Parameterization of Cirrus Cloud Formation in Large Scale Models:

Homogeneous Nucleation.

Donifan Barahona¹ and Athanasios Nenes¹,²*

¹School of Chemical and Biomolecular Engineering, Georgia Institute of Technology
²School of Earth and Atmospheric Sciences, Georgia Institute of Technology
311 Ferst Dr., Atlanta, GA, 30332, USA

*Corresponding author
Abstract

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 (also developed during this study) where the solution of equations is obtained 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 two and with an average relative error of -15%. If numerical model simulations are used to constraint the parameterization, error further decreases to 1 ± 28%.
1 Introduction

The effect of aerosols on clouds and climate is one of the major uncertainties in anthropogenic climate change assessment and prediction [IPCC, 2007]. Cirrus are of the most poorly understood systems, 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, i.e., 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 grow 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, shape), as well as by the thermodynamical state (i.e., relative humidity, pressure, 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 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 heterogeneous freezing has a stronger impact on cirrus formation over 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; DeMott, et al., 1998; Kärcher and Lohmann, 2003], and at temperatures higher than -38 °C where homogenous nucleation is not probable [Pruppacher and Klett, 1997; DeMott, et al., 2003]. On the other hand, 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, \(J\), i.e., the rate of generation of ice germs per unit of volume. Historically this has been accomplished through 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; DeMott, et al., 1997; 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, there is much to learn on the physical properties of
aqueous solutions and ice at low temperatures. 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 realized 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 a
three order of magnitude difference in the calculation of $J$, which is typical among
models at temperatures above -45 °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, and the precursor aerosol and
thermodynamic state. Empirical correlations derived from observations are available [i.e.,
Koenig, 1972]; their validity however for the whole spectra of cirrus formation
conditions present in a GCM is not guaranteed. 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 parameterization also takes into account 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 theoretically based, these
parameterizations are constrained to a particular set of parameters (i.e., deposition
coefficient, aerosol composition and characteristics) used during the model simulations,
the value of which is still uncertain. Kärcher and Lohmann [2002b; 2002a] introduced a
physically-based parameterization solving analytically the parcel model equations. In
their approach a “freezing time scale” is defined, related to the cooling rate of the parcel,
and used to approximate the 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 time scale, should be prescribed (also, the freezing pulse shape and freezing
time scale may still change with the composition and size of the aerosol particles). An
analytical fit of the freezing time scale based on Koop et al. [2000] data was provided by Ren and Mackenzie [2005]. Kärcher and Lohmann parameterization have 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].

In this work, we develop a new physically-based parameterization for ice formation from homogeneous freezing in which we relax the requirement of prescribed parameters. 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 size distribution, peak saturation ratio, and ice crystal concentration can be computed. The parameterization is then evaluated against a detailed numerical parcel model (also presented 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 even 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 then form an ice crystal distribution with its own composition and characteristics, which if superimposed, will represent the overall ice distribution. In this section 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 pressured to equilibrium vapor pressure over ice), and temperature, $T$, in an adiabatic parcel, with no initial liquid water present, are [Pruppacher and Klett, 1997].

$$\frac{dS_i}{dt} = -\frac{M_w p}{M_w p_i^s} \frac{dw_i}{dt} - (1 + S_i) \left[ \frac{\Delta H_s M_w}{RT^2} \frac{dT}{dt} - \frac{gM_a V}{RT} \right]$$

(1)

$$\frac{dT}{dt} = -\frac{gV}{c_p} - \frac{\Delta H_s}{c_p} \frac{dw_i}{dt}$$

(2)

where $\Delta H_s$ is the latent heat of sublimation of water, $g$ is the acceleration of gravity, $c_p$ is the heat capacity of air, $p_i^s$ is the ice saturation vapor pressure at $T$ [Murphy and Koop, 2005], $p$ is the ambient pressure, $V$ is the updraft velocity, $M_w$ 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

$$w_i = \frac{\rho_i}{\rho_a} \pi \int_{D_{c,\text{min}}}^{D_{c,\text{max}}} \int_{D_{o,\text{min}}}^{D_{o,\text{max}}} D_c^2 n_c(D_c, D_o) dD_c dD_o$$

(3)

