Parameterization of cirrus cloud formation in large-scale models: Homogeneous nucleation

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This work presents a new physically based parameterization of cirrus cloud formation for use in large-scale models which is robust, computationally efficient, and links chemical effects (e.g., water activity and water vapor deposition effects) with ice formation via homogenous freezing. The parameterization formulation is based on ascending parcel theory and provides expressions for the ice crystal size distribution and the crystal number concentration, explicitly considering the effects of aerosol size and number, updraft velocity, and deposition coefficient. The parameterization is evaluated against a detailed numerical cirrus cloud parcel model (developed during this study), the equations of which are solved using a novel Lagrangian particle-tracking scheme. Over a broad range of cirrus-forming conditions, the parameterization reproduces the results of the parcel model within a factor of 2 and with an average relative error of $-15\%$. If numerical model simulations are used to constrain the parameterization, error further decreases to $1\pm28\%$.


1. Introduction

The effect of aerosols on clouds and climate is one of the major uncertainties in anthropogenic climate change assessment and prediction [Intergovernmental Panel on Climate Change (IPCC), 2007]. Cirrus is one of the most poorly understood cloud types, yet they can strongly impact climate. Cirrus are thought to have a net warming effect because of their low emission temperatures and small thickness [Liou, 1986]. They also play a role in regulating the ocean temperature [Ramanathan and Collins, 1991] and maintaining the water vapor budget of the upper troposphere and lower stratosphere [Hartmann et al., 2001]. Concerns have been raised on the effect of aircraft emissions [Penner et al., 1999; Minnis, 2004; Stuber et al., 2006; IPCC, 2007] and long-range transport of pollution [Fridlind et al., 2004] changing the properties of upper tropospheric clouds, that is, cirrus and anvils, placing this type of clouds in the potentially warming components of the climate system.

Cirrus clouds form by the homogenous freezing of liquid droplets, by heterogeneous nucleation of ice on ice nuclei, and the subsequent growth of ice crystals [Pruppacher and Klett, 1997]. This process is influenced by the physicochemical properties of the aerosol particles (i.e., size distribution, composition, water solubility, surface tension, and shape), as well as by the thermodynamical state (i.e., relative humidity, pressure, and temperature) of their surroundings. Dynamic variability (i.e., fluctuations in updraft velocity) also impact the formation of cirrus clouds, potentially enhancing the concentration of small crystals [Lin et al., 1998; Kärcher and Ström, 2003; Hoyle et al., 2005].

The potential competition between homogeneous and heterogeneous freezing mechanisms has an important impact on cirrus properties. For instance, by enhancing ice formation at low relative humidity, heterogeneous effects may suppress homogeneous freezing and decrease the ice crystal concentration of the newly formed cloud [DeMott et al., 1994; Kärcher and Lohmann, 2002a; Gierens, 2003; Haag et al., 2003b]. It has been suggested that, in the absence of IN, homogeneous nucleation is not probable for polluted areas [Chen et al., 2000; Haag et al., 2003b; Abbatt et al., 2006], at low updraft velocities (less than 10 cm s$^{-1}$) [DeMott et al., 1997, 1998; Kärcher and Lohmann, 2003], and at temperatures higher than $-38^\circ$C [Pruppacher and Klett, 1997; DeMott et al., 2003]. Conversely, homogenous freezing is thought to be the prime mechanism of cirrus formation in unpolluted areas, high altitudes, and low temperatures [Heymsfield and Sabin, 1989; Jensen et al., 1994; Lin et al., 2002; Haag et al., 2003b; Cantrell and Heymsfield, 2005; Khvorostyanov et al., 2006].

A major challenge in the description of cirrus formation is the calculation of the nucleation rate coefficient, $J$, that is, the rate of generation of ice germs per unit of volume. Historically this has been addressed with application of classical nucleation theory [DeMott et al., 1997; Pruppacher and Klett, 1997; Tabazadeh et al., 1997], or using empirical correlations [i.e., Koop et al., 2000]. The
former requires the accurate knowledge of thermodynamic properties, such as surface and interfacial tensions, densities, and activation energies [Cantrell and Heymsfield, 2005]. With appropriate extensions [i.e., DeMott et al., 1994, 1997; Khvorostyanov and Sassen, 1998; Chen et al., 2000; Lin et al., 2002], theory included in cirrus formation simulations shows agreement with experimental measurements and field campaigns [i.e., Chen et al., 2000; Archuleta et al., 2005; Khvorostyanov et al., 2006]. Still, the physical properties of aqueous solutions and ice at low temperatures are subject to large uncertainty. Until now, the most reliable methods to calculate $J$ are based on laboratory measurements [Lin et al., 2002]. Koop et al. [2000] used experimental data to develop a parameterization showing $J$ as a function of water activity and temperature (rather than on the nature of the solute), which has been supported by independent measurements of composition and nucleation rate during field campaigns and cloud chamber experiments [i.e., Haag et al., 2003a; Möhler et al., 2003].

The formation of cirrus clouds is modeled by solving the mass and energy balances in an ascending (cooling) cloud parcel [e.g., Pruppacher and Klett, 1997]. Although models solve the same equations (described in section 2.1), assumptions about aerosol size and composition, $J$ calculation, deposition coefficient, and numerical integration procedure strongly impact simulations. This was illustrated during the phase I of the Cirrus Parcel Model Comparison Project [Lin et al., 2002]; for identical initial conditions, seven state-of-the-art models showed variations in the calculation of ice crystal concentration, $N_c$, (for pure homogeneous freezing cases) up to a factor of 25, which translates to a factor of two difference in the infrared absorption coefficient. Monier et al. [2006] showed that 3 orders of magnitude difference in the value of $J$, which is typical among models at temperatures above $-45^\circ C$, will account only for about a factor of two variation in $N_c$ calculation. The remaining variability in $N_c$ results from the numerical scheme used in the integration, the calculation of the water activity inside the liquid droplets at the moment of freezing, and the value of the water vapor deposition coefficient.

Introducing ice formation microphysics in large-scale simulations requires a physically based link between the ice crystal size distribution, the precursor aerosol, and the parcel thermodynamic state. Empirical correlations derived from observations are available [i.e., Koenig, 1972]; their applicability, however, for the broad range of cirrus formation presented in a GCM simulation is questionable. Numerical simulations have been used to produce prognostic parameterizations for cirrus formation [Sassen and Benson, 2000; Liu and Penner, 2005], which relate $N_c$ to updraft velocity and temperature (the Liu and Penner [2005] parameterization also accounts for the dependency of $N_c$ on the precursor aerosol concentration, and was recently incorporated into the NCAR Community Atmospheric Model (CAM3) [Liu et al., 2007]). Although based on theory, these parameterizations are constrained to the values of parameters (i.e., deposition coefficient, aerosol composition and characteristics) used during the parcel model simulations (the uncertainty of which is quite large). Kärcher and Lohmann [2002b, 2002a] introduced a physically based parameterization solving analytically the parcel model equations. In their approach, a “freezing timescale” is used (related to the cooling rate of the parcel) to obtain an approximated crystal size distribution at the peak saturation ratio through a function describing the temporal shape of the freezing pulse. This function, along with the freezing timescale, should be prescribed (the freezing pulse shape and freezing timescale may also change with the composition and size of the aerosol particles). An analytical fit of the freezing timescale based on Koop et al. [2000] data was provided by Ren and Mackenzie [2005]. The parameterization of Kärcher and Lohmann [2002a, 2002b] has been applied in GCM simulations [Lohmann and Kärcher, 2002] and extended to include heterogeneous nucleation and multiple particle types [Kärcher et al., 2006]. All parameterizations developed to date provide limited information on the ice crystal size distribution, which is required for computing the radiative properties of cirrus clouds [Liou, 1986].

This study presents a new physically based parameterization for ice formation from homogeneous freezing. The parameterization unravels much of the stochastic nature of the cirrus formation process by linking crystal size with the freezing probability, and explicitly considers the effects the deposition coefficient and aerosol size and number, on $N_c$. With this approach, the requirement of prescribed parameters is relaxed and the size distribution, peak saturation ratio, and ice crystal concentration can be computed. The parameterization is then evaluated against a detailed numerical parcel model (also developed here), which solves the model equations using a novel Lagrangian particle-tracking scheme.

