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A homogeneous freezing nucleation parameterization for cirrus clouds

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A

**HOMOGENEOUS FREEZING NUCLEATION
PARAMETERIZATION FOR CIRRUS CLOUDS**

A Thesis

Presented to

The Faculty of the Department of Meteorology

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Annette L. Walker

December 1995

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ABSTRACT

A Homogeneous Freezing Nucleation Parameterization For Cirrus Clouds

by Annette L. Walker

An ice nucleation scheme based on the physics of the homogeneous freezing nucleation process is developed for mesoscale models. Present ice initiation parameterizations are simple functions of ice saturation and/or temperature, based on heterogeneous nucleation, and valid only for middle tropospheric temperatures. In situ observations and theoretical calculations suggest the dominant mechanism in cirrus cloud ice crystal formation is not heterogeneous nucleation, but homogeneous nucleation of deliquescent sulfate aerosols. This process is strongly dependent on temperature and ice supersaturation. Since mesoscale model time steps can be longer than the length of the entire nucleation process, our parameterization includes a third dependence, the evolution of ice supersaturation. We integrate over the aerosol size distribution and nucleation process for a wide range of temperatures (-30.55 - -90 °C), ice saturations (0.985 - 1.385), and ice saturation tendencies (5.0×10^{-6} - 5.0×10^{-3} s $^{-1}$) to generate a lookup table containing the number of nucleated ice crystals.

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Finally, to my family and friends, I will give each of you a copy of my thesis along with a hand-written dedication.

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Chapter 1

Modelling Cirrus Clouds

1.1 Introduction

The radiative properties of cirrus clouds have important climate implications because of their great areal extent and the frequency of their occurrence. Having been formed by upper-level ridges, jet streams, mid-latitude cyclones, tropical cyclones, or by convective thunderstorms, cirrus clouds can extend horizontally for hundreds and sometimes thousands of kilometers [Liou, 1986; Dowling and Radke, 1990]. Depending upon the season and location, 20% to 50% of the globe can be covered by cirrus clouds [Dowling and Radke, 1990]. Climate studies have shown that cirrus clouds can have a positive or negative net radiative forcing [Cox, 1971; Liou, 1986; Ramanathan and Collins, 1991]. These studies indicated that cirrus cloud height and thickness determine whether the ground will be warmed or cooled in the presence of these clouds as compared to clear sky conditions.

Cirrus cloud radiative properties are intricately linked to the microphysical composition of the cloud, in particular the size, shape, and concentration of the ice crystals [Jensen et al., 1994; Stephens et al., 1990; Kinne and Liou, 1989]. Once the ice crystals

of a cirrus cloud have nucleated, any water vapor in excess of saturation will be rapidly spent in the growth of the crystals; therefore the size of the particles is dependent on how many ice crystals nucleate and compete for the available moisture [Jensen et al., 1994]. Radiatively, small ice particles have larger geometric areas per unit volume than large ice particles; hence, for a given ice water content, small numerous ice particles will reflect more sunlight than larger, less numerous ice particles [Kinne and Liou, 1989].

The lifetime of a cirrus cloud is related to the size and number density of the ice crystals which is important since the radiative impact of long lived clouds is obviously greater than short lived clouds. Tropical cirrus clouds made of numerous small ice crystals tend to persist on the order of days since their fall velocities are much lower than larger less concentrated cirrus uncinus ice crystals which precipitate out of the generating cell within an hour. Since the cirrus cloud ice particle size spectra is determined by ice production rates, the radiative properties of these clouds are indirectly linked to the number of ice crystals nucleated; therefore, to accurately model cirrus clouds and their subsequent impact on climate, one of the most important processes to parameterize is the nucleation of ice crystals.

1.2 Ice Initiation Schemes

In the middle and lower troposphere, ice crystals can form by four heterogeneous nucleation mechanisms: deposition, condensation-freezing, contact, and immersion [Pruppacher and Klett, 1978; Knight, 1979]. All four heterogeneous nucleation processes have an

associated ice nucleus which acts as a surface onto which water molecules can impinge to form aggregates with ice structures. In deposition nucleation, water vapor deposits directly onto the ice nucleus forming an ice lattice which becomes the ice crystal. For condensation-freezing nucleation, an ice nucleus acts as a condensation nucleus upon which water vapor condenses to form a supercooled water droplet. After the droplet has formed, water molecules reorient and attach themselves to the ice nucleus which causes the droplet to freeze. A contact nucleus initiates the ice phase upon collision with a liquid droplet. An immersion nucleus initiates the ice phase from within a supercooled water droplet. This type of ice nucleus becomes immersed in a droplet by colliding with the liquid droplet, then becoming embedded within the drop or by acting as the cloud condensation nucleus which formed the drop.

In regional and mesoscale models, ice nucleation algorithms are relatively simple functions of temperature or ice saturation and temperature. The most common scheme used in these models to determine the ice nuclei (IN) number concentration is Fletcher's approximation [Lin et al., 1990; Meyers et al., 1992; Grell et al., 1993]. Fletcher used measurements of ice nuclei made at temperatures ranging from 0°C to -25°C. Fletcher developed the following equation to determine the number of ice nuclei present at a given temperature

$$n_c = n_0 \exp[\beta(T_0 - T)] \quad (1.1)$$

where n_c is the number concentration of active ice nuclei, T is temperature, n_0 is 10^5 l^{-1} , β is $0.6 \text{ (}^\circ\text{C)}^{-1}$, and T_0 is the melting point of ice. Since the measurements for which Eqn.

1.1 is based were made at water saturation, only two of the four possible heterogeneous nucleation mechanism (deposition and condensation followed by freezing) are included.

Since little or no data is available for the upper troposphere, this nucleation parameterization, which is based on mid-tropospheric temperatures, has been extrapolated to the very low upper tropospheric temperatures (-85°C - -40°C) in which cirrus clouds form. However, problems arise when this approximation is extrapolated to upper tropospheric temperatures. Typically, at -20°C the atmosphere contains one ice nucleus per liter or 10^{-3} ice nuclei per cm^3 , and Fletcher's approximation is in agreement. For

Fig. 1.1: Number of ice nuclei calculated by Fletcher's approximation (Eqn. 1.1) for a temperature range through the depth of the troposphere.

temperatures below -40°C , the background aerosol distribution is $10\text{-}300\text{ cm}^{-3}$; but, Eqn. 1.1 predicts 10^3 cm^{-3} or more IN for this temperature range as seen in Fig. 1.1 [Pruppacher and Klett, 1978]. Clearly, Eqn. 1.1 is not valid at these temperatures.