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

$$\frac{dw_i}{dt} = \frac{\rho_i}{\rho_a} \pi \int_{D_{c,\text{min}}}^{D_{c,\text{max}}} \int_{D_{o,\text{min}}}^{D_{o,\text{max}}} D_c^2 \frac{dD_c}{dt} n_c(D_c, D_o) dD_c dD_o$$

(4)

where the term $D_c^2 \frac{d\hat{n}_c(D_c, D_o)}{dt}$ was neglected as instantaneous nucleation does not contribute substantially to the depletion of water vapor in the cloudy parcel. The growth term in equation (4) is given by [Pruppacher and Klett, 1997]

$$\frac{dD_c}{dt} = \frac{(S_i - S_{i,\text{eq}})}{\Gamma_1 D_c + \Gamma_2}$$

(5)

with

$$\Gamma_1 = \frac{\rho_i \tau_0}{4 \pi^2 \rho_a M_w} + \frac{\Delta H_{i,\text{f}} \rho_i}{4 k_a T} \left( \frac{\Delta H_{M_w}}{RT} - 1 \right)$$

$$\Gamma_2 = \frac{\rho_i \tau_0}{2 \rho_a M_w \sqrt{\frac{\pi \rho_a M_w}{RT}} \alpha_d}$$

(6)
where \(k_a\) is the thermal conductivity of air, \(D_v\) is the water vapor diffusion coefficient from the gas to ice phase, \(S_{v,eq}\) is the equilibrium ice saturation ratio, and \(\alpha_d\) is the water vapor deposition coefficient.

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

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

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

\[
\left. \frac{\partial n_c(D_c, D_o)}{\partial t} \right|_{D_c = D_o} = n_o(D_o, t) \frac{\partial P_f(D_o, t)}{\partial t} \equiv \psi(D_o, t) \quad ; \quad n_c(D_c, D_o, 0) = 0
\]

where \(n_o(D_o, t)\) 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]

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

and

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

\(J(t)\) is the homogeneous nucleation rate coefficient, and describes the number of ice germs formed per unit of volume of liquid droplets per unit of time [Pruppacher and Klett, 1997].
Equation (7) is a simplified version of the continuous general dynamic equation for 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.

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

\[
\frac{\partial n_o(D_o,t)}{\partial t} = - \frac{\partial}{\partial D_o} \left( n_o(D_o) \frac{dD_o}{dt} \right) - \psi(D_o,t) \tag{11}
\]

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 (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

Equations (1) to (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). At any \( t = t' \), the number of frozen aerosol particles is calculated using (9) and placed in a node of the particle tracking grid, in which their growth is followed. This group of ice crystals represents a particular solution of (7) for
the case in which all particles freeze at the same time and have the same size and composition. Since a particular solution of (7) can be obtained for each time step and droplet size, then the general solution of (7) is given by 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 \( n_o(D_o,t) \), a moving grid is employed, where frozen particles are removed from each size bin (which is in turn updated to its equilibrium size) after each time step.

Since all ice particles are allowed to grow to their exact sizes, the effect of numerical diffusion is small. The discretization of (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, an Euler integration scheme can be used without substantial losses in accuracy. This is at expense of setting a large grid: the total number of nodes in the particle tracking grid is the product of the number of time steps by the number of nodes of the liquid aerosol moving grid. 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],

\[
\frac{\partial n_o(D_o,s,D_o,t)}{\partial t} \bigg|_{D_o=D_o} = \frac{1}{D_{\text{upper}}-D_{\text{lower}}} \int_{D_{\text{lower}}}^{D_{\text{upper}}} n_o(D_o,t) \frac{\partial P_f(D_o,t)}{\partial t} \, dD_o \quad (12)
\]

