Dependence of homogeneous crystal nucleation in water droplets on their radii and its implication for modeling the formation of ice particles in cirrus clouds

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Abstract.
We propose an approximation for the total ice nucleation rate $J = J(T, R)$ in supercooled water droplets as a function of both droplet radius $R$ and temperature $T$, taking account of both volume-based and surface-stimulated nucleation modes. Its crucial idea is that, even in the surface-stimulated mode crystal nuclei initially emerge (as sub-critical clusters) homogeneously in the sub-surface layer, not “pseudo-heterogeneously” at the surface. This mode is negligible in large droplets, but becomes increasingly important with decreasing droplet size and is dominant in small droplets. The crossover droplet radius for the transition of homogeneous ice nucleation from the volume-based mode to the surface-stimulated mode nonmonotonically depends on $T$ from 233 K to 239.5 K, ranging there from $\approx 2 \mu m$ to $\approx 100 \mu m$. Using experimental data on ice nucleation rates in small droplets, we determine that the ice-air interfacial tension of basal facets of ice crystals monotonically increases from $\approx 89$ dyn/cm at $T = 234.8$ K to $\approx 91$ dyn/cm at $T = 236.2$ K.

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1 Introduction

Water is the most widespread and important chemical compound on Earth and hence, not surprisingly, most intensively studied.\textsuperscript{1,2} In the atmosphere, water is present in both vapor and condensed phases (liquid or solid aqueous particles).\textsuperscript{3,4} Atmospheric aerosol and cloud particles influence Earth’s global climate in various ways, e.g., by affecting the solar and terrestrial radiation balance, providing heterogeneous/catalytic surfaces for chemical reactions of some atmospheric species, removing some chemical compounds from atmosphere via precipitations, etc... These effects depends on the radiative and other physical and chemical properties of the aerosol and cloud particles.\textsuperscript{4} Therefore, it is necessary for both global and regional climate models to adequately predict the evolution of physico-chemical properties of atmospheric aerosols depending on atmospheric conditions.

One of the most important processes drastically affecting the radiative and catalytic properties of water particles in the atmosphere is the freezing of supercooled liquid droplets into ice.\textsuperscript{5} This phenomenon constitutes the core of the formation of wispy cirrus clouds (typically found at heights above 6 km).\textsuperscript{6} Since the radiative properties of ice and its ability to act as catalytic surface for heterogeneous chemical reactions differ drastically from those of liquid water, the formation of cirrus clouds is accompanied by significant changes in Earth’s radiative budget and possible heterogeneous chemical reactions involving atmospheric gaseous species.\textsuperscript{7,8} Thus it is important to be able to predict under what set of environmental conditions supercooled water droplets freeze into ice.

If no foreign (heterogeneous) centers are present in liquid water, it can be supercooled to temperatures below the melting temperature of ice and remain liquid for some time. For the crystallization process to start, an ice-like cluster of critical size (crystal nucleus) must first appear in water. Without heterogeneous centers, the formation of a crystal nucleus is a very rare event. Such nuclei do form due to density and structure fluctuations in liquid; this process is called nucleation (heterogeneous
nucleation if heterogeneous centers are present in liquid, otherwise homogeneous nucleation).

Although many phase transformations in aerosols and droplets occur via heterogeneous nucleation,\textsuperscript{4} in a number of important cases atmospheric particles appear to freeze homogeneously.\textsuperscript{9–13} The homogeneous freezing of supercooled aqueous droplets at temperatures below about -30°C can occur anywhere in the atmosphere from the surface layer (resulting in ice fogs\textsuperscript{14}) to the upper troposphere (in cirrus clouds); such low temperatures are required for the freezing of water aerosols/droplets when there are not enough preexisting centers in the air capable of nucleating ice.\textsuperscript{9–11}

The crystal nucleation rate is one of the most important characteristics of crystallization. It constitutes an integral element of any regional or global climate model. In what follows, we will consider homogeneous crystallization of pure water droplets and propose an analytical expression for the crystal nucleation rate in water droplets as an explicit function of the droplet radius and temperature. Although for bulk water the temperature dependence of the homogeneous crystal nucleation rate has been studied relatively well (see, e.g., ref.15 and references therein), this dependence for water droplets will be shown to significantly differ from the bulk one. Our approach allows one to also evaluate the ice-air interfacial tension using experimental data on the rate of homogeneous ice nucleation in water droplets.