In an attempt to correct the tendency of the Fletcher ice nuclei formula to overpredict ice crystal concentrations in very cold clouds and to incorporate the dependence on the degree of ice supersaturation, Cotton et al. (1986) combined the Fletcher formula with the Huffman and Vali (1973) equation to obtain the following hybrid equation

$$n_c = n_0 \left[\frac{(S_i - 1)}{S_0 - 1} \right]^b \exp(\beta T_{sup}) \quad (1.2)$$

where n_0 is 10^{-5} l^{-1} , $S_i - 1$ is the fractional ice supersaturation, $S_0 - 1$ is the fractional ice supersaturation at water saturation, b is 4.5, and T_{sup} is the degree of supercooling. Another empirically derived temperature and ice saturation dependent ice nuclei concentration (m^{-3}) parameterization has been developed by Flatau et al. (1989)

$$n_c = 0.956 + 0.12 |T| - (0.316 + 0.036 |T|) (S_i - 1) \quad (1.3)$$

which is valid for $T < -8^{\circ}\text{C}$ and T is in $^{\circ}\text{C}$. In the development of this scheme, Flatau et al. (1989) argued that Fletcher based his equation by “piecing together independent observations and averaging observations from different ice nuclei counters” while their work was based on consistent observations which measured both the temperature and relative humidity dependence.

During contact nucleation, the random collision of an ice nucleus by Brownian diffusion, thermophoresis, or diffusiophoresis with a supercooled droplet initiates the

freezing process. A parameterization which describes each one of these forces and how they lead to ice nucleation has been developed by Young (1974). The essential equation in his approach is the temperature dependent approximation used to calculate the number of active contact nuclei given by

$$n_a = n_{a0}(270.16 - T_c)^{1.3} \quad (1.4)$$

where n_{a0} can be a constant equal to 0.2 cm^{-3} or allowed to vary with height and T_c (K) is the cloud droplet temperature.

The measurement of ice nuclei which contribute to immersion freezing is difficult, and data on this type of ice nuclei are sparse [Knight, 1979; Cotton et al., 1986]. Measurement techniques used to detect these ice nuclei have difficulty in distinguishing these ice nuclei from contact ice nuclei in continuous flow chambers. In methods used to reconstruct the freezing process which formed the ice crystal from the supercooled droplet by observing the ice nucleus within the hydrometeor have not been successful, since ice nuclei which act as condensation-freezing nuclei are hard to separate from ice nuclei which act as immersion freezing nuclei. For modelling purposes, the number of crystals formed by this mechanism is assumed to be contained within Fletcher's approximation and the derivatives of his equation or by the contact freezing nucleation mechanism.

1.3 Dominant Nucleation Mode

Most of the ice nucleation schemes available use heterogeneous nucleation mechanisms for ice crystal initiation. These algorithms are based on empirical studies and are valid for

mid-tropospheric temperatures. In the upper troposphere at temperatures less than -40°C , in situ observations and theoretical calculations [Heymsfield and Sabin, 1989; Sassen and Dodd, 1988; Jensen et al., 1994] suggest the dominant mode of ice nucleation is not heterogeneous nucleation, but homogeneous freezing of sulfate haze particles. Heterogeneous nucleation is less likely to occur in the upper troposphere since most IN originate at the surface and activation of IN in cloud formation in the mid and lower regions of the troposphere would lead to their removal before reaching the upper troposphere. The scarcity of IN in the upper troposphere is also evident in the existence of supercooled droplets (-30°C - -38°C) in wave clouds and at the bases of cirrostratus clouds [Sassen et al., 1985; Heymsfield and Sabin, 1989; Heymsfield and Miloshevich, 1993].

The strongest empirical and theoretical evidence that homogeneous freezing is the mode of nucleation responsible for the formation of ice crystals in cirrus clouds has been presented in a recent paper by Heymsfield and Miloshevich (1995). In their analysis of orographic wave clouds and cirrus clouds sampled in FIRE II, they found that ice nucleation in the orographic water clouds below -34°C could be detected, regardless of the ice nucleating mechanism, by “following simultaneous and abrupt changes in cloud properties: disappearance of liquid water; decrease in relative humidity from near water-saturation to near ice-saturation; increase in mean cloud particle size; decrease in particle concentration; and a temperature effect resulting from the release of latent heat due to the freezing and rapid growth of ice crystals.” The best evidence in their measurements in support of

homogeneous nucleation is the “absence of high concentrations of ice crystals above -33°C in water-supersaturated regions, in contrast to high ice concentrations observed below -35°C [which] indicates the presence of relatively few IN and a relatively insignificant role of heterogeneous ice production.” In addition, Heymsfield and Miloshevich (1995) observed freezing rates to occur at specific temperatures and relative humidities, a result in agreement with homogeneous nucleation theory. They note heterogeneous ice nucleation would be more likely to occur over a broader range of temperatures and relative humidities since the ice nucleating efficiency of IN depends on the microstructure and composition of the IN, which have a wide range of natural variability. Consequently, to accurately parameterize the formation of ice crystals for cirrus cloud modelling, an ice initiation scheme based on our understanding of the physics of homogeneous freezing nucleation is absolutely necessary.

1.4 Statement of Problem and Approach

The goal of this study is to develop an ice nucleation scheme for use in mesoscale and regional models based on the physics of the homogeneous freezing nucleation process. Using classical theory, we derived an equation which diagnoses the number of ice crystals formed by the freezing of deliquescent sulfate aerosols for given temperatures, ice saturations, and cooling rates. The rationale for including the cooling rate comes from detailed cirrus model simulations, which suggest that the number of aerosols that nucleate to form ice crystals is controlled by the availability of water vapor in the surrounding

environment. Thus, as a parcel rises and the temperature decreases, supersaturation with respect to ice will increase. The removal of the available water vapor occurs by the growth of pre-existing ice crystals which formed in the first stages of the nucleation process. Ultimately, the termination of nucleation is regulated by the depletion of water vapor by the ice crystals [Heymsfield and Sabin, 1989; Sassen and Dodd, 1989; Jensen and Toon, 1994].