2. Numerical Cirrus Parcel Model

Homogenous freezing of liquid aerosol droplets is a stochastic process resulting from spontaneous fluctuations of temperature and density within the supercooled liquid phase [Pruppacher and Klett, 1997]. Therefore, only the fraction of frozen particles at some time can be computed (rather than the exact moment of freezing). At anytime during the freezing process, particles of all sizes have a finite probability of freezing; this implies that droplets of the same size and composition will freeze at different times, so freezing of a perfectly monodisperse droplet population will result in a polydisperse crystal population. This conceptual model can be extended to a polydisperse droplet population; each aerosol precursor “class” will form an ice crystal distribution with its own composition and characteristics, which if superimposed, will represent the overall ice distribution. In the following sections, the formulation of a detailed numerical model, taking into account these considerations, is presented. The equations of the model share similar characteristics with those proposed by many authors [Pruppacher and Klett, 1997; Lin et al., 2002, and references therein] as the ascending parcel framework is used for their development.

2.1. Formulation of Equations

The equations that describe the evolution of ice saturation ratio, $S_i$ (defined as the ratio of water vapor pressure to equilibrium vapor pressure over ice), and
temperature, \( T \), in an adiabatic parcel, with no initial liquid water present, are [Pruppacher and Klett, 1997]

\[
\frac{dS_i}{dt} = - \frac{M_p}{M_a p_i} \frac{dw_i}{dt} - \frac{1}{1} \left[ \frac{\Delta H_i M_o}{RT^2} \frac{dT}{dt} - \frac{gM_o}{RT} \right].
\]  

(1)

\[
\frac{dT}{dt} = - \frac{gV}{c_p} \frac{\Delta H_e}{c_p} \frac{dw_i}{dt},
\]  

(2)

where \( \Delta H_e \) is the latent heat of sublimation of water, \( g \) is the acceleration of gravity, \( c_p \) is the heat capacity of air, \( p_i \) is the ice saturation vapor pressure at \( T \) [Murphy and Koop, 2005], \( p \) is the ambient pressure, \( V \) is the updraft velocity, \( M_o \) and \( M_a \) are the molar masses of water and air, respectively, and \( R \) is the universal gas constant. For simplicity, radiative cooling effects have been neglected in equation (2), although in principle they can be readily included. By definition, the ice mixing ratio in the parcel, \( w_i \), is given by

\[
w_i = \frac{\rho_i}{\rho_a} \frac{\pi}{6} \int_{D_{0,\text{min}}}^{D_{0,\text{max}}} \int_{D_{0,\text{min}}}^{D_{0,\text{max}}} D_i^2 n_i(D_c, D_o) dD_c dD_o,
\]  

(3)

where \( \rho_i \) and \( \rho_a \) are the ice and air densities, respectively, \( D_i \) is the volume-equivalent diameter of an ice particle (assuming spherical shape), \( D_o \) is the wet diameter of the freezing liquid aerosol, \( n_i(D_c, D_o) = \frac{dN_i(D_o)}{dD_c} \) is the ice crystal number distribution function, \( N_i(D_o) \) is the number density of ice crystals in the parcel formed at \( D_o \); \( D_{0,\text{min}} \) and \( D_{0,\text{max}} \) are the limits of the droplet size distribution, and \( D_{c,\text{min}} \) and \( D_{c,\text{max}} \) are the limits of the ice crystal size distribution. Taking the time derivative of equation (3) we obtain

\[
\frac{dn_i}{dt} \frac{dD_o}{dt} = \frac{\rho_i}{\rho_a} \frac{\pi}{2} \int_{D_{0,\text{min}}}^{D_{0,\text{max}}} \int_{D_{0,\text{min}}}^{D_{0,\text{max}}} D_i^2 \frac{dn_i(D_c, D_o)}{dD_c} dD_c dD_o,
\]  

(4)

where the term \( D_i^2 \frac{dn_i(D_c, D_o)}{dD_c} \) was neglected as instantaneous nucleation does not substantially deplete water vapor from the cloudy parcel. The growth term in equation (4) is given by [Pruppacher and Klett, 1997]

\[
\frac{dD_o}{dt} = \left( S_i - S_{\text{eq}} \right) \Gamma_1 D_c + \Gamma_2,
\]  

(5)

with

\[
\Gamma_1 = \frac{\rho_i RT}{4\rho_a p_i D_o M_o} + \frac{\Delta H_e \rho_i}{4 k_a T} \left( \frac{\Delta H_i M_o}{RT} - 1 \right)
\]

\[
\Gamma_2 = \frac{\rho_i RT}{2\rho_a k_a T} \sqrt{\frac{2\pi M_o}{RT}} \frac{1}{\alpha_d},
\]  

(6)

where \( k_a \) is the thermal conductivity of air, \( D_o \) is the water vapor diffusion coefficient from the gas to ice phase, \( S_{\text{eq}} \) is the equilibrium ice saturation ratio, and \( \alpha_d \) is the water vapor deposition coefficient on ice.

[11] The crystal size distribution, \( n_o(D_c, D_o) \) is calculated by solving the condensation equation [Seinfeld and Pandis, 1998]

\[
\frac{\partial n_o(D_c, D_o)}{\partial t} = - \frac{\partial}{\partial D_o} \left( n_o(D_c, D_o) \frac{dD_o}{dt} \right)
\]  

(7)

subject to the boundary and initial conditions (neglecting any change of volume upon freezing),

\[
\frac{\partial n_o(D_c, D_o)}{\partial t} \bigg|_{D_o=D_{0,\text{min}}} = n_o(D_c, D_{0,\text{min}}) \frac{dP_f(D_o, t)}{dt} \equiv \psi(D_o, t);
\]

\[
n_o(D_c, D_{0,\text{min}}, 0) = 0,
\]  

(8)

where \( n_o(D_c, D_o) \) is the liquid aerosol size distribution function, \( \psi(D_o, t) \) is the nucleation function (which describes the number concentration of droplets frozen per unit of time), and \( P_f(D_o, t) \) is the cumulative probability of freezing, given by [Pruppacher and Klett, 1997]

\[
P_f(D_o, t) = 1 - \exp \left( -\frac{\pi}{6} \int_0^t D_o^3 J(t) dt \right)
\]  

(9)

and

\[
\frac{\partial P_f(D_o, t)}{\partial t} = \frac{\pi}{6} D_o^3 J(t) \exp \left( -\frac{\pi}{6} \int_0^t D_o^3 J(t) dt \right),
\]  

(10)

where \( J \) is the homogeneous nucleation rate coefficient, being the number of ice germs formed per unit volume of liquid per unit of time [Pruppacher and Klett, 1997].

[12] Equation (7) is a simplified version of the continuous general dynamic equation applied to the ice crystal population [Gelbard and Seinfeld, 1980; Seinfeld and Pandis, 1998], where the nucleation term has been set as a boundary condition to facilitate its solution. This can be done since the size of the ice particles equals the size of the precursor aerosol only at the moment of freezing.

[13] The evolution of the liquid droplets size distribution, \( n_o(D_o, t) \), is calculated using an equation similar to equation (7),

\[
\frac{\partial n_o(D_o, t)}{\partial t} = - \frac{\partial}{\partial D_o} \left( n_o(D_o) \frac{dD_o}{dt} \right) - \psi(D_o, t).
\]  

(11)

The first term of the right-hand side of equation (11) represents the growth of aerosol liquid particles by condensation of water vapor, and the second term the removal of liquid particles by freezing. Boundary and initial conditions for equation (11) are simply the initial aerosol size distribution and the condition of no particles at zero diameter.