where \( \overline{D_o} \) is the assumed size of the frozen particles. If all aerosol particles freeze at the same size, the integral in (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 recognizing that the freezing process occurs after some threshold \( S_i \) is reached [Sassen
and Benson, 2000; Kärcher and Lohmann, 2002b]; therefore the initial time step is set to 
$2V^{-1}$ s, and reduced to 0.05$V^{-1}$ s (with $V$ in m s$^{-1}$) when the nucleation event starts ($J > 10^4$
$m^{-3}s^{-1}$), only after which the growth of ice particles is 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 5-6).
$D_o$ was assumed as the equilibrium size at $S$, given by Köhler theory [Pruppacher and
Klett, 1997], and solved iteratively using reported 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 for which 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]). $J$
was calculated using the Koop et al. [2000] parameterization due to its simplicity and its
widely accepted accuracy for a broad range of atmospheric conditions [i.e., Abbatt, et al.,
2006] (in principle any model for $J$ can be used.) 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, $N_o = 200$ 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 $\alpha_{d} = 1$, these simulations are intended to provide a common basis for comparison with other models. 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 $N_{c}$ (cm$^{-3}$) of 0.20, 2.87, 24.06, for the cases Ch004, Ch020 and Ch100, 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 $N_{c}$ around 1.71 cm$^{-3}$ for $T$ between -43 and -53 °C, and $N_{c}$ around 0.78 cm$^{-3}$ for $T$ between -53 and -63 °C with $V$ mainly below 1 m s$^{-1}$, at formation conditions consistent with a homogeneous nucleation mechanism [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 may presuppose a rather simplistic view of the cirrus formation process, and overlook other 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 within the range 20 to 263 K [i.e., Haynes, et al., 1992; Wood, et al., 2001]. Due to these considerations $\alpha_{d}$ is considered in this work a highly uncertain parameter for which more study is required.
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; such link defines $n_c(D_c, D_o)$ at each time 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 $D_c$ down to $D_o$ (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

$$n_c(D_c, D_o) = -\overline{n}_o(D_o) \frac{\partial P_f(S_o')}{\partial D_c}$$

(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 $D_c$, that come from liquid aerosol particles of size $D_o$. $\overline{n}_o(D_o)$ is the average $n_o(D_o)$ during the freezing interval, and is taken to be constant since freezing occurs over a very narrow $S_i$ range [Kärcher and Lohmann, 2002b] and $N_c$ is usually much less than $N_o$ [i.e., Lin, et al., 2002]. 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).
Calculation of $S_o'$ is key for solving equation (13); this is done by combining equations (1) and (2),

$$\frac{dS_i}{dt} = \alpha VS_i - \beta \frac{dw_i}{dt}$$  \hspace{1cm} (14)

where $\alpha = \frac{g\Delta H_s M_w}{c_p RT^2}$, $\beta = \frac{M_o p}{M_w p_i} \gg \frac{\Delta H^2 M_w}{c_p RT^2}$. Before the nucleated ice crystals substantially impact saturation (“free growth”, Figure 3), $\frac{dw_i}{dt} \approx 0$, and the integration of (14) from $S_o'$ to $S_{i,\text{max}}$ gives

$$t - t_o \approx \frac{1}{\alpha V} \left( 1 - \frac{S_o'}{S_{i,\text{max}}} \right)$$  \hspace{1cm} (15)

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 $S_{i,\text{max}}$; for $S_i \rightarrow S_{i,\text{max}}$ 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 $D_c$ (Figure 3), which is found by integration of (5),

$$t - t_o = \frac{1}{(S_i - 1)} \left[ \frac{\Gamma_1}{2} (D_c^2 - D_o^2) + \Gamma_2 (D_c - D_o) \right]$$  \hspace{1cm} (16)

where $S_i$ has been assumed as constant as nucleation occurs in a very narrow $S_i$ range (i.e., Figure 5). The calculation of $P_f (S_o')$ using equation (9) requires the knowledge of $J$ as an explicit function of $S_o'$; this can be further simplified given that nucleation occurs on
a very narrow interval of saturation so that $J(S_i)$ can be approximated related to $J(S_{i,\text{max}})$

$$\ln \frac{J(S_i)}{J(S_{i,\text{max}})} \approx k(T)(S_i - S_{i,\text{max}})$$  \hfill (17)

$k(T)$ is obtained by fitting the Koop et al. [2000] data for $J$ between $10^8$ and $10^{22} \text{m}^{-3}\text{s}^{-1}$,

$$k(T) = 0.01046 T^2 - 3.489 T + 405.6$$  \hfill (18)

with $T$ in K. Using (14) and (17), (9) is solved under the assumption of free growth to give

$$P_f(D_o, S'_o) \approx \frac{1}{\alpha V S_{i,\text{max}}} \int_{S_o}^{S'_o} v_o J(S) dS = \frac{J(S_{i,\text{max}})v_o}{\alpha V k(T) S_{i,\text{max}}} \exp[-k(T)(S_{i,\text{max}} - S'_o)]$$  \hfill (19)

where $v_o = \frac{\pi D_o^3}{6}$, and the approximation $1 - \exp\left(-\int_0^t v_o J(t) dt\right) \approx \int_0^t v_o J(t) dt$ has been used.