2 Volume-based and surface-stimulated modes of homogeneous crystal nucleation in droplets

Until 2002, homogeneous crystallization in liquids had been assumed to initiate within the volume of the supercooled liquid,\textsuperscript{4,16,17} even when the latter was in the dispersed state (aerosols or droplets); the role of the droplet surface in its crystallization had been ignored. However, after re-examining some laboratory data on the homogeneous freezing of aqueous nitric acid droplets, Tabazadeh \textit{et al.}\textsuperscript{18}
suggested crystal nucleation to occur “pseudo-heterogeneously” at the air-droplet interface. Similar conclusions were drawn after re-analyzing experimental data on the freezing of pure water droplets. Moreover, using the classical nucleation theory (CNT), Djikaev et al. developed a thermodynamic theory of surface-stimulated crystal nucleation. It 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 (“surface-stimulated” mode) is thermodynamically favored over its formation with all the facets within the liquid phase (“volume-based” mode).

2.1 Two contributions to the kinetics of crystal nucleation in droplets

For both unary and multicomponent droplets, this condition coincides with the condition for the partial wettability of at least one of the crystal nucleus facets by the liquid. Neglecting the contributions from line tensions, the criterion for whether crystal nucleation in a supercooled droplet is or is not thermodynamically stimulated by the surface has the form

\[ \sigma_{sv}^{\Lambda} - \sigma_{lv}^{\Lambda} < \sigma_{ls}^{\Lambda}, \]

where \( \sigma_{lv}^{\Lambda} \) is the liquid-vapor surface tension, whereas \( \sigma_{ls}^{\Lambda} \) and \( \sigma_{sv}^{\Lambda} \) are the interfacial tensions of crystal facet \( \Lambda \) in the liquid and in the vapor, respectively. This effect was experimentally observed for several systems, including water-ice at temperatures at or below 0°C.

Taking this into account, it was suggested that the total crystal nucleation rate \( J \) in experiments on droplet freezing should contain two contributions, one due to the volume-based mode of crystal nucleation, where a crystal nucleus forms with all the facets within the liquid phase, and the other to the surface-stimulated mode, where one of the facets of a crystal nucleus constitutes a part of the droplet surface. The latter mode can become important when the crystallizing liquid is in a dispersed state (which is the case with the freezing of atmospheric aerosols and droplets and
many experiments); since smaller droplets have a higher surface-to-volume ratio than larger ones, surface-stimulated crystal nuclei will appear more often in the former than in the latter (or in bulk).

However, it was argued\textsuperscript{28} that the formation of a crystal nucleus with one of its facets at the droplet surface \textit{cannot start} preferentially \textit{at} the surface, because the latter does not have any sites which would make the ordering of the surrounding \textit{surface} molecules thermodynamically more favorable than the ordering of interior molecules. On the contrary, the crystal surface layer remains disordered far below the melting temperature due to weaker constraints on surface-located molecules which have a reduced number of neighbors and hence a higher vibrational amplitude compared to bulk ones. Consequently, a thin disordered layer forms on the crystal surface at temperatures far below the melting one. This phenomenon (premelting) has been well established both experimentally and via molecular dynamics simulations (see ref.\textsuperscript{29} and references therein). Moreover, it was experimentally observed\textsuperscript{30,31} that the premelting of the (0001) face of hexagonal ice occurs at about 200 K, far below the lowest temperature reported for the homogeneous freezing of atmospheric droplets.

Although a crystal nucleus with one facet at a droplet-vapor interface \textit{cannot begin} its formation (as a subcritical crystal) at the droplet surface, the surface of the droplet \textit{can} still stimulate crystal nucleation therein (under condition (1)), but a crystal cluster has to emerge \textit{homogeneously} in a spherical layer adjacent to the droplet surface. When this crystal becomes large enough (due to density and structure fluctuations), one of its facets hits the droplet surface and becomes a nucleus owing to a drastic change in its thermodynamic state.\textsuperscript{28} Any crystalline cluster, starting its evolution with its center in the “surface-stimulated nucleation” layer, has a potential to become a nucleus (by means of fluctuations) once one of its facets, satisfying eq.\,(1), meets the droplet surface. Originally proposed in ref.\textsuperscript{27}, this idea was verified in later experiments\textsuperscript{32} and molecular dynamics simulations.\textsuperscript{33} Recently we have furthered this idea and applied it to the freezing of aqueous nitric acid droplets.\textsuperscript{34,35}