2.2. Numerical Solution of Parcel Model Equations

[14] Equations (1)–(11) are solved numerically using a Lagrangian particle-tracking scheme; this uses a particle-tracking grid for the ice crystal population (the growth of groups of ice crystals is followed after freezing) coupled to a moving grid scheme (the liquid aerosol population is divided into bins the size of which is changing with time),
for the liquid aerosol population (Figure 1). For each time step, the number of frozen aerosol particles is calculated using equation (9) and placed in a node of the particle-tracking grid, after which their growth is subsequently followed. This group of ice crystals represents a particular solution of equation (7) for which all particles freeze at the same time, and have the same size and composition. Since a particular solution of equation (7) can be obtained for each time step and droplet size, the general solution of equation (7) is obtained from the superposition of all generated ice crystal populations during the freezing process; \( w_i \) can then be calculated and equations (1)–(4) readily solved. To describe the evolution of \( n_s(D_o, t) \), a moving grid is employed, where frozen particles are removed from each liquid drop size bin in each time step.

The particle tracking scheme allows ice particles to grow in each node of the particle-tracking grid (no sorting after each time step is needed); thus, the effect of numerical diffusion on the simulation is minimized without losing information about ice crystal composition. The discretization of equation (7) transforms the partial differential equation into a system of ordinary differential equations, each of which represents the growth of a monodisperse ice crystal population. Thus, simple integration schemes can be used without compromising solution accuracy, although a large number of points may be required (the total number of nodes in the particle-tracking grid is the number of time steps times the number of nodes of the liquid aerosol moving grid). However, the particle-tracking grid size can be substantially reduced by grouping the newly frozen particles in a fewer number of sizes [i.e., Khvorostyanov and Curry, 2005],

\[
\frac{\partial n_s(D_o, T_{ao}, t)}{\partial t} \bigg|_{D_o - D_o'} = \frac{1}{D_{upper} - D_{lower}} \int_{D_{lower}}^{D_{upper}} n_s(D_o, t) \frac{\partial P_i(D_o, t)}{\partial t} dD_o, \tag{12}
\]

where \( D_{ao}' \) is the assumed size of the frozen particles. If all aerosol particles freeze at the same size, the integral in equation (12) is evaluated over the entire size spectrum of the liquid aerosol population. A further reduction in the size of the particle-tracking grid is achieved by considering that the freezing process occurs after a water vapor saturation threshold is reached [Sassen and Benson, 2000; Kärcher and Lohmann, 2002b]. The initial time step size in the model is set to 2 s, and reduced to 0.05 s (with \( V \) in m s \(^{-1} \)) when ice nucleation starts \( (J > 10^7 \text{ m}^{-3} \text{ s}^{-1}) \) and growth of ice particles needs to be accounted for.

2.3. Baseline Simulations

The formulation of the parcel model was tested using the baseline protocols of Lin et al. [2002]. Pure ice bulk properties were used to calculate the growth terms (equations (5) and (6)). \( D_o \) was assumed to be the equilibrium size at \( S \), given by Köhler theory [Pruppacher and Klett, 1997], and solved iteratively using reported solution bulk density and surface tension data [Tabazadeh and Jensen; 1997; Myhre et al., 1998]. This assumption may bias the results of the parcel model simulations at low \( T \) and high \( V \) [Lin et al., 2002]. Alternatively, the aerosol size can be calculated using explicit growth kinetics, although the water vapor uptake coefficient from the vapor to the liquid phase is uncertain [Lin et al., 2002] (recent measurements indicate a value between 0.4 and 0.7 [Gershenzon et al., 2004]). Although any model can be employed for \( J \), the Koop et al. [2000] parameterization was used owing to its simplicity and its widely accepted accuracy for a broad range of atmospheric conditions [i.e., Abbatt et al., 2006]. The dry aerosol population was assumed to be pure H\(_2\)SO\(_4\), lognormally distributed with geometric mean diameter, \( D_{g,dry} = 40 \) nm, geometric dispersion, \( \sigma_{g,dry} = 2.3 \), and total number concentration, \( N_g = 200 \text{ cm}^{-3} \). The runs were performed using 20 size bins for the liquid aerosol; the newly frozen particles were grouped into 4 size classes, producing a grid between 1500 and 2000 nodes; numerical results showed that little accuracy was gained by using a finer grid (not shown). Runs of the parcel model using a regular PC (2.2 GHz processor speed and 1 GB of RAM), usually took between 5 and 12 min.

Figure 2 shows results of the performed simulations for the protocols of Lin et al. [2002] and \( \alpha_d = 1 \). The value of \( \alpha_d \) is still uncertain and may impact \( N_c \) [Lin et al., 2002]. Simulations using \( \alpha_d = 0.1 \) (not shown) produced \( N_c \) of 0.20, 2.87, 24.06, for the cases Ch004, Ch020, and Ch100.
(using the nomenclature of Lin et al. [2002]) respectively, and 0.043, 0.535, and 5.98 for the cases Wh004, Wh020 and Wh100, respectively. Results from the INCA campaign summarized by Gayet et al. [2004] indicate $N_c/C_{24}/C_{0}/C_3$ for $T$ between $43$ and $53$°C ($V$ was mainly below 1 m s$^{-1}$, at conditions favorable for homogeneous freezing) [Haag et al., 2003b]. These values are consistent with a low value for $\alpha_d$ (around 0.1) which is supported by independent studies [Gierens et al., 2003; Hoyle et al., 2005; Khvorostyanov et al., 2006; Monier et al., 2006]. However, direct comparison of the parcel model with experimental results is a rather simplistic view of the cirrus formation process, and overlooks other important effects (i.e., variation in aerosol characteristics, $V$ and $T$ fluctuations [Kärcher and Ström, 2003; Kärcher and Koop, 2005]). Theoretical calculations and direct experimental observations have reported $\alpha_d$ values from 0.03 to 1 at temperatures ranging from 20 to 263 K [i.e., Haynes et al., 1992; Wood et al., 2001]. Owing to these considerations, $\alpha_d$ is explicitly introduced in the parameterization.

3. Parameterization of Ice Nucleation and Growth

3.1. Parameterization of $n_c(D_c, D_o)$

The ultimate goal of this study is to develop an approximate analytical solution of equations (5)–(12) to predict number and size of ice crystals as a function of cloud formation conditions. For this, a link should be established between ice particle size and their probability of freezing at the time of nucleation, so that $n_c(D_c, D_o)$ can be defined at each instant during the freezing pulse. $n_c(D_c, D_o)$ is determined for a given $S_i$ profile by tracing back the growth of a group of ice crystals particles of size $D_o$ down to $D_c$ (Figure 3). In the following derivation we assume that most of the crystals are nucleated before maximum saturation ratio, $S_{i,max}$, is reached (the implications of this assumption are discussed in section 4). We start by writing a solution of equation (7) in the form

$$n_c(D_c, D_o) = -\pi_o(D_o) \frac{dP_f(S_o)}{dD_c}$$

(13)

where $S_o$ is a value of $S_i < S_{i,max}$ at which the ice crystals were formed and $P_f(S_o)$ represents the current fraction of crystals of size $D_o$, that come from liquid aerosol particles of size $D_o$. $\pi_o(D_o)$ is the average $n_o(D_o)$ during the freezing interval, and is taken to be constant since $N_c$ is usually much less than $N_o$ [i.e., Lin et al., 2002] and freezing occurs over a very narrow $S_i$ range [Kärcher and Lohmann, 2002b]. Since in a monotonically increasing $S_i$ field $P_f(S_o)$ decreases with increasing $D_c$ (as explained below), a negative sign is introduced in equation (13).

Figure 3. Sketch of the parameterization concept. Circle represents the supercooled liquid droplet, and hexagon represents the ice crystal.
Calculation of $S'_0$ is key for solving equation (13); this is done by combining equations (1) and (2),
\[
\frac{dS}{dt} = \alpha v S - \beta \frac{dw_i}{dt},
\]
where $\alpha = \frac{g\Delta H_s M_e}{c_p R^2} - \frac{g M_e}{RT}$, $\beta = \frac{M_p p_i}{c_p R^2}$. Before the nucleated ice crystals substantially impact saturation (known as “free growth,” Figure 3), $\frac{dw_i}{dt} \approx 0$, and the integration of equation (14) from $S'_0$ to $S_{i,max}$ gives
\[
t - t_o \approx \frac{1}{\alpha V} \left(1 - \frac{S'_0}{S_{i,max}}\right),
\]
where the approximation $\ln(x) \approx x - 1$ has been used. Equation (15) is similar to the “upper bound” expression derived by Twomey [1959] for liquid water clouds. Numerical simulations (section 4) support that “free growth” holds up to $S_i$ values very close $S_{i,max}$; for $S_i \rightarrow S_{i,max}$ however, equation (15) may underestimate $t - t_o$ and its effect is discussed in section 4.