The lower integration limit, $S_o$, in (19) represents the beginning of the freezing pulse, assumed to be where $P_f(D_o, S_o) < 10^{-6} P_f(D_o, S_{i,\text{max}})$, i.e.,

$$\exp[-k(T)(S_{i,\text{max}} - S'_o)] \gg \exp[-k(T)(S_{i,\text{max}} - S_o)]$$. The integration is not very sensitive to the latter assumption, as most of the ice crystals form for $S_i$ close to $S_{i,\text{max}}$ [i.e., Kärcher and Lohmann, 2002a]. Combining (15) and (16) to find $S_{i,\text{max}} - S'_o$, and replacing into (19) gives

$$P_f(D_o, D_c) = \frac{J(S_{i,\text{max}})v_o}{\alpha V k(T) S_{i,\text{max}}} \exp[-\mu \Gamma(D_c, D_o)]$$  \hfill (20)
where \( \mu = \frac{\alpha V k(T) S_{i,\text{max}}}{(S_{i,\text{max}} - 1)} \), and \( \Gamma(D_c, D_o) = \frac{\Gamma_1}{2} (D_c^2 - D_o^2) + \Gamma_2 (D_c - D_o) \). The ice number distribution function at \( S_{i,\text{max}} \) is obtained after computing \( \frac{\partial P_f(D_o, D_c)}{\partial D_c} \) from (20) and substituting into (13)

\[
n_c(D_c, D_o) = \overline{\nu}_o(D_o) \frac{J(S_{i,\text{max}}) \nu_o}{(S_{i,\text{max}} - 1)} \left( \Gamma_1 D_c + \Gamma_2 \right) \exp\left[ - \mu \Gamma(D_c, D_o) \right]
\]

Since ice particles attain large sizes after freezing, the spectrum of \( D_c \) values spans over several orders of magnitude \([\text{i.e., DeMott, et al., 1994; Monier, et al., 2006}]. \) Typically variation in \( D_o \) is much smaller; furthermore, \( P_f \) reaches significant values only in a fraction of the liquid droplets (generally those with larger sizes and low solute concentrations \([\text{Pruppacher and Klett, 1997}]\)). With this, the value of \( \exp\left[ - \mu \Gamma(D_c, D_o) \right] \) will be dominated by variation in \( D_c \), and the approximation \( \exp\left[ - \mu \Gamma(D_c, D_o) \right] \approx \exp\left[ - \mu \Gamma(D_c, D_o) \right] \) can be used. Obtaining the crystal size distribution then is done by integration of (21) over the contribution from each droplet size class,

\[
n_c(D_c) \bigg|_{S_{i,\text{max}}} = \overline{\nu}_o(D_o) \frac{J(S_{i,\text{max}})}{(S_{i,\text{max}} - 1)} \left( \Gamma_1 D_c + \Gamma_2 \right) \exp\left[ - \mu \Gamma(D_c, D_o) \right] \int \overline{\nu}_o(D_o) \nu_o \, dD_o
\]

which for a lognormal distribution of \( \overline{\nu}_o(D_o) \) gives

\[
n_c(D_c) \bigg|_{S_{i,\text{max}}} = \frac{N_o \overline{\nu}_o e^{g/2 \ln^2 \sigma_o} J(S_{i,\text{max}})}{(S_{i,\text{max}} - 1)} \left( \Gamma_1 D_c + \Gamma_2 \right) \exp\left[ - \mu \Gamma(D_c, D_o) \right]
\]

or
\[ n_c(\ln D_c)_{\text{Si,max}} = \frac{dN_c}{d \ln D_c} \bigg|_{\text{Si,max}} = N_o \bar{\nu}_o e^{9/2 \ln^2 \sigma_g} D_c J(S_{i,max}) \frac{D_c}{(S_{i,max} - 1)} \exp\left[-\mu \Gamma(D_c, \bar{D}_o)\right] \]

(23b)

where \( \bar{\nu}_o = \frac{\pi}{6} D_o^{3/2} \) and \( \sigma_g \) is the geometric dispersion of the droplet size distribution.