In this model, the total rate of crystal nucleation as the sum of the contributions from both
volume-based and surface-stimulated modes, can be written as\textsuperscript{28,34,35}

\[ J = \left[1 + (1 - (h_\lambda/R)u)^3 \right] \left( e^{-\frac{1}{2}(u-1)W_*/k_BT} - 1 \right) J_v \]  \quad (2)

where the parameter \( u = (\sigma^s_v - \sigma^l_v)/\sigma^l_s \) and \( h_\lambda \) is the height of a pyramid whereof the apex is at the center of the volume-based crystal nucleus and the basis is the facet \( \lambda \), satisfying eq.(1); \( J_v \) is the rate of volume-based crystal nucleation. In the framework of CNT,

\[ J_v = \frac{k_BT}{h} \rho e^{\Delta G_d/k_BT} e^{-W_*/k_BT}, \]  \quad (3)

where the density of molecules in the droplet is assumed to be uniform up to the dividing surface, and \( W_* \) is the work of formation of a volume-based crystal nucleus.

3 The dependence of the total rate of homogeneous ice nucleation in droplets on their radii and temperature

Current atmospheric models assume that homogeneous crystallization of an aerosol or a droplet always initiates therewithin\textsuperscript{4,16,17,22} at the nucleation rate \( J_v \), thus neglecting the ability of the droplet surface to stimulate crystal nucleation. In order to take into account this effect and thus increase the accuracy of atmospheric models (in their predictions of aerosol/droplet freezing events), it is necessary to treat the crystal nucleation in a droplet as potentially occurring due to both volume-based and surface-stimulated modes, with the combined rate \( J \) given by eq.(2).

The combined crystal nucleation rate \( J \) depends on both droplet radius \( R \) and temperature \( T \). Implementing it into an atmospheric model requires \( J \) to be a known function of both \( T \) and \( R \): \( J = J(T, R) \). While the dependence of \( J \) on \( R \) is simple, it depends on \( T \) not only explicitly, but also implicitly via the parameters \( u \) and quantities \( h_\lambda, W_* \), and \( J_v \).
For the $T$ dependence of the volume-based crystal nucleation rate, $J_v$, Koop and Murray\textsuperscript{15} proposed a simple and very accurate approximation. They constrained the key terms in CNT for crystal nucleation (diffusion activation energy and ice-liquid interfacial energy) with physically consistent approximations of all involved quantities. The only adjustable parameter in their model is the water-ice interfacial tension at one temperature which is determined by fitting CNT predictions to laboratory data on the rate of homogeneous ice nucleation between 233.6 K and 238.5 K. They obtained:

$$J_v(T) = 10^{x(T)} \text{[cm}^{-1}\text{s}^{-1}],$$

(4)

where the function $x(T)$ is the sixth-order polynomial in $T - T_m$ with known coefficients (see eq.(A9a) and Table VII in ref.15) and $T_m = 273.15$ K is the melting temperature of ice.

The $T$-dependence of $W_\ast$ can be determined via a classical expression\textsuperscript{4,22,36}

$$W_\ast = W_\ast(T) = \frac{(16\pi/3)[\sigma ls(T)]^3[m_W/\rho_1(T)]^2}{[\Delta q(T) \ln(T/T_m)]^2},$$

(5)

where $m_W/\rho_1(T) = v_1(T)$ is the volume per molecule of water in ice, $m_W$ is the mass of a water molecule, and $\rho_1(T)$ is the mass density of ice (given, e.g., in Table I of ref.15); for the water-ice interfacial tension $\sigma ls(T)$ and enthalpy of crystallization of water $\delta q(T) < 0$ per molecule as functions of $T$ one can use the approximations also from ref.15 (see eqs.(A1)-(A3) and Table III therein).

Note that eq.(5) assumes that the crystal nucleus approximately has a spherical shape with the effective\textsuperscript{16,20} water-ice interfacial tension $\sigma ls$ (or, equivalently, that all the facets of an ice nucleus have the same interfacial water-ice tension, $\sigma ls$). Accordingly, this assumption is implied in eq.(4).