By definition, $t - t_o$ should equal the time for growth of the ice particles from $D_o$ to $D_e$ (Figure 3), which is found by integration of equation (5),
\[
t - t_o = \frac{1}{(S_i - 1)} \left[ \frac{1}{2} (D_e^2 - D_o^2) + \Gamma_1 (D_e - D_o) \right],
\]
where $S_i$ has been assumed constant. This is supported by parcel model simulations that suggest that nucleation occurs in a very narrow $S_i$ range (i.e., Figure 5). The calculation of $P_f(S'_0)$ using equation (9) requires the knowledge of $J$ as an explicit function of $S_i$; this can be further simplified given that nucleation occurs on a very narrow interval of saturation so that $J(S_i)$ can be approximated with $J(S_{i,max})$ [i.e., Khvorostyanov and Curry, 2004],
\[
\ln \frac{J(S_i)}{J(S_{i,max})} \approx k(T) (S_i - S_{i,max}).
\]
k(T) is obtained by fitting the Koop et al. [2000] data for $J$ between $10^8$ and $10^{22} \text{ m}^{-3} \text{ s}^{-1}$,
\[
k(T) = 0.0240 T^2 - 8.0357 + 934.0,
\]
with $T$ in K. $k(T)$ can also be derived for any aerosol type and composition using classical nucleation theory [Khvorostyanov and Sassen, 1998; Khvorostyanov and Curry, 2004]. Using equations (14) and (17), equation (9) is solved under the assumption of free growth to give
\[
P_f(D_o, S'_0) \approx \frac{1}{\alpha v S_{i,max}} \int_{S_i}^{S'_0} v_o J(S) dS = \frac{J(S_{i,max}) v_o}{\alpha V k(T) S_{i,max}} \exp[-k(T)(S_{i,max} - S'_0)],
\]
where $v_o = \pi D_o^3 / 6$, and the approximation $1 - \exp(-\int_0^t v_o J(t) dt) \approx \int_0^t v_o J(t) dt$ has been used. The lower integration limit, $S_o$, in equation (19) represents the beginning of the freezing pulse, assumed to be where $P_f(D_o, S_o) < 10^{-6}$, $P_f(D_o, S_{i,max})$, that is, $\exp[-k(T)(S_{i,max} - S'_0)] \approx \exp[-k(T)(S_{i,max} - S_o)]$. The integration is not very sensitive to the latter assumption, as most of the ice crystals form for $S_i$ close to $S_{i,max}$ [i.e., Kärcher and Lohmann, 2002a]. Combining equations (15) and (16) to find $S_{i,max} - S_o$ and replacing into equation (19) gives
\[
P_f(D_o, D_e) = \frac{J(S_{i,max}) v_o}{\alpha V k(T) S_{i,max}} \exp[-\mu \Gamma(D_e, D_o)],
\]
where $\mu = \frac{\alpha V (T) S_{i,max}}{S_{i,max} - 1}$, and $\Gamma(D_e, D_o) = \frac{1}{2}(D_e^2 - D_o^2) + \Gamma_1 (D_e - D_o)$. The ice number distribution function at $S_{i,max}$ is obtained after computing $\frac{\partial P_f(D_o, D_e)}{\partial D_e}$ from equation (20) and substituting into equation (13),
\[
n_e(D_e, D_o)|_{S_{i,max}} = \pi_o(D_o) J(S_{i,max}) V_o (\Gamma_1 D_e + \Gamma_2) \exp[-\mu \Gamma(D_e, D_o)].
\]
Since ice particles attain large sizes after freezing, the spectrum of $D_e$ values spans over several orders of magnitude [i.e., DeMott et al., 1994; Monier et al., 2006]. Typically variation in $D_e$ is much smaller and is further reduced because $P_f$ is significant only for a fraction of the liquid droplets (generally those with larger sizes and low solute concentrations [Pruppacher and Klett, 1997]). With this, the value of $\exp[-\mu \Gamma(D_e, D_o)]$ will be dominated by variation in $D_e$, so that $\exp[-\mu \Gamma(D_e, D_o)]$ can be approximated with $\exp[-\mu \Gamma(D_e, D_o)]$. Obtaining the crystal size distribution then is done by integration of equation (21) over the contribution from each droplet size class,
\[
n_e(D_e)|_{S_{i,max}} = \frac{J(S_{i,max})}{(S_{i,max} - 1)} (\Gamma_1 D_e + \Gamma_2) \exp[-\mu \Gamma(D_e, D_o)]
\]
\[
	imes \int \pi_o(D_o) v_o dD_o.
\]
which for a lognormal distribution of $\pi_o(D_o)$ gives
\[
n_e(D_e)|_{S_{i,max}} = \frac{dN_e}{d \ln D_e}|_{S_{i,max}} = \frac{N_o \sigma e^{\frac{1}{2} \ln^2 \sigma}}{\sigma_0 \ln \sigma_0} J(S_{i,max}) (\Gamma_1 D_e + \Gamma_2) \exp[-\mu \Gamma(D_e, D_o)],
\]
or
\[
n_e(|\ln D_e|)|_{S_{i,max}} = \frac{dN_e}{d |\ln D_e|}|_{S_{i,max}} = \frac{N_o \sigma e^{\frac{1}{2} \ln^2 \sigma}}{\sigma_0 \ln \sigma_0} J(S_{i,max}) (\Gamma_1 D_e + \Gamma_2) \exp[-\mu \Gamma(D_e, D_o)],
\]
where $\sigma_o = \pi D_o^3$ and $\sigma_0$ is the geometric dispersion of the droplet size distribution. Equation (23) is the final
expression used for the ice crystal size distribution at \( S_{i,\text{max}} \). Equations (21)–(23) demonstrate the probabilistic character of ice nucleation: at any time particles of all sizes have finite freezing probabilities; that is, the population of ice crystals of a given size \( D_c \) results from the freezing of droplets with different sizes at different times. As a result, the freezing of a monodisperse aerosol size population produces a polydisperse ice crystal population. Since \( S_i \) increases monotonically with time before reaching \( S_{i,\text{max}} \), the number of crystals generally increases as \( D_c \) decreases. For a given droplet size, \( P_f(D_{o}, S_i) \) will increase with time so that the number of newly formed crystals will increase. These crystals in turn will have less time to grow before \( S_i \) reaches \( S_{i,\text{max}} \); in other words, the most recently formed crystals will have the largest probability of freezing, \( P_f(D_c = D_{o}, S_{i,\text{max}}) \). The maximum in the distribution may be shifted to \( D_c > D_{o} \) if the timescale for the growth of the newly formed particles is larger than the timescale of change of probability (section 4).

3.2. Calculation of \( N_c \) at \( S_{i,\text{max}} \)

The deposition rate of water vapor upon ice crystals can be approximated by substituting equation (23) into equation (4),

\[
\frac{dN_c}{dt} = \frac{\rho_i}{\rho_o} 2 N_o v_o \frac{\varphi}{2} \frac{1}{2} \frac{1}{\pi} J(S_{i,\text{max}}) \int_{D_{c,\text{max}}}^{D_c} \frac{D_c^2}{D_c^2 - D_o^2} \exp \left[ -\frac{\mu}{2\Gamma} (D_c^2 - D_o^2) \right] dD_c,
\]

where \( D_{c,\text{max}} \) is the equivalent diameter of the largest ice crystal at \( S_{i,\text{max}} \) (calculated in section 3.3) and \( \Gamma \) is calculated using the approach of Fountoukis and Nenes [2005],

\[
\Gamma = \frac{D_{c,\text{max}}}{D_c} = \frac{1 + \frac{\ln (\Gamma_2 + \Gamma_1 D_{c,\text{max}})}{\Gamma_1}}{\frac{\ln (\Gamma_2 + \Gamma_1 D_{c,\text{max}})}{\Gamma_1}}.
\]

where \( \gamma \) is a correction factor defined in section 3.3. Integration of equation (24) gives

\[
\frac{dN_c}{dt} = \frac{\rho_i}{\rho_o} 2 N_o v_o \frac{\varphi}{2} \frac{1}{\pi} J(S_{i,\text{max}}) \exp \left[ -\frac{\mu}{2\Gamma} (D_c^2 - D_o^2) \right] \left[ \frac{\varphi}{2} \frac{1}{\pi} J(S_{i,\text{max}}) \right]^{3/2}.
\]