Equation (23) is the final expression used for the size distribution of the ice crystals at \( S_{i,max} \). Equations (21-23) demonstrate the probabilistic character of ice nucleation: at any time particles of all sizes have finite freezing probabilities; i.e., the population of ice crystals of a given size \( D_c \) results from the freezing of droplets with different sizes. From this, the freezing of a monodisperse aerosol size population produces a polydisperse ice crystal population. Since for values below \( S_{i,max} \), \( S_i \) increases monotonically with time, 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 \( S_{i,max} \); that is, the most recently formed crystals will have the largest probability of freezing, i.e., \( P_f(D_c = \bar{D}_o, S_{i,max}) \). The maximum in the distribution may be shifted to \( D_c > \bar{D}_o \) if the time scale for the growth of the newly formed particles is larger than the timescale of change of probability (see section 4).

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

The deposition rate of water vapor upon ice crystals can be approximated by substituting equation (23) into (4),
\[ \frac{dw_i}{dt} = \rho_i \frac{\pi}{\rho_a} N_o \bar{\nu}_o e^{9/2n^2 \sigma o} J(S,_{i,\text{max}}) \int_{D_o}^{D_{c,\text{max}}} D_c^2 \exp \left[ -\frac{\mu}{2\Gamma} (D_c^2 - D_o^2) \right] dD_c \]  

(24)

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 given by [i.e., Fountoukis and Nenes, 2005]

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

(25)

Integration of (24) gives

\[ \frac{dw_i}{dt} = \rho_i \frac{\pi}{\rho_a} N_o \bar{\nu}_o e^{9/2n^2 \sigma o} J(S,_{i,\text{max}}) \frac{e^{\frac{\mu}{2\Gamma} \bar{n}_o^2}}{4 \left( \frac{\mu}{2\Gamma} \right)^{3/2}} \left[ \sqrt{\pi} \text{erf} \left( \frac{\mu}{2\Gamma} \right) - 2 \left( \frac{\mu}{2\Gamma} \right)^{1/2} D_{c,\text{max}} e^{\frac{\mu}{2\Gamma} \bar{n}_o^2} \right] \]  

(26a)

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

\[ \frac{dw_i}{dt} = \rho_i \frac{\pi}{\rho_a} N_o \bar{\nu}_o e^{9/2n^2 \sigma o} J(S,_{i,\text{max}}) \frac{e^{\frac{\mu}{2\Gamma} \bar{n}_o^2}}{4 \left( \frac{\mu}{2\Gamma} \right)^{3/2}} \left( \frac{2\mu}{\pi\Gamma} \right)^{3/2} \]  

(26b)

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

\[ \alpha V S,_{i,\text{max}} = \beta \frac{\rho_i}{\rho_a} N_o \bar{\nu}_o e^{9/2n^2 \sigma o} J(S,_{i,\text{max}}) \frac{e^{\frac{\mu}{2\Gamma} \bar{n}_o^2}}{4 \left( \frac{\mu}{2\Gamma} \right)^{3/2}} \]  

(27)
the fraction of frozen particles, \( f_c \), at \( S_{i,\text{max}} \) is found at the maximum \( P_f \), given by (20)

\[
f_c = \frac{1}{N_o} \int \bar{n}_o(D_o) P_f(D_o = \bar{D}_o, D_o) dD_o = \frac{\bar{v}_o e^{\frac{\beta}{2}}}{\alpha \eta \sigma_i} J(S_{i,\text{max}})
\]

combining (27) and (28) we arrive at,

\[
f_c = \frac{\rho_a}{\rho_i} \frac{[k(T)]^{1/2}}{\beta N_o} \left( \frac{2 \alpha \eta \sigma_i}{\pi \Gamma(S_{i,\text{max}} - 1)} \right)^{3/2} \exp \left( -\frac{\alpha V k(T) S_{i,\text{max}}}{2 \Gamma(S_{i,\text{max}} - 1) \bar{D}_o^2} \right)
\]