The nucleation process, from initiation of ice nucleation to depletion of supersaturation by growing ice crystals, occurs on a time-scale of a few minutes; mesoscale model time steps are typically 1-20 minutes. An ice nucleation scheme for a large-scale model requires specification of the number of ice crystals nucleated during a time step Δt as a function of the grid-box state variables such as temperature and saturation. If the model time step is short enough such that the grid-box saturation is not significantly affected by the growth of new ice crystals during the time step, then the cooling rate will not affect the number of ice crystals nucleated. However, if the mesoscale model time step is long enough to allow vapor depletion, a parameterization such as ours must be used to account for this change and the impact it has on the final ice number density.

In Chapter 2, the theory of homogeneous freezing nucleation, the equations necessary to calculate the homogeneous freezing nucleation rate, and the physical quantities needed for those equations are discussed. In addition, homogeneous nucleation theory as applied to the freezing of solution droplets is given. Chapter 3 will describe the development of the homogeneous freezing nucleation parameterization. For a wide range

of vertical velocities (cooling rates), temperatures, and ice saturations, a parcel model is used to investigate the impact the ice saturation tendency has on the number of aerosols which freeze. The results using our parameterization are then compared to the ice crystal number densities calculated by an explicit cloud model [Jensen et al., 1994] for a few select temperatures. The final product of our parameterization is a three dimensional lookup table containing the number of ice crystals nucleated for a range of atmospheric conditions in which cirrus clouds form. Chapter 4 addresses the further development of our homogeneous freezing nucleation parameterization to include the effects of heterogeneous nucleation. This chapter also includes the requirements necessary to use the lookup table and a discussion of implementing our parameterization into a cloud resolving model.

Chapter 2

Homogeneous Nucleation

2.1 Classical Theory

a. Pure Water

The classical theory of homogeneous nucleation provides a method of calculating the freezing rate of pure, supercooled water droplets. Homogeneous freezing of a pure water droplet is strongly dependent upon the temperature of the system, in addition to the droplet volume. Embryos are clusters of water molecules that have joined together by collisions. Classical theory assumes that at any given time, the size distribution of embryos existing within a droplet can be described by a Boltzmann distribution. The onset of droplet freezing begins with the growth of an ice embryo which occurs when water molecules next to the embryo reorient and incorporate themselves into the ice lattice. This process is dependent upon the surface energies of the ice embryo and the surrounding liquid. Depending on the temperature, the embryo itself may only be a few water molecules or a cluster of 100 or more water molecules [Knight, 1979; Pruppacher and Klett, 1978]. Classical homogeneous nucleation theory assumes the ice embryo may be

treated as a sphere with characteristic macroscopic properties of bulk ice such as surface tension and density.

As the ice embryo grows, water molecules diffuse across the ice-water interface. Turnbull and Fischer [1949] showed that the flux of molecules across this phase boundary w_{diff} is given by

$$w_{diff} = \frac{N_c kT}{h} \exp\left(-\frac{\Delta F^+}{kT}\right) \quad (2.1)$$

where N_c is the number of water molecules in contact with a unit ice surface area, k is Boltzmann's constant, T is temperature, h is Planck's constant, and ΔF^+ is the phase change activation energy. Once an embryo has reached a critical size, the addition of another water molecule will decrease the energy barrier to nucleation, and it will grow unabated producing a macroscopic phase change (i.e. the liquid droplet freezes and becomes an ice crystal) at which point the embryo is referred to as a germ. Classical theory has shown the temperature required for the embryos to form and become critical germs inside pure water droplets is approximately -40°C .

The homogeneous freezing nucleation rate for pure, bulk water is the number of critical ice germs formed per cubic centimeter of water per second. Assuming steady state conditions and using Eqn. 2.1, Pruppacher and Klett (1978) derived the homogeneous freezing nucleation rate J ($\text{cm}^{-3} \text{s}^{-1}$) as

$$J = 2N_c \left(\frac{\rho_w kT}{\rho_i h} \right) \left(\frac{\sigma}{kT} \right)^{1/2} \exp\left[-\frac{\Delta F^+ + \Delta F_s}{kT}\right] \quad (2.2)$$

where ρ_w and ρ_i are the water and ice densities, respectively, and $\sigma_{i/w}$ is the surface energy between ice and supercooled water. The work against surface forces required to form a critical ice germ ΔF_g is given by

$$\Delta F_g = \frac{4}{3} \pi \sigma_{i/w} a_g^2 \quad (2.3)$$

and the germ radius a_g can be expressed as

$$a_g = \frac{2M_w \sigma_{i/w}}{L_m \rho_i \ln(T_0 / T_e)} \quad (2.4)$$

where M_w is the molecular weight of water, L_m is the latent heat of melting, T_0 is the melting temperature of ice (273.16 K), and T_e is the ambient temperature. The overbars denote that the values of the ice density and latent heat are averaged from T_0 to T_e . The magnitude of the pre-exponential factor in Eqn. 2.2 is on the order of $10^{35} \text{ cm}^{-3} \text{ s}^{-1}$ and varies slowly for a given temperature; therefore, the exponential term dominates variations in the calculated freezing rate.

The phase change activation energy is one of the most poorly known physical quantities in the nucleation rate equation. ΔF^+ has been estimated from measurements of the self diffusion coefficient and the viscosity of water at temperatures greater than -30°C [Pruppacher and Klett, 1978]. For the temperature range $-30^\circ\text{C} \leq T \leq 0^\circ\text{C}$, their fit to laboratory data for ΔF^+ is

$$\Delta F^+ = 5.5 \exp(-1.330 \times 10^{-2} T + 2.74 \times 10^{-4} T^2 + 1.085 \times 10^{-6} T^3). \quad (2.5)$$

where ΔF^+ is in erg cm^{-2} and T is in $^\circ\text{C}$.

Another physical quantity that is difficult to determine by experimental techniques is $\sigma_{i/w}$. All laboratory measurements have shown, that the surface tension between ice and supercooled water decreases with decreasing temperature. The following relation describes the variation of $\sigma_{i/w}$ with temperature based on several laboratory measurements [see Pruppacher and Klett, 1978]:

$$\sigma_{i/w} = 28.5 + 0.25T, \quad (2.6)$$

where $\sigma_{i/w}$ is in erg cm^{-2} and T is in $^{\circ}\text{C}$.

b. Solution Droplets

Ice crystal nucleation can occur by the homogeneous freezing of solution droplets. In subsaturated conditions, aerosols can take on water or deliquesce forming solution droplets in stable equilibrium with the ambient water vapor. As the relative humidity increases, the aerosols take on more water, and the solution concentration of the droplets decreases. Freezing nucleation occurs when the solution becomes sufficiently dilute. Even though the aerosols are not pure supercooled water droplets, the rate at which they freeze can be described by homogeneous nucleation theory since ice nuclei are not present to initiate ice crystal production, and germ formation within the solution occurs by water molecules forming ice-like clusters.