An order of magnitude estimation based on parcel simulations (not shown) suggest that \( D_o \approx 10^{-7} \text{ m} \), \( D_{c,\text{max}} \approx 10^{-5} \text{ m} \) and \( \mu \approx 10^{10} \text{ m}^{-2} \). Therefore, the bracketed term in equation (26a) tends to approach \( \sqrt{\pi} \) in most conditions, that is,

\[
\frac{dN_c}{dt} = \frac{\rho_i}{\rho_o} 2 N_o v_o \frac{\varphi}{2} \frac{1}{\pi} J(S_{i,\text{max}}) \exp \left[ -\frac{\mu}{2\Gamma} (D_c^2 - D_o^2) \right] \left[ \frac{\varphi}{2} \frac{1}{\pi} J(S_{i,\text{max}}) \right]^{3/2}.
\]

after substitution of equation (26b) into equation (14), at \( \frac{dS_i}{dt} = 0 \),

\[
\alpha V S_{i,\text{max}} = \beta \frac{\rho_i}{\rho_o} N_o v_o \frac{\varphi}{2} \frac{1}{\pi} \frac{1}{(2\mu \sqrt{\pi} J(S_{i,\text{max}}))^{3/2}}.
\]

the fraction of frozen particles, \( f_c \), at \( S_{i,\text{max}} \) is found at the maximum \( P_f \), given by equation (20)

\[
f_c = \frac{1}{N_o} \int \frac{\pi v_o}{(D_o)} P_f(D_c = D_{o, i}) \frac{1}{D_o} dD_o = \frac{\pi v_o \sqrt{\varphi/2} \frac{1}{\pi} J(S_{i,\text{max}}) \exp \left( -\frac{\mu}{2\Gamma} (D_c^2 - D_o^2) \right)}{\alpha V k(T) S_{i,\text{max}}^{3/2}}.
\]

combining equations (27) and (28) we obtain,

\[
f_c = \frac{\rho_i}{\rho_o} \left[ \frac{k(T)^{1/2}}{\beta N_o} \right] \left[ \frac{1}{2} \left( \frac{\mu}{\pi} \frac{1}{(2\mu \sqrt{\pi} J(S_{i,\text{max}}))^{3/2}} \right) \right]^{3/2}.
\]

The exponential term in equation (29) approaches unity, which is a result of the assumption made in section (13) that freezing depletes a negligible amount of aerosol (i.e., \( n_i(D_o) \) is constant during the nucleation process). Since \( J(S_{i,\text{max}}) \) has been eliminated from equation (29), \( f_c \) is not strongly influenced by small variations in \( S_{i,\text{max}} \). Therefore, \( S_{i,\text{max}} \) can be taken as the saturation freezing threshold obtained by solving the parametrization of Koop et al. [2000] for \( J(S_{i,\text{max}}) = 10^{10} \text{ s}^{-1} \text{ m}^{-3} \), which represents an average of \( J(S_i, \text{max}) \) over a wide set of simulations (section 4), and is close to the nucleation rate of pure water at \( -38^\circ \text{C} \) [Pruppacher and Klett, 1997; Sassen and Benson, 2000]. The total number of crystals would be given by \( N_c = N_o f_c \); however, such a result is not limited by \( N_o \). Instead, lifting the assumption made in equation (19), \( f_c \) can be associated with the solution of the integral in equation (9); that is, \( f_c \approx \int_0^{\tau} \frac{\rho_i}{\rho_o} \frac{1}{N_o} J(t) dt \), so

\[
N_c = N_o e^{-\int f_c \frac{1}{N_o} J(t) dt}.
\]

where \( N_o e^{-\int f_c \frac{1}{N_o} J(t) dt} \) represents the number of remaining unfrozen droplets.

3.3. Calculation of \( D_{c,\text{max}} \)

\[ D_{c,\text{max}} \] is required for calculating the ice growth rate (equation (26b)). Two methods are used to calculate it. The first one is based on theoretical arguments (therefore \( \gamma = 1 \) in equation (25)), and assumes \( D_{c,\text{max}} \) as the diameter of the ice crystal at which \( P_f(D_c = D_{o, i}) \) is \( 10^{-6} \) (i.e., the size above which the number of crystals is below \( 10^{-6} \) \( N_c \)). With this, equation (20) can be solved for \( D_{c,\text{max}} \),

\[
D_{c,\text{max}} = 2 \frac{\Gamma_1}{\Gamma} D_{o, i} - 2 \ln(10^{-6}) (S_{i,\text{max}} - 1) /
\]

\[
\alpha V k(T) S_{i,\text{max}} \Gamma_1 = 0.
\]
Table 1. Conditions Used in Parameterization Evaluation

<table>
<thead>
<tr>
<th>Property</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T, , \text{K} )</td>
<td>200–235</td>
</tr>
<tr>
<td>( V, , \text{m s}^{-1} )</td>
<td>0.02–5</td>
</tr>
<tr>
<td>( \alpha_d )</td>
<td>0.05–1.0</td>
</tr>
<tr>
<td>( \sigma_{g,\text{dry}} )</td>
<td>1.7–2.3, 2.9</td>
</tr>
<tr>
<td>( N_a, , \text{cm}^{-3} )</td>
<td>10–5000</td>
</tr>
<tr>
<td>( D_{g,\text{dry}}, , \text{nm} )</td>
<td>20–160</td>
</tr>
</tbody>
</table>

where we have assumed \( D_{c,\text{max}} \gg D_o \) (supported by numerical simulations). Since \( \Gamma_2 \propto \frac{1}{\alpha_d} \) (equation (6)), the value of \( D_{c,\text{max}} \) would increase as \( \alpha_d \) decreases. For low values of \( \alpha_d \) ice crystals grow slowly, and noncontinuum effects limit the condensation rate; when ice become large enough, gas-to-particle mass transfer is in the continuum regime and the crystals grow quickly [Pruppacher and Klett, 1997]. When growth of the newly frozen ice crystals is delayed, water vapor water tends to preferentially condense on preexisting ice crystals. Slow uptake effects become important for \( \alpha_d \) lower than 0.1, that is, when \( \Gamma_2 \) becomes comparable to \( \Gamma_1 \) [Lin et al., 2002; Gierens et al., 2003]. Alternatively, \( D_{c,\text{max}} \) can be computed using an empirical fit to numerical simulations obtained with the parcel model,

\[
D_{c,\text{max}} = \min \left\{ \left( 1.6397 \times 10^{-14} T - 3.1769 \times 10^{-12} \right), \right.
\]

\[
V^{-0.65} \left( N_a D_{g,\text{dry}} \right)^{-0.373} ; 10^{-4} \right\}, \tag{32}
\]

where \( V \) is in \( \text{m s}^{-1} \), \( T \) is in K, \( N_a \) in \( \text{cm}^{-3} \) and \( D_{g,\text{dry}} \) in meters. For this case, \( \gamma = 1.33 \) in equation (25). Equation (32) was generated over a broad set of \( T, \, P, \, V, \, N_a, \, D_{g,\text{dry}}, \) and \( \alpha_d \) (Table 1, section 4). The \( T \) and \( V \) dependencies in equation (32) are introduced to adjust the effective growth of the particles for the “free growth” assumption (section 3.1). Variability in the formulation of equation (30) from aerosol property changes is not accounted for. Since \( n_e(D_c) \) is determined by the dry aerosol size distribution, a larger \( D_{g,\text{dry}} \) will enhance \( P_r \) as the total volume of the liquid aerosol particles is increased. This would produce a longer freezing pulse and increase \( N_c \). The same effect can be achieved by reducing the effective growth of the particles, and explains why \( D_{c,\text{max}} \) scales with the average volume of the dry aerosol population, that is, \( \sim (N_a D_{g,\text{dry}}^3)^{1/3} \) (equation (32)).

