{\mathrm{ss}} = I^{\mathrm{vb}}$.

According to (28), under given external conditions (temperature, pressure, etc.) the value of the "nucleation mode factor" α is determined by $\varepsilon = \eta/R$, i.e., by the size of the freezing droplet, R. The geometric factor $1 - (1 - \varepsilon)^{3}$ in α monotonically increases from 0 to 1 with increasing ε. However, the nucleation mode factor itself, α, may have a more complicated dependence on ε because of the exponential $\mathrm{e}^{-\Delta W_{*}}/kT$ in which ΔW_{*} is intrinsically related to ε via η.

4. Nucleation Mode Factor

According to the definition of the SSN layer, its thickness, denoted by η, is determined by the shape and orientation of the crystal nucleus and the physical characteristics of the crystal nucleus *and* droplet. They also determine the free energy of nucleus formation in both surface-stimulated and volume-based modes, $\tilde{W}_{*}$ and W_{*}, respectively (the droplet surface tension is involved only in $\tilde{W}_{*}$ but not in W_{*}). For a given droplet in a given thermodynamic state, η and W_{*} are completely independent of each other. However, both η and $\tilde{W}_{*}$ are determined by the shape *and* orientation of the crystal nucleus. Hence the dependence $\Delta W_{*} = \Delta W_{*}(\eta)$ which, according to (28), is likely to be a key factor in determining the ε dependence of I^{ss} (because $\varepsilon = \eta/R$) and, ultimately, the value of the nucleation mode factor α.

Consider first the case where crystal clusters (including the critical one, nucleus, which forms as a result of fluctuational growth of an initially subcritical cluster) have n facets each and assume that only one of these facets, e.g., facet λ, satisfies the condition of partial wettability, (17). Let us introduce the unit vectors n_{d} and n_{λ} as the external normal vectors to the droplet surface and facet λ, respectively. The angle Θ between n_{d} and n_{λ} determines the mutual orientation of the droplet surface and facet λ. Clearly, $0 \le \Theta \le \pi$ with $\Theta = 0$ corresponding to the λ-facet being parallel to the droplet surface and $\Theta = \pi$ their being "antiparallel".

If the only possible orientation of a crystal cluster were the one with $\Theta = 0$, then the λ-facet of any surface-stimulated nucleus would be a part of the droplet surface. Consequently, the thickness η of the SSN layer would be equal to $\tilde{h}_{\lambda}$ (the height of the λth pyramid, with facet λ its basis and point O its apex; see Figure 2) and (27) could be written as

$$I^{\mathrm{ss}} = [1 - (1 - \varepsilon_{\lambda})^{3}](-1 + \mathrm{e}^{-\Delta W_{*\lambda}/kT}) I^{\mathrm{vb}} \tag{29}$$

where $\varepsilon_{\lambda} = \tilde{h}_{\lambda}/R$, $\Delta W_{*\lambda} \equiv \tilde{W}_{*\lambda} - W_{*}$, and $\tilde{\ } W_{*\lambda}$ is the free energy of formation of a surface-stimulated nucleus with facet λ being a part of the droplet surface.

In reality, however, the orientations of crystal clusters are randomly distributed in the range from $0 \le \Theta \le 1$. Assuming this distribution to be uniform (because there are no obvious reasons for the contrary), its probability density is $p(\Theta) = 1/\pi$ with the normalization $\int_{0}^{\pi} \mathrm{d}\Theta \, p(\Theta) = 1$.