The exponential term in (29) approaches unity, which is a result of the assumption made in (13) that freezing depletes a negligible amount of aerosol (i.e., \( \bar{n}_o(D_o) \) is constant during the nucleation process). Since the term \( J(S_{i,\text{max}}) \) has been eliminated from (29), \( f_c \) is not strongly influenced by small variations in \( S_{i,\text{max}} \). Thus, \( S_{i,\text{max}} \) can be taken as the saturation freezing threshold obtained solving the Koop et. al. [2000] parameterization for \( J(S_{i,\text{max}}) = 10^{16} \text{ s}^{-1} \text{ m}^{-3} \), which is close to the nucleation rate of pure water at -38 °C [Pruppacher and Klett, 1997; Sassen and Benson, 2000], and represents an average of \( J(S_{i,\text{max}}) \) over a wide set of simulations (section 4). The total number of crystals would be given by, \( N_c = N_o f_c \), however such result will not be constrained by \( N_o \) as upper limit.

Instead, purposely contradicting the assumption made in (19), \( f_c \) can be associated with the solution of the integral in (9), i.e., \( f_c \approx \int_0^t v_o J(t) dt \) and then write

\[
N_c = N_o e^{-f_c} (1 - e^{-f_c})
\]

where \( N_o e^{-f_c} \) represents the number of remaining unfrozen droplets.


3.3 Calculation of $D_{c,s_{\text{max}}}$

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

$$D_{c,s_{\text{max}}}^2 + \frac{2\Gamma_2}{\Gamma_1}D_{c,s_{\text{max}}} = \frac{2\ln(10^{-6})(S_{i,\text{max}} - 1)}{\alpha V k(T)S_{i,\text{max}} \Gamma_1} = 0$$

(31)

where we have assumed $D_{c,s_{\text{max}}} >> D_o$ (supported by numerical simulations).

Since $\Gamma_2 \propto \frac{1}{\alpha_d}$ (Equation (6)), the value of $D_{c,s_{\text{max}}}$ would increase as $\alpha_d$ decreases. For low values of $\alpha_d$ ice crystals grow slowly, and non-continuum 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 condensate preferentially to preexisting ice crystals. Slow uptake effects became important for $\alpha_d$ lower than 0.1, i.e, when $\Gamma_1$ becomes comparable to $\Gamma_2$ [Lin, et al., 2002; Gierens, et al., 2003]. Alternatively, $D_{c,s_{\text{max}}}$ can be computed using an empirical fit to numerical simulations obtained with the parcel model,

$$D_{c,s_{\text{max}}} = \min\left\{1.6397 \times 10^{-14} T - 3.1769 \times 10^{-12} V^{-0.05} (N_o D_{g,\text{dry}})^{-0.373}; 10^{-4}\right\}$$

(32)

where $V$ is in m s$^{-1}$, $T$ is in K, $N_o$ in cm$^{-3}$ and $D_{g,\text{dry}}$ in m. Equation (30) was generated over a broad set of $T$, $p$, $V$, $N_o$, $D_{g,\text{dry}}$, and $\alpha_d$ (Table 1, section 4). The $T$ and $V$
dependencies in (32) are introduced to adjust the effective growth of the particles correcting for the “free growth” assumption (section 3.1). Additional variability not taken into account in the formulation of (30) is caused by the effect of variation in the aerosol properties. Since \( n_o(D_o) \) is in equilibrium with the dry aerosol size distribution, an increase \( D_{g,dry} \) will increase the total volume of the liquid aerosol particles therefore increasing \( P_f \). 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, which explains the approximated dependency of \( D_{c,S_{\text{max}}} \) on the average volume of the dry aerosol population, i.e., \( \sim \left( n_o D_{g,dry}^3 \right)^{1/3} \) (equation (32)).