3.4. Implementation of the Parameterization

As application of the parameterization is presented in Figure 4. Inputs are the conditions of cloud formation \( T, \, P, \, V, \) and the aerosol size distribution (i.e., \( N_a \) and \( D_{g,\text{dry}} \)); the outputs are \( N_c \) and ice crystal size distribution. To apply the parameterization, first \( \Gamma \) is calculated (equation (25)), using \( D_{c,\text{max}} \) computed from either equation (31) or (32), the latter being preferred. \( S_{i,\text{max}} \) is obtained by solving \( J(S_{i,\text{max}}) = 10^{16} \, \text{s}^{-1} \, \text{m}^{-3} \) [Koop et al., 2000], for which reported fits can be employed [i.e., Ren and Mackenzie, 2005]. \( N_c \) is calculated from equation (30) using \( f_c \) calculated from equation (29). After \( f_c \) is calculated, \( J(S_{i,\text{max}}) \) can be corrected using \( J(S_{i,\text{max}}) = f_c \alpha V k(T) S_{i,\text{max}} / \gamma_{\text{ref}} \theta/2\pi \sigma_c \) (equation (28)); \( n_e(D_c, \, D_o) \) is then obtained from equations (21)–(23).

4. Evaluation of the Parameterization

The parameterization was evaluated against the detailed numerical solution of the parcel model over a wide range of \( T, \, V, \, D_{g,\text{dry}}, \) \( N_a, \) and \( \alpha_d \) (Table 1), for a total of 1200 runs that reflect the uncertainty in \( \alpha_d \) [Lin et al., 2002] and the range of cirrus cloud formation conditions expected in a GCM simulation. The parcel model was run using initial \( S_{i} = 1.0 \); initial \( p \) was estimated from hydrostatic equilibrium at \( T \) using a dry adiabatic lapse rate. The dry aerosol was assumed to follow a lognormal size distribution and be composed of pure \( \text{H}_2\text{SO}_4 \). "Aged," “unperturbed,” and “perturbed” aerosol is represented by setting the geometric dispersion of the dry aerosol distribution, \( \sigma_{g,\text{dry}} \), to 1.7, 2.3, and 2.9, respectively [Seinfeld and Pandis, 1998]. The aerosol was assumed to be deliquesced and in equilibrium with \( S_i \) in all simulations. Calculated \( N_c \) ranged from 0.001 to 100 \( \text{cm}^{-3} \) and \( S_{i,\text{max}} \) varied between 1.4 and 1.6, which agrees with the reported values for cirrus formation by homogeneous freezing [i.e., Heymsfield and Sabin, 1989; Lin et al., 2002].

Two main assumptions were introduced in the development of the parameterization: (1) \( N_c \) is calculated at \( S_{i,\text{max}} \) rather than at the end of the freezing pulse, that is, \( N_c \approx N_c(\mid S_{i,\text{max}} \rangle \), and (2) the newly formed crystals have a negligible impact on \( S_i \) before \( S_{i,\text{max}} \) is reached (“free growth”). Figure 5 shows how these assumptions may impact the results of the parameterization for high and low \( V \) and \( T \) (1–0.04 \( \text{m s}^{-1} \), 233–203 K). By using free growth regime to estimate the evolution of \( S_i \) (Figure 5, dotted black line), \( S_{i,\text{max}} \) is overestimated by \( \sim 0.5\% \) at low \( V \) (Figures 5c and 5d) and \( \sim 2\% \) at high \( V \) (Figures 5a and 5b). At high \( T \) (Figures 5b and 5d) this overestimation does not impact parameterization performance, as \( S_{i,\text{max}} \) is low and small overestimations thereof do not significantly influence \( J(S_{i,\text{max}}) \). However, as \( T \) decreases and \( V \) increases, \( S_{i,\text{max}} \) reaches higher values during the parcel ascent; \( J \) is an unrealistic function of \( S_{i,\text{max}} \), and \( P_r \) becomes very sensitive to small changes in \( S_{i,\text{max}} \). As a result, an overestimation in \( N_c \) may be expected. Conversely, Figures 5c and 5d show that at low \( V, \, N_c(\mid S_{i,\text{max}} \rangle \) underestimates the actual \( N_c \) by nearly a factor of 2; since few ice crystals (low \( S_{i,\text{max}} \) are formed, it takes a longer time to deplete the available water vapor, resulting in longer freezing pulses. At high \( V \) (Figures 5a and 5b), \( N_c(\mid S_{i,\text{max}} \rangle \) is close to \( N_c \), since \( S_{i,\text{max}} \) is reached rapidly and a larger number of crystals is formed; this effect will be more important at low \( T \) as higher \( S_{i,\text{max}} \) values are reached.

4.1. Calculation of \( n_e(D_c) \)

[27] Figure 6 presents the parameterized \( n_e(D_c) \) (equation (23b)) for two representative cirrus cases, along with \( n_e(D_c) \), \( S_{i,\text{max}} \) obtained from parcel model simulations. Although the effect of the droplet size distribution parameters is explicitly considered in equation (23), it cancels out with its effect on \( f_c \) (which is a result of assuming constant \( \eta_c(D_c) \)), and a single crystal size distribution is obtained for the three values of \( \sigma_{g,\text{dry}} \) tested (although small variations in
**Input:** $p$, $T$, $V$, $\alpha$, and aerosol characteristics.

Calculate $D_c, S_{\text{max}}, \Gamma$

Estimate $S_{\text{max}}$ at $J(S_{\text{max}}) = 10^{16}$ m$^3$ s$^{-1}$

$$f_c = \frac{\rho_i}{\rho_s} \left[ \frac{k(T)}{\beta N_o} \right]^{1/2} \left[ \frac{2\alpha V S_{\text{max}}}{\pi \Gamma (S_{\text{max}} - 1)} \right]^{1/2} \exp \left[ -\frac{\alpha V k(T) S_{\text{max}}}{2\Gamma (S_{\text{max}} - 1)} \right]$$

Output: $N_c = N_o e^{-f_c} (1 - e^{-f_c})$

Re-calculate $J(S_{\text{max}}) = \frac{f_c \alpha V k(T) S_{\text{max}}}{V_c e^{2\ln^2 \alpha}}$

Output: $n_c(D_c)|_{S_{\text{max}}}$, equation (23)

**Figure 4.** Parameterization algorithm.

**Figure 5.** $S_i$ (solid lines, left axes) and $N_c$ (dash-dotted lines, right axes) evolution calculated by the parcel model. $T$ and $V$ conditions shown are (a) 233 K and 1 m s$^{-1}$, (b) 203 K and 1 m s$^{-1}$, (c) 233 K and 0.04 m s$^{-1}$, and (d) 203 K and 0.04 m s$^{-1}$. Dashed lines represent the time at which $S_{i,\text{max}}$ is reached, and dotted lines represent $S_i$ evolution under "free growth". $N_o = 200$ cm$^{-3}$, and $D_{g,dry} = 20$ nm.
may occur owing to differences in $T$ at $S_{i,max}$). The latter is not a critical issue, as $N_c$ variations with respect to $s_g$, dry are generally small (i.e., Figure 6). $D_o$ was approximated with the equilibrium size of $D_{g, dry}$ at $S_{i,max}$. $n_c(D_c)$ was calculated using the outline in section 3.4 (Figure 4), from which $J(S_{i,max})$ is corrected using equations (30) and (32) (therefore enforcing $N_c \approx \int n_c(D_c) dD_c$).

Generally, the parameterized $n_c(D_c)$ reproduces well the numerical results at $S_{i,max}$; however, the size of the ice crystals is underestimated (which is a result of the assumption of “free growth” which underestimates $t - t_w$; equation (15) and $N_c|_{S_{i,max}}$ is overestimated.” The adjusted $J(S_{i,max})$ will then be slightly below the obtained in numerical simulations to satisfy $N_c = N_c|_{S_{i,max}}$. Thus, the correction in $J(S_{i,max})$ produces a reduction in the peak of the ice crystal size distribution. The influence of these factors on the resulting effective radius of the cirrus cloud, and its radiative properties, will require the time integration of $n_c(D_c)$, and the comparison with numerical simulations at different stages after cloud formation. Although such a task may be readily achieved, it is out of the focus of this manuscript and will be undertaken in a future study.