Let $p_{\Theta\varepsilon}(\Theta)$ be the probability density that a crystal cluster has an orientation Θ and, at this orientation, the surface-stimulated nucleation occurs in a layer of (dimensionless) thickness ε. As mentioned above, for a given droplet under given external conditions ε can be a function of only Θ. Moreover, the droplet surface can stimulate the nucleation of crystal clusters only at one single orientation, $\Theta = 0$. Thus,

$$p_{\Theta\varepsilon}(\Theta) = p(\Theta)\, \delta(\Theta) = \frac{1}{\pi}\delta(\Theta) \tag{30}$$

The contribution I^{ss} from the surface-stimulated mode to the total pp rate of crystal nucleation, I, is now obtained by averaging $I^{\mathrm{ss}}(\varepsilon(\Theta))$, given by (27) and (28), over all the possible orientations of crystal clusters, i.e., as

$$I^{\mathrm{ss}} = \int_0^{\pi} \mathrm{d}\Theta\ [1 - (1 - \varepsilon(\Theta))^3](-1 + \mathrm{e}^{-\Delta W_*(\Theta)/kT})I^{\mathrm{vb}} p_{\Theta_\varepsilon}(\Theta) \tag{31}$$

Taking into account (30) and the equality $\varepsilon(0) = \varepsilon_\lambda$, one obtains

$$I^{\mathrm{ss}} = \frac{1}{\pi}[1 - (1 - \varepsilon_\lambda)^3](-1 + \mathrm{e}^{-\Delta W_{*\lambda}/kT})I^{\mathrm{vb}} \tag{32}$$

As is clear, the ability of a crystal cluster in the SSN layer to appear with facet λ not only parallel to the droplet surface but with any other orientation, with Θ uniformly distributed from 0 to π, decreases I^{ss} (and hence α) by a factor of $1/\pi$ compared to a hypothetical situation when all crystal clusters would evolve with their λ facets parallel to the droplet surface, i.e., with $\Theta = 0$.

Equation 32 is obtained for the case where every cluster of the nascent crystalline structure has only one facet (facet λ) satisfying the condition of partial wettability, (17). In more general situations, every cluster can have w facets ($1 \le w \le N$) partially wettable by the melt. Let these facets be numbered 1 through w. Every one of these facets contributes to the surface-stimulated mode of the pp-rate of crystal nucleation in the droplet. Because these contributions I_λ^{ss} ($\lambda = 1,..., w$) are independent of one another, each of them is determined by (32), so that the total "surface-stimulated" contribution I^{ss} to the pp-rate of crystal nucleation will be given by the sum $\Sigma_{\lambda=1}^{w} I_\lambda^{\mathrm{ss}}$, i.e.,

$$I^{\mathrm{ss}} = \sum_{\lambda=1}^{w} \frac{1}{\pi}[1 - (1 - \varepsilon_\lambda)^3](-1 + \mathrm{e}^{-\Delta W_{*\lambda}/kT})I^{\mathrm{vb}} \tag{33}$$

In a rough approximation, one can assume that

$$\tilde{h}_0 \equiv \tilde{h}_1 \approx \tilde{h}_2 \approx \ ... \ \approx \tilde{h}_w \tag{34}$$

and

$$\tilde{W}_{*0} \equiv \tilde{W}_{*1} \approx \tilde{W}_{*2} \approx \ ... \ \approx \tilde{W}_{*w} \tag{35}$$

The former assumption is reasonable if, for instance, all crystal nuclei have globular (not elongated) shape with aspect ratios close to 1, whereas the latter implies that the surface tensions of facets 1,..., w do not differ much from one another. With such approximations, (33) reduces to

$$I^{\mathrm{ss}} = \frac{w}{\pi}[1 - (1 - \varepsilon_0)^3](-1 + \mathrm{e}^{-\Delta W_{*0}/kT})I^{\mathrm{vb}} \tag{36}$$

where $\varepsilon_0 = \tilde{h}_0/R$ and $\Delta W_{*0} = \tilde{W}_{*0} - W_*$. This equation is convenient for rough numerical evaluations of I^{ss}. In a more complicated case where assumption (34) is not acceptable, but approximate equalities in (35) do hold, (33) acquires the form

$$I^{\mathrm{ss}} = \frac{1}{\pi}\left[w - \sum_{\lambda=1}^{w} (1 - \varepsilon_\lambda)^3\right](-1 + \mathrm{e}^{-\Delta W_{*0}/kT})I^{vb}... \tag{37}$$

where the factor in the square brackets is a relatively weak function of ε_λ ($\lambda = 1,..., w$) not exceeding w. Again, this form is more convenient than (33) to numerically evaluate the nucleation mode factor α.