The classical homogeneous freezing nucleation theory can be modified to describe the freezing of a solution droplet. The presence of the solute acts to depress the freezing

point of the aerosol and changes the thermodynamic equilibrium between the ice embryo, liquid, and vapor resulting in a modified germ radius [Pruppacher and Klett, 1978; equation (6-43)]

$$a_g = \frac{2M_w \sigma_{i/w}}{L_m \rho_i \ln(T_0 / T_e) + \rho_i RT \ln a_w} \quad (2.7)$$

where R is the universal gas constant, T is the solution drop temperature, and a_w is the activity of water in the solution. Water activity is defined as the ratio of the water vapor pressure over the solution to the vapor pressure over pure water. Since the solution vapor pressure is lower than the vapor pressure over water, a_w is always less than 1, the solution term in the denominator is always negative, and a_g is always larger for solution droplets. Hence, as a solution droplet grows, the concentration decreases, a_w increases causing a decrease in a_g and ΔF_g (Eqn. 2.3) which increases J .

2.2 Calculating Homogeneous Freezing Nucleation Rates

In the development of an ice initiation scheme for cirrus clouds, we used the preceding modified classical theory to calculate the freezing rates for deliquescent aerosols. To use this theory, ΔF^+ values for upper tropospheric temperatures ($T < -30^\circ\text{C}$) must first be approximated. To accomplish this, we have fit the calculated nucleation rates to laboratory measurements of droplet freezing nucleation rates [Hagen et al., 1981; DeMott and Rogers, 1990]. Using the nucleation rate expression given in Eqn. 2.2 and the equation for the surface tension given in Eqn. 2.6, we adjusted the phase change activation

energy until the resulting nucleation rate agreed well with the two laboratory data sets. The following fit describes the phase change activation energy for $-90^{\circ}\text{C} \leq T \leq -30^{\circ}\text{C}$,

$$\Delta F^+ = 1.29 \times 10^{-12} \exp[0.05(T + 36)]. \quad (2.8)$$

Fig. 2.1 shows the calculated homogeneous nucleation rates versus temperature using Eqn. 2.8 as compared to the two cloud chamber experiments. The laboratory nucleation rates are valid for temperatures ranging from -34°C to -45°C . Also plotted in the same graph are the freezing rates calculated by DeMott et al. (1994). DeMott et al. (1994) also used the homogeneous nucleation rate expression given by Eqn. 2.2, but instead of adjusting the phase change activation energy as we have chosen to do, they used ΔF^+ values estimated from viscosity measurements given by Eqn. 2.5 and fit the nucleation rates to the same set of laboratory data by adjusting σ_{iw} . The results from a cirrus cloud model which uses classical homogeneous nucleation theory are also presented in Fig. 2.1 [Heymsfield and Sabin, 1989].

The important feature to note in Fig. 2.1 is the difference between the three nucleation parameterizations upon extrapolation to the temperature range of interest (-85°C - -40°C) for cirrus generation. Even though pure water droplets do not exist at temperatures of -45°C and below, nucleation rates were calculated for this temperature range in order to find phase change activation energy values (i.e. Eqn. 2.8) which are necessary to calculate the freezing of solution droplets. Within the range of observed freezing nucleation rates (-45°C to -35°C), the three classical theory calculations generally agree

Fig. 2.1: Homogeneous freezing nucleation rates for pure water are plotted versus temperature. The solid, dashed, and dotted curves are the results calculated by this work, Heymsfield and Sabin (1989), and DeMott et al. (1994), respectively. Observed nucleation rates are indicated by points, and error bars were measured by Hagen et al. (1981) and DeMott and Rogers (1990).

with the observed values. Below -45°C , the extrapolation and fitting of physical parameters used to calculate freezing rates leads to the large differences between the theoretical calculations. Without laboratory measurements for nucleation rates below -45°C , the accuracy of the predicted theoretical values had been in question. In a recent study investigating the freezing point of sulfuric acid solutions at stratospheric temperatures, Bertram et al. (1995) have measured homogeneous nucleation rates of

dilute solutions down to -90°C . His measurements show that the behavior of the extrapolated theoretical freezing rates for pure water droplets is correct for low tropospheric temperatures even though many assumptions and approximations are made using classical theory to obtain these values.

In calculating the germ radius (Eqn. 2.7), we follow classical theory and assume T , the temperature of the solution, is equal to the ambient temperature, T_e . DeMott et al. (1994) argue that this assumption is incorrect and an additional correction factor is required to treat solution effects not included in the classical theory. Instead, they use “an effective temperature” which accounts for a slight increase in solution temperature due to nonideal ionic interactions between the solute and condensed water. However, the original experiments used to derive the effective temperature correction involved heterogeneous freezing of aerosols containing involatile components [Pruppacher and Klett, 1978]; hence, we feel it is inappropriate to apply this correction to calculations of homogeneous freezing. Fig. 2.2 shows the fraction F of aerosols frozen after 1 second versus water super-saturation based on our calculations and on those of DeMott et al. (1994). The use of the effective temperature has a large impact on the calculated freezing rates. Essentially, the water saturation required for homogeneous freezing predicted by DeMott et al. (1994) is about 15% larger than that predicted by our calculations.

Fig. 2.2: The log of the fraction F of aerosols frozen after 1 second at -50°C is plotted versus the saturation with respect to liquid water S for sulfate aerosols with sulfate masses ranging from 10^{-15}g to 10^{-12}g , decreasing in mass. The solid curves correspond to the classical theory calculations for solution drops, and the dashed curves are from DeMott et al. (1994) who included the solution effects on droplet temperature.