### 3.4 Implementation of the Parameterization

The application of the parameterization is presented in Figure 4. As input, one requires the conditions of cloud formation \( T, P, V, \) and \( \alpha_d \) and the aerosol characteristics (i.e., \( N_o \) and \( D_{g,dry} \)); the outputs are \( N_c \) and size distribution information. To apply the parameterization, first \( \Gamma \) is calculated (Equation (25)) using \( D_{v,S_{\text{max}}} \) estimated using either Equation (31) or (32), the latter being preferred. \( S_{l,\text{max}} \) is obtained by solving

\[
J(S_{i,\text{max}}) = 10^{16} \text{ s}^{-1} \text{ m}^{-3} \quad [\text{Koop, et al., 2000}], \quad \text{for which reported fits, relating } S_{l,\text{max}} \text{ at } J(S_{i,\text{max}}) = 10^{16} \text{ s}^{-1} \text{ m}^{-3} \text{ to } T, \text{ can be employed} \quad [\text{i.e., Ren and Mackenzie, 2005}]. \quad N_c \text{ is calculated from (30) using } f_c \text{ calculated from (29). After } f_c \text{ is calculated, } J(S_{i,\text{max}}) \text{ can be corrected using } J(S_{i,\text{max}}) = \frac{f_c \alpha V S_{i,\text{max}}}{V_o e^{9/2 \ln^2 \sigma_g}} \quad (\text{equation (27)) from where } n_c(D_e, D_o) \text{ is obtained (equations (21-23))}. \quad \text{There is still uncertainty regarding the values of } \alpha_d \text{ and the aerosol}
characteristics [Lin, et al., 2002]; the sensitivity of the parameterization results to these parameters is discussed in the next section.

4 Evaluation of the Parameterization

The parameterization was evaluated against the detailed numerical solution of the parcel model over a wide range of $T$, $V$, $D_{g, \text{dry}}$, $N_{\text{dry}}$, and $\alpha_d$ (Table 1), in a total of 1200 runs, covering the expected variation in cirrus cloud formation conditions in a GCM simulation. The parcel model was run using initial $S_i = 1.0$; initial $p$ was estimated as in hydrostatic equilibrium at $T$ using a dry adiabatic lapse rate. The dry aerosol population was assumed to be pure H$_2$SO$_4$, lognormally distributed. To test aged, unperturbed, and perturbed aerosol runs the geometric dispersion of the dry aerosol distribution, $\sigma_{g, \text{dry}}$ was selected to be 1.7, 2.3 and 2.9 respectively [Seinfeld and Pandis, 1998]. The liquid aerosol was assumed to be in equilibrium with $S_i$ in all simulations. Calculated $N_c$ ranged from 0.001 to 100 cm$^{-3}$ and $S_{i,\text{max}}$ varied between 1.4 and 1.6 which agrees the range on 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, i.e., the calculation of $N_c$ at $S_{i,\text{max}}$ rather than at the end of the freezing pulse, i.e., $N_c \approx N_c |_{S_{i,\text{max}}}$; and the assumption of negligible impact of the newly formed crystals 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 m s$^{-1}$, 233-203 K). By using free growth regime to estimate the evolution of $S_i$ (dotted black line),
$S_{i,\text{max}}$ is overestimated by about 0.5% at low $V$ (bottom left) to about 2% at high $V$ (top right). At high $T$ (right panels) such overestimation is not expected to exert a large influence in the performance of the parameterization as low values of $S_{i,\text{max}}$ are reached. Therefore the small overestimation in $S_{i,\text{max}}$ will not significantly influence $J(S_{i,\text{max}})$ (which is a very nonlinear function $S_{i,\text{max}}$). However, as $T$ decreases and $V$ increases, $S_{i,\text{max}}$ reaches higher values during the parcel ascent and small changes in $S_{i,\text{max}}$ significantly impact $J$ (hence $P_f$), for which an overestimation in $N_c$ may be expected. Conversely, Figure 5 shows that at low $V$ (bottom panels), $N_c\big|_{S_{i,\text{max}}}$ 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 $V$ (top panels) $N_c\big|_{S_{i,\text{max}}}$ 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 $n_c(D_c)$