Using eq.(18) from ref.21, one can show that, independent of the shape of the crystal nucleus, its volume $V_\ast$ as a function of $T$ can be found as

$$V_\ast = V_\ast(T) = 2W_\ast(T)v_1(T) [\Delta q(T) \ln(T/T_m)]^{-1}.$$

(6)

Adopting a more realistic assumption (compared to the assumption of sphericity) that the ice nucleus has a shape of a right hexagonal prism with an aspect ratio $\kappa$ and assuming that the basal facets of
the prism are those that satisfy the criterion of partial wettability, eq.(1), the quantity $h_\lambda$ (defined above) will be equal to the half-height of the prism. Thus, one can obtain for its $T$-dependence

$$h_\lambda = h_\lambda (T) = [\kappa^2 V_s (T)]^{1/3}/\sqrt{3}.$$  \hspace{1cm} (7)

For large enough droplets of radii $R \to \infty$, the RHS of eq.(2) reduces\textsuperscript{28,34,35} to $J_v$. Thus, if crystal nucleation rates $J_{\text{Large}}^{\text{exp}}$ are measured in experiments on large droplets, $J_{\text{Large}}^{\text{exp}} = J_v$. If, under identical experimental conditions, crystal nucleation rates $J_{\text{small}}^{\text{exp}}$ are measured in experiments on small droplets, then the rates $J_{\text{small}}^{\text{exp}}$ and $J_{\text{Large}}^{\text{exp}}$ will be related as

$$\frac{J_{\text{small}}^{\text{exp}}}{J_{\text{Large}}^{\text{exp}}} = \left[ 1 + (1 - (h_\lambda (T)/R)u(T))^3 \right] \left( e^{-\frac{1}{2}(u(T)-1)} W_s (T)/k_B T - 1 \right).$$  \hspace{1cm} (8)

Since the functions $W_s (T)$ and $h_\lambda (T)$ can be considered to be known (as outlined above), equation (8) can be solved with respect to $u$ at any temperature $T$, so that one can build an approximation for the function $u = u(T)$. Since (at any given $T$ and $R$) the RHS of eq.(8), i.e., the ratio $f(u) \equiv J/J_v$, is a nonmonotonic function\textsuperscript{34,35} of $u$, equation (8) can formally have two roots: one, $u'$, with $df(u)/du|_{u'} > 0$, and the other, $u_0 > u'$, with $df(u)/du|_{u_0} < 0$. However, the root $u'$ is not physically meaningful. Indeed, at constant $\sigma_{lv}$ and $\sigma_{ls}$, one can expect $J_{\text{small}}^{\text{exp}}$ to decrease with increasing $\sigma_{lv}$ hence, $df(u)/du$ must be negative.

As clear from eq.(2), knowing the functions $W_s (T)$, $h_\lambda (T)$, and $u(T)$, and using eq.(4), one can parameterize the total rate of crystal nucleation $J$ (containing the contributions from both volume-based and surface-stimulated modes) as a function of both droplet radius $R$ and temperature $T$:

$$J = J(T, R) = \left[ 1 + (1 - (h_\lambda (T)/R)u(T))^3 \right] \left( e^{-\frac{1}{2}(u(T)-1)} W_s (T)/k_B T - 1 \right) \times 10^x(T).$$  \hspace{1cm} (9)

This expression can be expected to more adequately describe the freezing of water droplets in cirrus clouds and thus improve the accuracy of both regional and global climate models.
3.1 Temperature dependence of the ice-air interfacial tension

The $T$-dependence of the parameter $u$ (according to its definition) is determined by the $T$-dependence of $\sigma_{ls}^\lambda$, $\sigma_{sv}^\lambda$, and $\sigma_{lv}^\lambda$. The function $\sigma_{ls}^\lambda(T)$ can be approximated as in ref.15, whereas for $\sigma_{lv}^\lambda(T)$ one can use an analytical fit of experimental data reported in ref.37. Thus, one can determine the ice-air interfacial tension $\sigma_{sv}^\lambda$ of the facet $\lambda$ as a function of temperature,

$$\sigma_{sv}^\lambda(T) = \sigma_{lv}^\lambda(T) + u(T)\sigma_{ls}^\lambda(T). \quad (10)$$

This method for determining the function $\sigma_{sv}^\lambda(T)$ requires the experimental data for ice nucleation rates in large and small droplets, $J_{\text{exp Large}}$ and $J_{\text{exp small}}$, to be for identical experimental conditions, droplets differing only in their size. Otherwise, the method provides only rough estimates for $\sigma_{sv}^\lambda$.