5. Numerical Evaluations and Experimental Perspective

To illustrate the above theory by numerical evaluations, consider the freezing of water droplets (surrounded by water vapor in air) at around $T = 233$ K (i.e., about −40 °C). The homogeneous and isothermal character of freezing is assumed. As reported by Defay et al.,[13] the rate of crystal nucleation in bulk supercooled water at this temperature is 7×10^{12} cm^{-3} s^{-1}, with the nucleation barrier height $W_* = 45\ kT$, the average (over all crystal facets) surface tension of liquid−solid (water−ice) interface σ^{ls} being about 20 dyn/cm (Table 18.1 in ref 12). The surface tensions of liquid−vapor and solid−vapor (ice−water vapor) interfaces at $T = 233$ K will be taken to be $\sigma^{\mathrm{lv}} = 88$ dyn/cm and $\sigma^{\mathrm{sv}} = 103$ dyn/cm, respectively. All these values of σ^{ls}, σ^{lv}, and σ^{sv} are consistent with the data provided in ref 2 (chapters 5.7 and 5.9, pp 145−161).

The wettability of a solid by a liquid (both in contact with a vapor) is determined by the contact angle, defined as the angle between the tangents to the liquid−vapor and solid−liquid interfaces at the three phase contact line. According to Young's relation,[13] which gives a connection between three interfacial tensions and contact angle, the above values of σ^{ls}, σ^{lv}, and σ^{sv} would correspond to the contact angle $\beta \simeq 19.4°$ (or $\cos\beta \simeq 0.943$). Therefore, at $T = 233$ K at least some of (if not all) the facets of an ice crystal are only partially wettable by liquid water. This is consistent with the experimental results of Elbaum et al.[16] who reported partial wettability of the basal facets of hexagonal ice ($\mathrm{I_h}$) at temperatures slightly below 0 °C. In those experiments,[16] 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,[47,48] so one can expect that at temperatures far below 0 °C at least some facets of water crystals remain only partially wettable even in the presence of air. Moreover, according to Cahn's theory,[47] perfect wetting of a solid by a liquid away from the critical point is not generally observed; i.e., condition (17) should be fulfilled for any substance at sufficiently low temperatures. That theory[47] can be also applied to the case where the solid is of the same chemical nature as the fluid phases (it is only assumed that the surface of the solid phase is sharp on an atomic scale, i.e., the transition from the solid density to the fluid is abrupt, and interactions between surface and fluid are sufficiently short-range). Cahn's theory is inapplicable at temperatures close to the fluid critical point, but temperatures involved in crystallization are usually far below that point.

For simplicity of numerical evaluations, let us assume that only the basal facet {0001} of the hexagonal ice crystal is partially wettable by water at $T = 233$ K. Denote the height of the basal pyramid of the crystal cluster 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 (15),

$$\frac{\tilde{h}_b}{h_{\mathrm{b}}} = \frac{95 - 80}{20} = 3/4 \tag{38}$$

Consequently, the ratio of the volumes of the surface-based and volume-formed clusters is

$$\frac{\tilde{V}_*}{V_*} \simeq \frac{\tilde{h}_b + h_{\mathrm{b}}}{2h_{\mathrm{b}}} \tag{39}$$

By virtue of (16), for the corresponding works of formation of crystal nuclei we obtain

$$\frac{\tilde{W}_*}{W_*} \simeq 0.875 \tag{40}$$

i.e., $\tilde{W}_* \simeq 39.3kT$. Thus, the decrease in the work of formation of the surface-stimulated crystal nucleus, as compared to that of the volume-based one, is $\Delta W_* \approx -5.7\ kT$.