### 4.2. Calculation of $N_c$

Figure 7 shows the comparison of $N_c$ predicted by the parcel model and the parameterization (equation (30)) using the theoretical calculation of $D_{c,max}$ (Figure 7, right; equation (31)) and using the empirical correlation for $D_{c,max}$ (Figure 7, left; equation (32)). The effects of assuming “free growth” and the approximation of $N_c$ as $N_c|_{S_{i,max}}$ are expected to cancel out at moderate $T$ and $V$. However, at low $V$ and high $T$ (hence low $N_c$), the parameterization tends to underestimate $N_c$ with respect to the parcel model results;

**Figure 6.** Crystal size distribution calculated by the parcel model and the parameterization at $S_{i,max}$: (left) $T = 213$ K, $V = 1.0$ m s$^{-1}$; (right) $T = 233$ K, $V = 0.2$ m s$^{-1}$. $\sigma_{g, dry}$ is the geometric dispersion of the aerosol size distribution.

**Figure 7.** Ice crystal number concentration calculated by the parcel model and the parameterization. $D_{c,max}$ was calculated using either (left) equation (32) or (right) equation (31). Gray scale represents the value of $\alpha_d$ used in the calculations; dashed lines represent ±50% error.
the opposite tendency occurs at very high \( V (>2 \text{ m s}^{-1}) \) and low \( T \) (hence, high \( N_c \)). The behavior at these \( T, V \) extremes is not typical of cirrus formation [i.e., Heymsfield and Sabin, 1989; Gayet et al., 2004], hence not expected to be a source of significant bias in GCM simulations. Overall, using the theoretically calculated \( D_{c,\text{max}} \) gives a parameterized \( N_c \) that agrees within a factor of 2 of the parcel model simulations, with a mean relative error about 29% (for all runs in Table 1). When using the empirically calculated \( D_{c,\text{max}} \) (equation (32)), the parameterized \( N_c \) is much closer to the numerical parcel model (average relative error 1% ± 28%), as equation (32) allows more flexibility in reproducing the parcel model results, and accounts for the additional variability due to the effect of aerosol size and number.

4.3. Comparison Against Other Parameterizations

[29] The new parameterization is evaluated against several published schemes for different combinations of \( V, N_o, D_{g,\text{dry}}, T, \) and \( \alpha_d \). The parameterizations used in this section are those of Liu and Penner [2005] (LP2005), Sassen and Benson [2000] (SB2000), Kärcher and Lohmann [2002a] (KL2002), and Fountoukis and Nenes [2005]. SB2000 is based on an empirical fit to numerical simulations relating \( N_c \) to \( T \) and \( V \). A similar approach is used in LP2005 where an additional dependency on \( N_o \) is included. In both cases, \( J \) is calculated through classical nucleation theory (the latter using the effective temperature method [i.e., DeMott et al., 1994]). KL2002 is physically based and employs the freezing timescale and the threshold supersaturation as input parameters. It resolves explicitly the dependency of \( N_o \) on \( T, V, \alpha_d, \) and \( D_o \), and uses \( N_c \) as upper limit for \( N_c \). Although the freezing of polydisperse aerosol is discussed in KL2002, not explicit solution is presented; their monodisperse solution is therefore used for comparison. The freezing timescale and supersaturation threshold are calculated using the analytical fits to Koop et al. [2000] data provided by Ren and Mackenzie [2005]. \( D_o \) in this case was taken as in equilibrium with the volume-weighted geometric mean diameter of the dry size distribution. By using this definition of \( D_o \), the best agreement between the parcel model simulations and the results of the KL2002 parameterization was obtained. The three parameterizations were compared to the solution of equation (30) using theoretically calculated \( D_{c,\text{max}} \) (equation (31) (although termed “theoretical”, \( k(T) \) was derived from an empirical fit to \( J \)), and using the empirically adjusted \( D_{c,\text{max}} \) (equation (32), termed “adjusted”). \( D_o \) was calculated as the equilibrium size of \( D_{g,\text{dry}} \) at \( S_{\text{max}} \). All parameterizations are evaluated using \( T \) obtained at \( S_{\text{max}} \) from the parcel model simulations. \( \alpha_d \) was set to 0.1 and 1.0 to test both diffusionally and nondiffusively limited cases (see section 3.3).

4.3.1. Dependency on \( V \)

[30] Figure 8 presents \( N_c \) predicted from all parameterizations at \( T_o = 213 \) (Figure 8, left; \( T \) between 208.6 and 209.4 K) and 233 K (Figure 8, right; \( T \) between 228.8 and 229.2 K), and \( \alpha_d = 0.1 \) (black line) and 1.0 (gray line). At \( T_o = 233 \) K, all parameterizations agree fairly well when \( \alpha_d = 0.1 \) and \( V < 1 \text{ m s}^{-1} \). At higher \( V \), KL2002 and LP2005 predict a larger \( N_c \), whereas SB2000 predicts a lower \( N_c \) with respect to the parcel model results and becomes significant when \( V > 3 \text{ m s}^{-1} \). At these conditions the adjusted parameterization follows the parcel model very well, whereas the theoretical parameterization slightly underpredicts \( N_c \) at low \( V \). Runs made using \( \alpha_d = 1 \) (gray line) showed a good agreement between the parcel model and KL2002, the adjusted and theoretical parameterizations. This is not surprising, as equation (29) bears the same dependency on \( V \) and \( p_i^g \), reported by KL2002 in their “fast growth” solution (i.e., \( N_c \propto V^{3/2}) \), and further emphasized by more recent work [Gierens, 2003; Ren and Mackenzie, 2005]. At high \( f_c \) (i.e., low \( T, \) low \( \alpha_d \), and high \( V \)) the exponential term in equation (30) dampens the effect of \( V \) (also because \( D_{c,\text{max}} \) scales with \( V \) and \( N_c \) scales almost linearly with \( V \)). Results for \( \alpha_d = 1 \) lie below those of LP2005 and
SB2000, who used lower $\alpha_d$ values for their numerical simulations (LP2005 used $\alpha_d = 0.1$ and SB2000 used $\alpha_d = 0.36$ [Lin et al., 2002]). At $T_o = 213$ K and $\alpha_d = 0.1$ (Figure 8, left, black line), the parameterizations agree only for $V$ below 0.3 m s$^{-1}$ whereas for large $V$ they diverge, with KL2002 giving the largest $N_c$ over the whole $V$ interval. At very high $V$ (>3 m s$^{-1}$) the adjusted parameterization underpredicts $N_c$ with respect to the parcel model results, which is a result of the exponential term introduced in equation (30). As with $T_o = 233$ K, KL2002, the adjusted and theoretical parameterizations agree well with the numerical results when $\alpha_d = 1$, and $T_o = 213$ K (Figure 8, left, gray line).

### 4.3.2. Dependency on $N_o$

[31] Figure 9 presents $N_c$ as a function of $N_o$ for $V = 0.2$ m s$^{-1}$ (Figure 9, left) and $V = 1.0$ m s$^{-1}$ (Figure 9, right) and $T_o = 213$ K (black line) and 233 K (gray line); $D_{g, dry}$ was set to 40 nm and $\alpha_d$ to 0.1. In all cases of Figure 9, LP2005 and the adjusted parameterization show the best agreement with the parcel model results. Still, at $T_o = 213$ K, $V = 1.0$ m s$^{-1}$, and $N_o$ below 20 cm$^{-3}$, the adjusted parameterization underpredicts with respect to the numerical results and LP2005 overpredicts. In both cases the difference with the parcel model results is about 50%, which is not critical as these very low $N_o$ are atypical of cirrus forming conditions [i.e., Pruppacher and Klett, 1997]. In all cases of Figure 9, KL2002 predicts larger $N_c$ than the parcel model; however, the difference becomes much smaller at large $N_o$. SB2000 predicts $N_c$ close to the average of the parcel model results at $T_o = 213$ K; when $T_o = 233$ K, SB2000 is close to the parcel model results at large $N_o$. The theoretical parameterization tends to agree better with the parcel model results at high $N_o$. As proposed by LP2005, the parcel model results can be reasonably well expressed in the form $N_c = a N_o^b$ where $a$ and $b$ are functions of $T$, $V$, $D_{g, dry}$ and $\alpha_d$. The dependency of $N_c$ on $N_o$ generally increases when $T$ and $\alpha_d$ decrease and when $V$ increases. For the cases of Figure 9, $b$ lies between 0.19 ($T_o = 233$ K, $V = 0.2$ m s$^{-1}$) and 0.61 ($T_o = 213$ K, $V = 1$ m s$^{-1}$). This is consistent with experimental and numerical studies that report a factor of 2 to 4 increase in $N_c$ for a tenfold increase in $N_o$ [i.e.,Heymsfield and Sabin, 1989; Jensen and Toon, 1994; Seifert et al., 2004].