4 Numerical Calculations

To accurately apply the proposed method for determining the dependence of the total ice nucleation rate $J$ in droplets on their radii $R$ and temperature $T$, experimental data used in eq.(8) for ice nucleation rates in large and small droplets, $J_{\text{exp Large}}$ and $J_{\text{exp small}}$, must be for identical experimental conditions, droplets differing only in their size. Since such “ideal” data are not available, for ice nucleation in large droplets we used eq.(4) and assumed $J_{\text{exp Large}} \approx J_v$. For ice nucleation in small droplets, we used experimental data\textsuperscript{38} for droplets of radii $R \approx 0.5, 1.7$, and $2.9 \, \mu m$ at different $T$’s.

Alternatively, if there are two sets of experiments on the freezing of water droplets, one set for droplets of radius $R_1$ and the other for droplets of radius $R_2$, with $J_{R_1}^{\text{exp}}$ and $J_{R_2}^{\text{exp}}$ being the respective ice nucleation rates, an approximation for the function $u(T)$ can be obtained by numerically solving the equation

$$\frac{J_{R_1}^{\text{exp}}}{J_{R_2}^{\text{exp}}} = f(u)|_{T,R_1} f(u)|_{T,R_2}$$
(t experimental temperatures $T$, instead of solving eq.(8). Again, in the ideal case, experiments for both $R_1$ and $R_2$ should be at identical experimental conditions.

Note that the aspect ratio $\kappa$ entering eq.(10) via eqs.(7) and (8), is not a variable quantity. The thermodynamics and kinetics of crystal nucleation constrain the size and shape of the ice nucleus with a unique, “native” aspect ratio $\kappa_\ast$, determined by the conditions that the free energy of formation of a crystal cluster have an extremum (saddle point) for the nucleus and by Wulff’s relations.\textsuperscript{4,16,20–22,28} Although the morphology of tiny ice crystal nuclei in liquid water has not been investigated thoroughly so far, some interesting studies have been reported (see, e.g., ref.39 and ref.4, pp.145-161 and references therein). Equilibrium (hexagonal) ice crystals are most likely to have the shape of a regular hexagonal prism. Using the estimates for the interfacial tensions $\sigma_{ls}^{p}$ and $\sigma_{ls}^{b}$ of the prismatic and basal facets, respectively, of such ice crystals in supercooled liquid water (ref.4, p.160) in Wulff’s relations allow one to obtain their approximate aspect ratio $\kappa \approx 0.8$.

Ice nucleation in supercooled water most likely proceeds via the formation of nuclei of metastable non-hexagonal ice modifications (reportedly cubic\textsuperscript{40} or stacking-disordered\textsuperscript{15,41,42}). However, one can expect that the aspect ratio of such ice nuclei will be also roughly equal to 0.8, because it is determined via the ratio $\sigma_{bs}^{p}/\sigma_{ls}^{p}$ in Wulff’s relations which differs little between these three ice modifications due to relatively small differences between their corresponding interfacial tensions.\textsuperscript{4,15} We have thus assumed $\kappa \approx 0.8$.

In Figure 1 the combined ice nucleation rate $J = J(T, R)$ in supercooled water droplets is plotted as a ratio $J/J_\nu$ vs droplet radius $R$ at various $T$. The nucleation rates $J$ were calculated according eq.(9), with the functions $h_\lambda(T)$ and $W_\ast(T)$ provided by eqs.(7) and (5), respectively. For the functions of temperature $\sigma_{ls}^{p}$, $\rho_\nu(T)$, and $\Delta q(T)$ in eqs.(5)-(7), we have adopted the Koop-Murray approximations.\textsuperscript{35} The latter were also used in numerically solving eq.(8) (with respect to $u$) for the experimental data of Earle et al.\textsuperscript{38} to construct the function $u(T)$, wherefor we obtained the following
quadratic approximation

\[ u = u(T) = -1809.88 + 15.2553T - 0.0321355T^2 \quad (233 \text{ K} < T < 240 \text{ K}). \] (11)