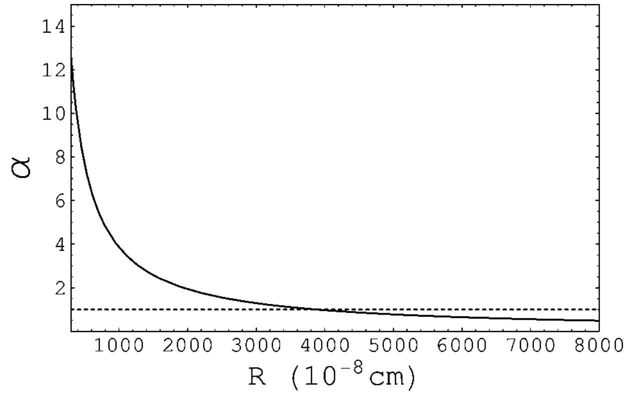

Figure 4. Nucleation mode factor $\alpha = I^{ss}/I^{vb}$ (given by (36) with $w = 2$) as a function of R for crystal nucleation in water droplets at $T = 233$ K.

Let us now evaluate the thickness of the SSN layer, η, which still depends on the size and habit of crystal nuclei even after averaging over Θ in (31). According to (6), the work of formation of a volume-formed crystal nucleus can be rewritten in the form

$$W_* = \frac{1}{3}\sigma_{ls}A_* \tag{41}$$

where σ_{ls} is the average (over all the crystal facets) interfacial tension of the nucleus and A_* is its total surface area.[11,12] The total surface area of an I_h crystal (shaped as a right prism) is $A = 12h_b a + 3 \cdot 3^{1/2}a^2$, where a is the side length of the basal facet (for a regular hexagon a is also equal to its radius) and h_b is the half-height of the prism.

As mentioned, for crystallization in pure water $W_* \approx 45kT$ and $\sigma_{ls} \approx 20$ dyn/cm at $T = 233$ K. On the other hand, at this temperature the "crystal-liquid" interfacial free energies of the basal and prismal facets are $\sigma_b^{ls} \simeq 19.2$ dyn/cm and $\sigma_p^{ls} \simeq 20.5$ dyn/cm, respectively (see ref 2, pp 145−161). Therefore, according to Wulff's relations (4), $h_b \simeq 0.81a$ and (41) leads to $h_b \approx 9.8 \times 10^{-8}$ cm, which, according to (38), corresponds to the SSN layer of thickness $\eta = \tilde{h}_b \approx 7.4 \times 10^{-8}$cm.

The nucleation mode factor α can be estimated from (36) with $w = 2$. Its dependence on the radius of the droplet is presented in Figure 4. As clear, the surface-stimulated mode can considerably enhance crystal nucleation in droplets with radii even exceeding 1 μm. For example, for droplets of radius $R = 0.15$ μm the nucleation mode factor $\alpha = 2.7$, whereas for droplets of radius $R = 2$ μm the nucleation mode factor $\alpha = 0.2$. These estimates suggest that homogeneous crystal nucleation in water droplets with radii smaller than $R \approx 0.2$ μm occurs predominantly in the surface-stimulated mode, whereas the volume-based mode prevails in droplets with radii greater than $R \approx 2$ μm. Both the surface-stimulated and volume-based modes apparently provide contributions of the same order of magnitude to the total pp-rate of crystal nucleation in droplets with radii in the range approximately from 0.2 to 2 μm. Similar evaluations can be carried out for the case where all the facets of I_h crystals are only partially wettable. Assuming that for the I_h prism facets ΔW_* is approximately the same as for the basal ones, it is clear from (36) that in this case the nucleation mode factor α may be greater than 1 even for droplets with $R > 10$ μm (i.e., the surface-stimulated mode may dominate crystal nucleation even in such relatively large droplets).