### 4.3.3. Dependency on $D_{g, dry}$

[32] Figure 10 presents $N_c$ as a function of $D_{g, dry}$ for $T_o = 213$ K (Figure 10, left) and $T_o = 233$ K (Figure 10, right), and $\alpha_d = 0.1$ (black line) and $\alpha_d = 1$ (gray line); for these simulations $V = 1.0$ m s$^{-1}$ and $N_o = 200$ cm$^{-3}$. To apply KL2002, $D_{g, dry}$ was converted into the volume-weighted mean diameter in equilibrium with $S_{t, max}$. In all conditions of Figure 10, parcel model results suggest $N_c$ scales almost linearly with $D_{g, dry}$, which is also found by the combination of equations (29) and (32). This was also observed in LP2005 and is a result of the increased $P_f$ due to the larger volume of the liquid aerosol particles in equilibrium with the aerosol dry distribution (see section 3.3 and equation (9)). An inverse tendency predicted by KL2002 ($N_c \propto D_{g, dry}^{-1}$), and also by the theoretical parameterization (although with a much weaker dependence). In the latter, the effect of increased $P_f$ is not accounted for owing to the assumption of an infinite aerosol source (section 3.1, equation (13)). Although LP2005 does not take into account this dependency, it predicts $N_c$ in agreement with parcel model results at $D_{g, dry} = 80$ nm, and $\alpha_d = 0.1$. SB2000 predictions agree with the parcel model results at $D_{g, dry} = 40$ nm and $T_o = 213$, and at $D_{g, dry} = 120$ nm and $T_o = 233$, when $\alpha_d = 0.1$. The dependence of $N_c$ with $D_{g, dry}$ is much stronger in the left than in the right panel of Figure 10, which suggests once more that size effects would be more important at low $T$ and high $V$. In all cases of Figure 10, the adjusted parameterization closely reproduces the parcel model results. While the comparison of the different parameterizations was carried out over a comprehensive set of conditions, common values of $D_{g, dry}$ often ranges between 40 and 100 nm (and between 100 and 500 cm$^{-3}$ for $N_o$) [e.g., Heymsfield and Miloshevich, 1995; Gayet et al., 2004]. Figures 8–10 show that the effect of $T$ and $V$ variations on $N_c$ is much stronger than that of $D_{g, dry}$.
and \( N_o \). The relative importance of each parameter remains to be assessed in global model studies.

5. Summary and Conclusions

[33] To address the need for improved ice cloud physics in large-scale models, we have developed a physically based parameterization for cirrus cloud formation, which is robust, computationally efficient, and links chemical effects (e.g., water activity and uptake effects) with ice formation via homogenous freezing. This was accomplished by tracing back the growth of ice crystals to their point of freezing, relating their size to freezing probability. Using this approach, an expression for the ice crystal size distribution is derived, the integration of which yields the number concentration.

[34] The parameterization is evaluated against the predictions of a detailed numerical parcel model developed during this study. The parcel model equations were integrated using a Lagrangian particle-tracking scheme; the evolution of the ice crystal size distribution is described by the superposition of growing of monodisperse crystal populations generated by the freezing of single classes (of same size and composition) of supercooled droplets.

[35] Two versions of the parameterization are developed and evaluated; one based solely on theoretical arguments, and one with adjustments in the ice crystal growth rate using numerical parcel simulations. When compared against the predictions of the numerical parcel model over a broad set of conditions, the theoretically based parameterization for \( N_c \) robustly reproduced the results of the parcel model within a factor of two and with an average relative error of about 29%. When numerical simulations are used to adjust the ice crystal growth rate, the relative error was reduced to 1 ± 28%, which is remarkable given the simplicity of the final expression obtained for \( N_c \) and the broad set of conditions tested, and the complexity of the original parcel equations.

[36] The new parameterization presented in this work offers an analytical and physically based relationship between the parameters affecting cirrus ice formation via homogeneous freezing. The prediction skill of the parameterization is robust across a wide range of parameters (e.g., \( \alpha_d \), aerosol characteristics). As shown in Figure 7, the accuracy with which the parameterization reproduces the parcel model results is independent of these parameters. In this regard, only the KL2002 parameterization shares this characteristic; the presented parameterization, however, (1) explicitly links the variables that control the freezing timescale of the particles and (2) successfully reproduces the effect of the aerosol number on \( N_c \).

[37] The results given are applicable for cirrus formation on predominantly homogenous freezing conditions. Frequently, heterogeneous freezing and competition between multiple particle types can significantly impact cloud formation. Both the numerical model and the parameterization can be readily extended to include these processes, and will be the focus of future work.

Notation

\begin{align*}
\alpha, \beta & \quad \text{parameters defined in equation (14).} \\
\alpha_d & \quad \text{water vapor deposition coefficient on ice.} \\
c_p & \quad \text{heat capacity of air.} \\
\Delta H_v & \quad \text{heat of sublimation of water.} \\
D_{c, \text{max}} & \quad \text{diameter of the largest ice particle at } S_{i,\text{max}}. \\
D_v & \quad \text{volume sphere-equivalent diameter of an ice particle.} \\
D_{g,\text{dry}} & \quad \text{geometric mean diameter of the dry aerosol size distribution.} \\
D_o & \quad \text{diameter of a liquid aerosol particle.} \\
D_c & \quad \text{bulk water vapor diffusion coefficient.} \\
f_c & \quad \text{fraction of frozen particles at } S_{i,\text{max}}. \\
g & \quad \text{acceleration of gravity.} \\
\Gamma(D_o, D_c) & \quad \text{growth function defined in equation (20).} \\
\Gamma & \quad \text{effective growth parameter defined in equation (25).}
\end{align*}
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$k(T)$ constant defined in equation (18).

$\kappa_a$ thermal conductivity of air.

$\mu$ parameter defined in equation (20).

$M_{w}, M_a$ molar masses of water and air, respectively.

$n_i(D_o, t)$ ice crystal size distribution function originated at $D_o$.

$n_i(D_i)$ ice crystal size distribution function.

$n_0(D_i)$ liquid aerosol size distribution function.

$\pi_i(D_o)$ average liquid aerosol size distribution function during freezing.

$N_{i,S}$ ice crystal number concentration at $S_{i,max}$.

$N_i$ aerosol number concentration.

$P$ ambient pressure.

$p_i$ ice saturation vapor pressure.

$P_c, P_i(D_o, t)$ cumulative probability of freezing.

$\rho_i, \rho_a$ ice and air densities, respectively.

$R$ universal gas constant.

$\sigma_{g}$ geometric dispersion of the liquid aerosol size distribution.

$\sigma_{g, dry}$ geometric dispersion of the dry aerosol size distribution.

$S_i$ water vapor saturation ratio with respect to ice.

$S_{i, eq}$ equilibrium ice saturation ratio.

$S_{i, max}$ maximum ice saturation ratio.

$S_i$ ice saturation ratio at the beginning of freezing.

$S'_i$ ice saturation ratio at which an ice crystal was formed.

$T$ temperature.

$t$ time.

$t_f$ time of freezing.

$V$ updraft velocity.

$v_o$ volume of a liquid droplet of size $D_o$.

$w_i$ ice mass mixing ratio.

$\psi(D_o, t)$ ice nucleation function.

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