In Fig.1, the solid curve is for \( T = 235 \text{ K} \), dashed curve for \( T = 237 \text{ K} \), dash-dotted curve for \( T = 239 \text{ K} \), and dotted curve for \( T = 239.3 \text{ K} \). As clear, at any fixed \( T \) the ratio \( J/J_v \) is a monotonically decreasing function of \( R \). Starting from large values for smallest \( R \), it sharply decreases with increasing \( R \) and asymptotically approaches 1 as \( R \to \infty \), when \( J \to J_v \). At some droplet radius \( R_v^s = R_v^s(T) \), the curve crosses the horizontal line \( J/J_v = 2 \). In droplets of radius \( R = R_v^s \), the contributions from the surface-stimulated mode and volume-based modes (\( J_v^s \) and \( J_v \), respectively) to the total rate of ice nucleation are equal to each other, \( J_v^s = J_v \), so that \( J = J_v^s + J_v = 2J_v \). Thus, the radius \( R = R_v^s \) determines the crossover radius for the transition of homogeneous ice nucleation in supercooled droplets from being dominated by the volume-based mode (with \( J_v^s < J_v \) in droplets of radii \( R > R_v^s \)) to being dominated by the surface-stimulated mode (with \( J_v^s > J_v \) in droplets of radii \( R < R_v^s \)).

Figure 2 presents the \( T \)-dependence of the crossover radius \( R_v^s \). In the range \( 233 \text{ K} < T < 239.5 \text{ K} \) the function \( R_v^s = R_v^s(T) \) is non-monotonic and non-trivial. One can observe a sharp increase in \( R_v^s \) as \( T \) approaches 239.5 K from left, as well as a local maximum of about 70\( \mu \text{m} \) at \( T \approx 233.5 \text{ K} \). However (as seen in the inset in Fig.2), in the most interesting temperature range (for freezing of atmospheric droplets) \( 234.5 \text{ K} < T < 238.5 \text{ K} \) the crossover radius \( R_v^s \) is in the range from 2\( \mu \text{m} \) to 7\( \mu \text{m} \), attaining its global minimum of about 2\( \mu \text{m} \) for temperatures from 236 K to 237.5 K.

The dependence of the combined homogeneous ice nucleation rate \( J \) in supercooled water droplets (calculated using eq.(9)) on the droplet radius \( R \) and temperature \( T \) is illustrated in Figure 3. The rate \( J \) as a function of \( R \) at constant \( T \) is plotted in Fig.3a (dark solid curve is for \( T = 235 \text{ K} \), dotted for \( T = 236 \text{ K} \), dashed for \( T = 237 \text{ K} \), light solid for \( T = 238 \text{ K} \), and dash-dotted for \( T = 239 \text{ K} \).
At any temperature, $J(T, R) \rightarrow J_v(T)$ as $R \rightarrow \infty$, i.e., in large droplets the contribution from the surface-stimulated mode to $J$ tends to zero. For such (large) droplets, the $T$-dependence of $J(T, R)$ reduces to the $T$-dependence of its contribution from the volume-based mode, $J_v(T)$, given by eq.(4).

These results are further illustrated in Figure 3b, showing $J$ as a function of $T$ for droplets of a given radius $R$; different curves correspond to different $R$’s as indicated in the Figure panel. The lowest curve represents infinitely large droplets, i.e., the function $J(T, \infty) = J_v(T)$. The smaller the droplet, the larger the contribution $J_s^v$ from the surface-stimulated mode to $J$, and it can exceed the contribution $J_v$ from the volume-based mode by two orders of magnitude for $R \lesssim 0.5 \mu$m.

Figure 4 shows the temperature dependence of the ice-air interfacial tension $\sigma_{sv}^\lambda$ of the basal facet $\lambda$ of ice nuclei obtained by using the experimental data for $J_{\text{exp small}}$ for small droplets of radii $R = 1, 1.7, \text{ and } 2.9 \mu$m. The results for $\sigma_{sv}^\lambda$ at each temperature represent the average over three values extracted from each experimental set (for droplets of three different radii). Despite relatively large uncertainties in reported temperatures $T$ and nucleation rates $J_{\text{exp small}}$, one can observe relatively smooth, monotonic, linear-like dependence of $\sigma_{sv}^\lambda$ on $T$, with the interfacial tension $\sigma_{sv}^\lambda$ increasing from about 89 dyn/cm to 91 dyn/cm as the temperature increases from $T = 234.8$ to $T = 236.2$.