Currently there is both experimental and simulational evidence suggesting that it is thermodynamically more favorable for water-to-ice nucleation to proceed via the formation of cubic ice (I_c) crystal nuclei rather I_h nuclei (see, e.g., refs 49 and 50). Depending on the external conditions, I_c nuclei may or may not acquire a hexagonal shape upon their further growth.[50] Numerical evaluations for I_c nuclei can be also performed as above. Even though there are no reliable data on the interfacial free energy of the dominant facets of I_c, it is assumed[49] to be roughly the same as that for the basal plane of hexagonal ice, hence one can expect the nucleation mode factor for I_c to be of the same order of magnitude as for I_h.

Although the above numerical estimates are approximate because of insufficiently accurate data on the interfacial tensions involved in the model, laboratory techniques currently available for studying crystal nucleation in droplets make it possible to carry out the experimental verification of the above theory. Indeed, modern experimental methods[2,26] can provide data on the dependence of the pp-rate of crystal nucleation in droplets on their radius, i.e., I as function of R. According to the above model, one can expect that there must exist such a constant A that for $R \leq 1$ μm the LMS fit of the experimental dependence I^{exp} vs R with the function $(1 + A/R)BR^3$ (B is another constant) is much more accurate than with the function BR^3 and the inaccuracy of the latter compared to the former should be aggravating with decreasing R.

6. Concluding Remarks

The thermodynamics of surface-stimulated crystal nucleation was previously developed for both unary[11] and multicomponent droplets[12] (for which the theory is more complicated not only due to the presence of several components but also due to the surface adsorption of all components as well as their dissociation into ions) 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 and multicomponent droplets, this criterion coincides with the condition of partial wettability of at least one of the crystal facets by the melt. However, so far the kinetic aspects of this phenomenon had not been studied at all.

In this paper we have presented a kinetic theory of homogeneous crystal nucleation in unary droplets taking into account that a crystal nucleus can form not only in the volume-based mode but also in the surface-stimulated one. We have invoked experimental and simulations-based evidence showing that surface-stimulated crystal nucleation is *not* a particular case of heterogeneous nucleation. On the contrary, it is a particular case of homogeneous crystal nucleation hence its thermodynamic similarities with heterogeneous nucleation can be misleading because the kinetics of this process cannot be treated by using the formalism of heterogeneous nucleation on foreign surfaces.

Even in the surface-stimulated mode the crystal nucleus initially emerges (as a subcritical cluster) homogeneously in the droplet subsurface layer, not pseudo-heterogeneously at the droplet surface. A homogeneously emerged subcritical crystal cluster can become a surface-stimulated nucleus when, after growing large enough owing to density and structure fluctuations, one of its facets meets the droplet surface and both are parallel to each other. This effect gives rise to an additional contribution to the total rate of crystal nucleation in a droplet (the conventional contribution arises from the volume-based crystal nucleation). We have derived an expression for the total per-particle rate of crystal nucleation in the droplet in the framework of CNT. The theory has been presented only for unary droplets, but its generalization to multicomponent droplets is possible although not straightforward.

As a numerical illustration of the proposed theory, we have considered crystal nucleation in water droplets at $T = 233$ K. Our results suggest that that the surface-stimulated mode can markedly enhance the per-particle rate of crystal nucleation in water droplets as large as 10 μm in radius. We have also roughly outlined a simple way to carry out the experimental verification of the proposed theory.

However complex a theory of homogeneous crystal nucleation in droplets may be, the presence of foreign particles, serving as nucleating centers, makes the crystal nucleation phenomenon (and hence its theory) even more involved. Numerous aspects of heterogeneous crystal nucleation still remain obscure. For example, 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 *touching* the droplet surface) than in the immersion mode (particle *immersed* in the droplet).[2] Underlying physical reasons for this enhancement have remained unclear, but as little as might be known about the phenomenon of surface-stimulated (homogeneous) crystal nucleation, it strongly suggests that the droplet surface can enhance heterogeneous nucleation in a way similar to the enhancement of the homogeneous process. The thermodynamics and kinetics of both contact and immersion modes of heterogeneous crystal nucleation in droplets is the subject of our current research.

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