2.3 Aerosol Composition

Our current understanding of aerosol composition in the free troposphere is limited. In previous studies on cirrus cloud formation, the swelling and subsequent freezing of ammonium sulfate aerosols to form ice crystals has been considered. However, we have chosen to use sulfuric acid aerosols for the following reasons: In a recent study, Heymsfield and Miloshevich (1995) investigate the freezing of sulfuric acid solution

droplets to produce ice particles. In their analysis of the composition of solution droplets sampled in orographic wave clouds, they suggest that a component of the background aerosol distribution which acted as condensation nuclei for the cirrus clouds was not composed of ammonium sulfate. Further evidence that sulfuric acid particles compose the upper tropospheric background aerosol distribution is given by Goodman (personal communication) who suggests these aerosols are ammoniated only after in situ sampling and during laboratory analysis. The importance of the sulfate composition, and subsequent impact on ice nucleation, is the relative humidity required to deliquesce either sulfate aerosol. Ammonium sulfate will not take on water until the relative humidity with respect to water is greater than 80% [Tang et al., 1978], corresponding to an ice supersaturation of about 48% at -65°C ; i.e., very high ice supersaturation are required to deliquesce ammonium sulfate aerosols. In comparison, sulfuric acid aerosols are always in equilibrium with the water vapor; and therefore form solution drops of varying concentrations for any temperature and saturation, even for the cold upper tropospheric temperatures. Another advantage to the use of sulfuric acid is that the activities of water in sulfuric acid solution of varying concentration have been measured by Gmitro and Vermeulen (1964) for temperatures down to -90°C . These activities are used in our calculations of the critical germ radii. Measurements for water activities in ammonium sulfate solutions are only available for room temperatures.

In our calculations, we assume the deliquesced aerosols are composed of pure binary sulfuric solutions, $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$. It is likely the aerosols in the upper troposphere are

sometimes multicomponent solutions, containing electrolytes such as ammonium sulfate, sulfuric acid, and nitric acid. Recent laboratory studies focused on processes in the polar stratosphere suggests that the relative compositions of sulfuric acid and nitric acid in ternary solution aerosols can dramatically affect freezing nucleation rates [Molina et al., 1993]. Our current understanding of aerosol composition in the free troposphere is limited; hence, we have not included ternary solution effects in the ice nucleation parameterization. We note that the variations in aerosol composition are potentially important for ice nucleation in cirrus cloud formation.

Chapter 3

Parameterization

3.1 Introduction

Homogeneous freezing nucleation will be initiated with the increase in ice saturation above unity accompanied by growth and dilution of the deliquescent aerosols. Given the probability of existence of ice embryos, the largest aerosols freeze first. If supersaturated conditions persist, smaller aerosols will eventually freeze. Homogeneous nucleation theory provides equations to calculate the rate of ice crystal production given the aerosol size distribution, temperature, and ice saturation. Detailed cirrus model simulations have shown that nucleation terminates when the growth of the newly nucleated ice crystals and the pre-existing ice crystals (the aerosols which were the first to freeze) have depleted the available vapor [Heymsfield and Sabin, 1989; Sassen and Dodd, 1989; Jensen and Toon, 1994]. From initiation of ice nucleation to depletion of supersaturation by growing crystals, the entire nucleation process occurs on a time scale of a few minutes.

An ice nucleation scheme for a large-scale model requires specification of the number of ice crystals nucleated during a time step Δt as a function of the grid-box state

variables such as temperature and saturation. Synoptic mesoscale model time steps are typically 1-20 minutes; hence, the impact of vapor depletion during the time step by nucleation of new ice crystals will be important in some cases. If the model time step is short enough such that the grid-box saturation is not significantly affected by the growth of new ice crystals during the time step, then a parameterization based on temperature and saturation alone is appropriate. However, if the newly nucleated ice crystals impact the grid-box saturation by depleting available water vapor during the time step, then the evolution of ice saturation must be included in an ice nucleation parameterization or the number of ice crystals nucleated will be overestimated.

In the development of our ice initiation scheme, we follow the approach taken by DeMott et al. (1994) who developed an ice nucleation parameterization based on the classical theory of homogeneous freezing nucleation. The net rate of ice crystal production for a particular temperature and saturation can be expressed as

$$\frac{dN_i}{dt} = \int_0^{\infty} J(r, s_i, T) N_{CN}(r) dr \quad (3.1)$$

where J is the homogeneous freezing nucleation rate (s^{-1}) at ice supersaturation s_i , r is the aerosol radius, and $N_{CN}(r)$ is the sulfate aerosol size distribution. This expression differs from Eqn. 2.2 in that it is the nucleation rate for a population of aerosols of varying sizes. With the assumption that saturation and temperature are not affected by the new ice crystals nucleated during a time step, DeMott et al. (1994) derived the following expression for the number of ice crystals which nucleate in a time step Δt :

$$N_i = \int_0^{\infty} (1 - e^{-J(r,s_i,T)V(r)\Delta t}) N_{CN}(r) dr. \quad (3.2)$$

where $V(r)$ is the volume of the solution droplet. In the development of our parameterization, we modify their approach by including the time rate of change in ice saturation.

3.2 Development of the Ice Nucleation Scheme

a. Size Distribution and Equilibrium Radii

For our nucleation parameterization, the aerosol size distribution upon which water condenses to form solution droplets was taken from measurements made over Japan at 8-11 km during the Global Backscatter Experiment (GLOBE) shown in Fig. 3.1. This distribution appears to be typical of the upper troposphere background aerosol [Pueschel et al., 1994]. However, some measurements taken during the GLOBE experiment showed a marked variability in number densities for aerosols with radii measuring less than 0.3 μm . The background aerosol size distribution can be described by a lognormal function where the total number of aerosols is 300 cm^{-3} , the maxima of the size distribution occurs at $r_0 = 0.02 \mu\text{m}$, and the standard deviation is 2.3. We truncated the size distribution such that aerosols with radii larger than 1 μm were not included.