### 4.1 Concluding remarks

Thus, we have proposed a relatively simple approximation for the total rate of homogeneous ice nucleation rate in supercooled water droplets as a function of both droplet radius and temperature. It contains the contributions from both the surface-stimulated and volume-based modes of ice nucleation and thus more adequately describes the freezing of supercooled water droplets in cirrus clouds. This approximation can improve the accuracy of both regional and global climate models once implemented therein (in a parameterized form).

The crucial idea of our method is that, even in the surface-stimulated mode, when a crystal
nucleus forms with one of its facets at the droplet surface, it initially emerges (as a subcritical cluster) *homogeneously* in the subsurface layer, not “pseudo-heterogeneously” at the surface. This mode is negligible for large droplets, but becomes increasingly important with decreasing droplet size and is dominant in small droplets. We have proposed a definition of a crossover radius for the transition of homogeneous ice nucleation in droplets from the volume-based mode to the surface-stimulated one and determined its temperature dependence. We have also determined the solid-vapor interfacial tension of the basal facets of ice crystals (assumed to be shaped as hexagonal prisms) using experimental data on ice nucleation rates in small droplets.

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Captions

to Figures 1 to 4 of the manuscript “DEPENDENCE OF HOMOGENEOUS CRYSTAL NUCLEATION IN WATER DROPLETS ON THEIR RADIi AND ITS IMPLICATION FOR MODELING THE FORMATION OF ICE PARTICLES IN CIRRUS CLOUDS.” by Y. S. Djikaev and E. Ruckenstein.

Figure 1. The dependence of the ratio $J(T, R)/J_v(T)$ in supercooled water droplets on the droplet radius $R$ at three different temperatures: 235 K (solid curve), 237 K (dashed curve), 239 K (dash-dotted curve), and 239.3 K (dotted curve).

Figure 2. The temperature dependence of the crossover radius $R_v$ for the transition of ice nucleation in supercooled water droplets from the volume-based mode (at $R > R_v$) to the surface-stimulated mode (at $R < R_v$).

Figure 3. The dependence of the combined ice nucleation rate $J$ in supercooled water droplets on the droplet radius $R$ and temperature $T$. a) $J$ as a function of $R$ at constant $T$; different curves correspond to different temperatures as marked. b) $J$ as a function of $T$ for droplets of given radius $R$; different curves correspond to different droplet radii $R$ as indicated in the Figure panel.

Figure 4. The temperature dependence of the ice-air interfacial tension $\sigma_{\lambda v}^{4v}$ of the basal facet $\lambda$ of ice crystal nuclei obtained by using the experimental data for the homogeneous ice nucleation rates $J_{\text{small}}^{\exp}$ in small supercooled water droplets of radii 1 $\mu$m, 1.7 $\mu$m, and 2.9 $\mu$m.
Figure 1: The dependence of the ratio $J(T, R)/J_o(T)$ in supercooled water droplets on the droplet radius $R$ at three different temperatures: 235 K (solid curve), 237 K (dashed curve), 239 K (dash-dotted curve), and 239.3 K (dotted curve).
Figure 2: The temperature dependence of the crossover radius $R'_c$ for the transition of ice nucleation in supercooled water droplets from the volume-based mode (at $R > R'_c$) to the surface-stimulated mode (at $R < R'_c$).
Figure 3: The dependence of the combined ice nucleation rate $J$ in supercooled water droplets on the droplet radius $R$ and temperature $T$. a) $J$ as a function of $R$ at constant $T$; different curves correspond to different temperatures as marked. b) $J$ as a function of $T$ for droplets of given radius $R$; different curves correspond to different droplet radii $R$ as indicated in the Figure panel.
Figure 4: The temperature dependence of the ice-air interfacial tension $\sigma_{\lambda}^{sv}$ of the basal facet $\lambda$ of ice crystal nuclei obtained by using the experimental data\textsuperscript{38} for the homogeneous ice nucleation rates $J_{\text{exp small}}$ in small supercooled water droplets of radii $1 \, \mu m$, $1.7 \, \mu m$, and $2.9 \, \mu m$. 

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\sigma_{\lambda}^{sv} \text{(dyn/cm)} \quad \text{T (K)} 
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