The deliquescence of the sulfuric acid aerosols in equilibrium with the ambient water vapor and the growth of aqueous solution drops in ice sub/supersaturated

Fig. 3.1: Lognormal aerosol size distribution based on measurements taken from the Global Backscatter Experiment (+ : Ames wire impactor; Δ : active scattering spectrometer (Pueschel et al., 1994)).

conditions is described by the following form of Köhler's equation [Pruppacher and Klett, 1978; Eqn. 6-26b]

$$\ln S = \frac{2M_w \sigma_{s/a}}{RT \rho_w a} - \frac{v \Phi_s m_s M_w / M_s}{(4\pi a^3 \rho_s / 3) - m_s} \quad (3.3)$$

where S is the saturation ratio with respect to water, M_w is the molecular weight of water, $\sigma_{s/a}$ is the surface tension of the solution against the air, a is the drop radius, v is the number of ions which the salt dissociates into, Φ_s is the osmotic coefficient for aqueous

solution, m_s is the mass of solute, M_s is the molecular weight of solute, and ρ_s is the solute density. Solving Eqn. 3.3 with an iterative technique, we calculated the equilibrium radii for the deliquesced aerosols for various temperatures, water vapor saturations, and initial aerosol radii.

b. Parcel Model

The essence of our nucleation parameterization is the consideration of the time rate of change in the ice saturation during the nucleation process. Using some simple considerations posed by Pruppacher and Klett (1978) on the equilibrium behavior of ice particles, we determined that the variation in ice supersaturation is controlled by the growth of existing ice crystals and the cooling rate of a parcel:

$$\frac{ds_i}{dt} = -\frac{A\rho_i 4\pi r_i^2 g_o N_i}{M_w} - \frac{ds_i}{dT} \frac{dT}{dt} \quad (3.4)$$

where A is Avogadro's number, r_i is the ice crystal radius (assuming a monodispersed crystal size distribution), and g_o is the growth kernel defined in Eqn. 3.8 [Toon et al., 1989]. In the derivation of Eqn. 3.4, we assumed zero flux of water vapor into the parcel. Early in the nucleation process (see Fig. 3.2), few ice crystals are present, so the second term on the right hand side of Eqn. 3.4 dominates the change in ice supersaturation, and the ice supersaturation increases (represented by the thin solid line in the figure) as the temperature decreases. When enough ice crystals nucleate, the first term on the right hand side of Eqn. 3.4 dominates and the saturation tendency becomes negative. Shortly

afterwards, nucleation terminates, and in Fig. 3.2, this is shown by the leveling off of thick solid curve. By integrating Eqn. 3.1 and Eqn. 3.4, the number of ice crystals nucleated for evolving ice supersaturation conditions can be calculated. By integrating through the entire nucleation process, a maximum saturation s_p and ice number density N_p can be found for any final temperature and cooling rate. By integrating through the entire nucleation process, a maximum saturation s_p and ice number density N_p can be found for any final temperature and cooling rate.

Fig. 3.2: A simplified example of the behavior of the ice supersaturation S_i and the ice number density N_i over time during the nucleation process in a cooling parcel. The solid curves (thin: ice supersaturation; thick: ice number density) represent tendencies which include the depletion of water vapor during the nucleation process. The dashed curves are tendencies (thin: ice supersaturation; thick: ice number density) which do not include the depletion of water vapor during the nucleation process. The peak ice supersaturation and ice number density found by integrating Eqn. 3.1 and 3.4 are given by s_p and N_p , respectively. The predicted large-scale model peak ice supersaturation s_m and ice number density N_m , are indicated.

The basic requirement for a large-scale model ice nucleation parameterization is to calculate the number of ice crystals nucleated as a function of the grid-box temperature, saturation, and cooling rate. If the grid-box saturation predicted by the model is below s_p corresponding to the model temperature and cooling rate, then the vapor will not be significantly depleted and Eqn. 3.2 should give an accurate estimate of the number of ice crystals generated. However, depending on the numerical stability scheme and hierarchy of physical processes calculated within the large-scale model, calculated ice supersaturations can exceed the limiting peak supersaturation, s_p . In Fig. 3.2, the thin dashed line shows how the predicted large-scale model ice supersaturation steadily increases over time. If the model saturation s_m is larger than $(s_p(T, dT/dt))$, then Eqn. 3.2 would overestimate the number of ice crystals nucleated, and is shown in Fig. 3.2 as N_m . The actual number of ice crystals nucleated is equal to the peak ice number density found by integrating Eqn. 3.1 and Eqn. 3.4. This is shown in the figure as N_p .

To calculate N_p , we integrate Eqn. 3.1 and Eqn. 3.4 until N_i reaches a maximum and the ice supersaturation is decreasing due to vapor depletion by growing ice crystals. Equation 3.4 can be rewritten as

$$\frac{ds_i}{dt} = -\frac{Ap_i 4\pi G_0 r_g N_i}{M_w} - S_i \quad (3.5)$$

where

$$r_g \equiv \frac{1}{N_i} \int_0^\infty \left(\frac{dN_i}{dr} \right) r dr. \quad (3.6)$$

Since the growth kernel, g_0 , is inversely proportional to r , we have substituted $G_0 = g_0 r$ to remove the particle size dependence from the growth kernel and include it in the effective radius of an ice crystal r_g . S_i is the rate of change of s_i at the beginning of the time step (i.e. before any *new* ice crystals have nucleated). S_i includes both the increase in saturation due to cooling and changes in saturation due to growth or sublimation of pre-existing ice crystals. Two processes can change r_g : First, existing ice crystals will grow by deposition of vapor. The growth rate due to this process is given by

$$\frac{dr_g}{dt} = g_0 S_i n_{vap,i} \quad (3.7)$$

where

$$g_0 = \frac{DF_v M_w}{r_i \rho_i A} \quad (3.8)$$

In the above expression $n_{vap,i}$ is the saturation vapor density over ice. The growth kernel includes diffusional effects D and corrects for ventilation around the particle F_v . For more information on the growth kernel, the reader is referred to Toon et al. (1989). Second, nucleation of new ice crystals due to freezing of the aerosols will decrease the effective radius. In our numerical scheme, we first calculate the change in N_i due to nucleation of new ice crystals. Then we adjust r_g with

$$(r_g)_{\Delta t+1} = \frac{N_i r_g + \Delta N_i r_{new}}{N_i + \Delta N_i} \quad (3.9)$$

where r_{new} is the radius of the new ice crystals nucleated in the current time step. Second, r_g is increased due to deposition growth according to Eqn. 3.7.

c. Comparison with an Explicit Cloud Model

In our development of the simple parcel model described above, many assumptions and simplifications have been made. An exact calculation of the nucleation process and the dynamical modification of the ice supersaturation requires the use of a detailed cloud microphysics model which is able to simulate the evolution of the aerosol, solution droplet, and ice crystal size distributions and the water vapor budget. To compare and to validate our parcel model, we compared our results with those of a one-dimensional explicit cloud model by Jensen et al. (1994). Three distinct aerosol types are treated in this model: condensation nuclei, solution drops, and ice crystals. Each particle type is divided into 40 size bins with equivalent volume radii ranging from 0.01 to 1000.0 μm . The volume of a particular size bin i is 2.331 times that in size bin $i-1$. Hence, the first bin has the finest radius resolution. A continuity equation for each size bin and each aerosol type is solved at each time step. Water vapor is treated as a fully interactive element in the model, and the water vapor continuity equation is also solved at each time step. Microphysical processes included in the model are nucleation, condensation, deposition, evaporation, sublimation, coagulation, sedimentation, advection, and diffusion. The model time step is variable since during rapid nucleation Δt must be smaller than 1 second to maintain stability, and during periods without nucleation or ice crystal growth, it can be set to relatively large values. For a more detailed discussion of the numerical algorithms

and analytic expressions of the microphysics, the reader is referred to Jensen and et al. (1994).

The results from our approximate calculation and from the size-resolving cloud model [Jensen et al., 1994] are shown in Figs. 3.3 and 3.4. Both figures show the time evolution of ice crystal number density and saturation for a cooling rate of 100 K/day, corresponding to an updraft velocity of about 20 cm s^{-1} . A vertical velocity that is about three times larger than typical synoptic scale lifting. Figs. 3.3 and 3.4 had initial starting temperatures of -47°C and -88°C respectively, and with no pre-existing ice. The comparisons were made at -47°C and -88°C . These temperatures were chosen because the warmer example reflects a case of ice formation for cirrus clouds during winter in the mid-latitudes and the colder example corresponds to cirrus that form in situ near the tropopause in the tropics. These temperatures correspond to the 9.1 and 16.9 km vertical levels of the explicit cloud model.

Figs. 3.3 and 3.4 show the variation in ice supersaturation and the ice number density versus time over the entire nucleation process. As previously stated, the increase in ice supersaturation depends on the parcel cooling rate and the depletion of the available water vapor by the growth of the existing ice crystals. Both Figs. 3.3 and 3.4 show how the ice supersaturation reaches a peak s_p after which ice crystal nucleation quickly terminates and the number of ice crystals reaches a maximum value N_p . For a mesoscale model time step of 10 minutes, the ice saturation tendency would continue to increase along the slope as indicated during the first four minutes in Fig. 3.3 and the first two

Fig. 3.3: The supersaturation with respect to ice S_i and the ice number density N_i are plotted versus time for a parcel-model nucleation simulation at -47°C . The solid curves are results from a model simulation, and the dashed curves correspond to our simplified model of the nucleation process. The peak saturation s_p and ice density N_p are indicated.

minutes in Fig. 3.4. At the end of the 10 minute time step, if the depletion of vapor by the existing ice crystals is not accounted for and using the grid-box state variables (T, S_i) , the end result will be an overestimate of the number of ice crystals nucleated during that time interval. Finally, both Figs. (3.3) and (3.4) demonstrate that the time-evolution of ice saturation and the final ice number density predicted by the simple box model agree well with the result from the explicit cloud model even though several assumptions and

simplifications were made in the development of the parcel model and the microphysics contained within it.

Fig. 3.4: The supersaturation with respect to ice and the ice number density are plotted versus time for a parcel-model nucleation simulation at -88°C . The solid curves are results from a model simulation, and the dashed curves correspond to our simplified model of the nucleation process.

The number of ice crystals nucleated for a one minute time step is plotted versus ice saturation for various temperatures in Fig. 3.5. The solid curves are based on Eqn. 3.2 (no vapor depletion by new crystals). The dashed curves show the results of including the detailed evolution of saturation as ice crystals are nucleated. We have developed our parameterization to be valid over a wide range of temperatures (-30.55°C - -90°C), ice

Fig. 3.5: The number of ice crystals nucleated in one minute is plotted versus saturation with respect to ice and various temperatures. The solid curves were generated by neglecting depletion of vapor during the nucleation process (i.e. using Eqn. 3.2). The dashed curves correspond to calculations for which the number of ice crystals was limited by depletion of vapor. For each temperature, a peak saturation and ice number density exists. When the large-scale model predicts a saturation larger than this peak value, the number of ice crystals nucleated is limited to the peak ice number density.

saturation (0.985 - 1.385), and ice saturation tendencies ($5.0 \times 10^{-6} \text{ s}^{-1}$ - $5.0 \times 10^{-3} \text{ s}^{-1}$).

These conditions correspond to mid-latitude and tropical environments in which cirrus clouds form. The ice saturation tendencies correspond to vertical velocities ranging from large-scale synoptic lifting (5 cm s^{-1}) and to wave cloud motions (2 m s^{-1}). As Fig. 3.5 shows, the nucleation cutoff values (s_p and N_p) increase with increasing saturation

tendency. If the saturation is increasing relatively slowly, then few ice crystals can nucleate before vapor depletion terminates nucleation. In the case of large increases in ice saturation with time, high number densities result as both the large and the small aerosols nucleate. The calculated number densities presented in Fig. 3.5 agree well with measured peak number densities from in situ measurements of cirrus clouds, mountain wave clouds, and tropical cirrus anvils [Heymsfield et al., 1990; Heymsfield and Miloshevich, 1995; Knollenberg et al., 1993]. Fig. 3.5 also shows that with decreasing temperatures, the nucleation of aerosols occurs at lower ice supersaturation values.

3.3 Lookup Table

As discussed above, for each temperature, ice saturation, and ice saturation tendency, we calculate a peak saturation and peak ice crystal number density. If the saturation predicted by the large-scale model is larger than that peak saturation, we limit the number of ice crystals nucleated to the corresponding N_p and write this value to a lookup table; if this condition is not satisfied, then the number of ice crystals nucleated using Eqn. 3.2 is written in the lookup table. For the temperature, ice saturation, and ice saturation tendency ranges, we chose the respective incremental resolutions: 0.5°C, 0.005, and 0.81 s⁻¹, corresponding to 597,861 possible atmospheric scenarios in which cirrus clouds could form.

The advantage of using our parameterization is two-fold. First, to run the explicit cloud model [Jensen et al., 1994] for each of the 597,861 cases would be computationally

prohibitive. Second, our ice nucleation scheme (which parameterizes all the explicit microphysics involved in the nucleation process) requires no additional calculations by the mesoscale model in which it is implemented. The calculated grid-box temperature, ice saturation, and ice saturation tendency are sent to the lookup table, which can be included in the model code as a subroutine, and the number of ice crystals nucleated for these conditions will be passed back to the main program. The end result of our parameterization is a (121 X 81 X 61) dimensioned array containing the number of ice crystals nucleated for a range of temperatures, ice saturations, and ice saturation tendencies.

Chapter 4

Conclusion

4.1 Heterogeneous Nucleation

The calculations presented here assume that the dominant ice nucleation mechanism is homogeneous nucleation. The impact on the number of ice crystals nucleated in the presence of condensation-freezing, deposition, contact, or immersion nuclei was not considered. If these ice nuclei have not been removed by cloud formation processes lower in the troposphere and have been transported to the upper troposphere or are injected at these levels by the exhaust of jet aircraft, they can either increase or decrease the total ice number density. Depending on the available number of ice nuclei, for large vertical motions which lead to high ice saturations and ice saturation tendencies, homogeneous freezing of deliquescent aerosols will occur, in addition to those ice crystals nucleated by heterogeneous mechanisms. For large scale synoptic lift where the vertical velocities are small and low ice saturations and ice saturation tendencies are produced, the presence of condensation-freezing and deposition nuclei will decrease the number of ice crystals formed by homogeneous freezing. The heterogeneous nuclei will act as a sink for the

available water vapor and will lower the peak ice supersaturation. The background sulfate aerosols are therefore prevented from diluting and freezing. In the further development of our parameterization, the effects of heterogeneous nucleation on the ice number density will be addressed.

4.2 Application of Parameterization

a. Ice Supersaturation

Realistic estimates of ice supersaturations and their tendencies at cloud-motion scales are required by our nucleation parameterization. By design, regional and mesoscale models are driven by synoptic scale motions and resolve weather phenomena on a horizontal grid ranging in size from 20 to 70 km. Average values for vertical velocity, temperature, and saturation are used over one grid-box. The cloud-forming dynamics, e.g., updrafts and downdrafts that cool and heat parcels of air creating super- and subsaturated areas, necessary to drive our parameterization occur on scales too small for these models to resolve. For example, if the atmosphere is saturated at -35°C to -45°C , a cooling of 2°C to 3°C is required to raise the ice saturation by 35% or to 1.35. Assuming a moist adiabatic lapse rate, for this cooling to occur the parcel must be vertically displaced approximately half a kilometer with speeds of 130 to 85 cm s^{-1} . By comparison at the resolution of mesoscale models, vertical motions are on the order of a few tens of centimeters per second. Under these conditions, cirrus clouds will still be simulated in mesoscale models, but their formation will be delayed until sufficient cooling and ice supersaturations can occur. Thus,

there is a mismatch between the dynamics produced by mesoscale models and those required by our microphysical scheme. An approach to overcome this problem is to incorporate a probability distribution function of vertical velocities into the mesoscale models to allow for finer resolution of the grid-box state variables and the ice saturation tendency.

b. Ice Crystal Number Prediction Equation

For each mesoscale model time step, our parameterization gives the number of newly nucleated ice crystals for a given temperature, ice saturation, and saturation tendency. Hence, to use our ice scheme an ice crystals number prediction equation is required to separate the newly nucleated ice crystals from those ice crystals formed in previous time steps. Having knowledge of the number of ice crystals present in each stage of a model simulation is essential for the microphysical, radiative, and mass transport calculations for cirrus clouds. Presently, mesoscale models do not include an ice crystal number prediction equation in their cloud microphysics subroutines; therefore, the absence of this equation needs to be addressed.

c. Cloud Resolving Models

Large eddy simulation (LES) models or cloud resolving models are able to resolve cloud scale motions; hence, these models could generate ice supersaturations necessary to drive our parameterization. The physical processes included in these models cover a wide range

of scales: from hundredths of a micron for nucleation to tens of kilometers for turbulence and dynamics. These three dimensional models have been applied to studies of liquid phase convective clouds and severe storms [Clark, 1979; Kogan, 1991]. Although LES models are used to study mix-phase clouds that contain both supercooled water droplets and ice crystals, the cloud microphysical parameterizations employed in these models are unrealistic since they do not consider the role of ice crystals. These models have the capability of resolving ice supersaturations on the time scales and with the cloud motions required to drive our parameterization. LES model time steps are much smaller than those of mesoscale models; therefore, for these models the impact of vapor depletion during the evolution of ice initiation would be inconsequential. However, these models offer the opportunity to test our parameterization for cirrus cloud case studies.

Appendix A

List of Symbols

a	Drop radius
A	Avogadro's number
a_g	Critical ice germ radius
a_w	Activity of water in the solution
b	Constant in ice nuclei equations
D	Diffusional effects during growth of g_o
ΔF^+	Phase change activation energy
ΔF_g	The work against surface forces required to form a critical ice germ
F_v	Ventilation correction
g_o	Growth kernel
h	Planck's constant
J	Homogeneous freezing nucleation rate

k	Boltzmann's constant
L_m	Latent heat of melting
m_s	Mass of solute
M_s	Molecular weight of solute
M_w	Molecular weight of water
n_0	Constant in ice nuclei equations
n_a	Number of active contact nuclei
n_{a0}	Constant in ice nuclei equation
n_c	Number concentration of ice nuclei
$n_{vap,i}$	Saturation vapor density over ice.
N_c	Number of water molecules in contact with a unit ice surface area
$N_{CM}(r)$	Sulfate aerosol size distribution
N_m	Maximum (peak) ice crystal number density predicted by large-scale model
N_p	Maximum (peak) ice crystal number density
r	Aerosol radius
r_0	Maxima of the sulfate aerosol size distribution
r_g	Effective radius
r_i	Ice crystal radius
r_{new}	Radius of the new ice crystals nucleated in current time step
R	Universal gas constant
s_i	Ice supersaturation

s_m	Maximum (peak) ice saturation predicted by large-scale model
s_p	Maximum (peak) ice saturation
S	Water supersaturation ratio
$S_0 - 1$	Fractional ice supersaturation at water saturation
S_i	Ice supersaturation
$S_i - 1$	Fractional ice supersaturation
S_t	Rate of change of s_i at the beginning of the time step
t	time
Δt	Model time step
T	Temperature or solution drop temperature
T_0	Melting point of ice
T_c	Cloud droplet temperature
T_e	Ambient temperature
T_{sup}	Degree of supercooling
β	Constant in ice nuclei equation
v	Number of ions which the salt dissociates into
ρ_i	Ice density
ρ_s	Solute density
ρ_w	Water density
σ_{iw}	Surface energy (tension) between ice and supercooled water

σ_{sa} Surface tension of the solution against the air

Φ_s Osmotic coefficient for aqueous solution

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