The parameterized $n_c(D_c)$, equation (23b), is presented for two representative cases in Figure 6, along with $n_c(D_c)\big|_{S_{i,\text{max}}}$ obtained from parcel model simulations. Although the effect of the droplet size distribution parameters is explicitly considered in (23) it cancels out with its effect on $f_c$ (which is a result of the assumption constant $\bar{n}_o(D_o)$), and a single crystal size distribution is obtained for the three values of $\sigma_{g,\text{dry}}$ tested (although small variations in $n_c(D_c)\big|_{S_{i,\text{max}}}$ may occur due to differences in $T$ at $S_{i,\text{max}}$), this is not critical as $N_c$ variations with respect to $\sigma_{g,\text{dry}}$ are generally small (i.e., Figure 6). $\bar{D}_o$ was
assumed as the equilibrium size of $D_{g,\text{dry}}$ at $S_{i,\text{max}}$. $n_c(D_c)$ was calculated using the procedure outlined in section 3.4 (Figure 4) in which $J(S_{i,\text{max}})$ is corrected using equations (30) and (32) (therefore enforcing $N_c \approx \int_{D_c=D_{g,\text{mm}}}^{D_c=S_{i,\text{max}}} n_c(D_c) dD_c$). Generally, the parameterized $n_c(D_c)$ reproduces well the numerical results at $S_{i,\text{max}}$, however, it predicts a continuous size distribution down to $\overline{D}_n$, which differs from the numerical results. This can be explained due to the discrete nature of the size distribution (and of the numerical method). After freezing, the newly formed ice crystals “jump” to larger sizes leaving gaps in the distribution, and eliminating part of the left-tail of the size distribution. Due to the continuous nature of the parameterized $n_c(D_c)$, it would tend to overpredict $N_c|_{S_{i,\text{max}}}$.

The adjusted $J(S_{i,\text{max}})$ will then be slightly below the obtained in numerical simulations to satisfy $N_c = N_c|_{S_{i,\text{max}}}$. This works well in the cold case ($T=213$, $V=1$ m s$^{-1}$, Figure 6, left) as more crystals are to be produced after $S_{i,\text{max}}$ is reached. However in the warm case ($T=233$, $V=0.2$ m s$^{-1}$, Figure 6, right), the freezing pulse is shorter and the correction in $J(S_{i,\text{max}})$ produces a reduction in the peak of the 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 future works.
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 $D_{c,s_{\text{max}}}$ (right, equation (31)) and using the empirical correlation for $D_{c,s_{\text{max}}}$ (left, equation (32)). The effects of the assumption of “free growth” and the approximation of $N_c$ as $N_c \big|_{s_{\text{max}}}$ 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; the opposite tendency occurs at very high $V$ (>2 m s$^{-1}$) and low $T$ (hence, high $N_c$). This latter is not significant as such conditions are not typical of cirrus formation [i.e., Heymsfield and Sabin, 1989; Gayet, et al., 2004]. In summary, using the theoretically calculated $D_{c,s_{\text{max}}}$ gives a parameterized $N_c$ always within a factor of 2 of the $N_c$ predicted by the parcel model with a mean relative error about -15% (for all runs in Table 1). When using the empirically calculated $D_{c,s_{\text{max}}}$ (equation (32)) is used, 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 effect of aerosol size and number.

4.3 Comparison Against Other Parameterizations

The parameterization results were compared to those of several reported works for different combinations of $V$, $N_\alpha$, $D_{g,\text{dry}}$, $T$, and $a_d$. The parameterizations used in this section are those of Liu and Penner [2005, hereafter LP2005], Sassen and Benson [2000, hereafter SB2000], and Kärcher and Lohmann, [2002a, hereafter, KL2002; 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 $N_c$ on $T$, $V$, $\alpha_d$, and $D_o$, and uses $N_o$ as upper limit for $N_c$. Although the freezing of polydisperse aerosol is discussed in KL2002 not explicit solution is presented, therefore their monodisperse solution is 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 $D_{c,max}$, equation (31) (termed “theoretical”, still $k(T)$, equation (18), has been derived from an empirical fit to $J$), and using the empirically adjusted $D_{c,max}$ equation (32), (termed “adjusted”). $D_o$ was calculated as the equilibrium size of $D_{g,dry}$ at $S_{i,max}$. All parameterizations are evaluated using $T$ obtained at $S_{i,max}$ from the parcel model simulations. $\alpha_d$ was set to 0.1 and 1.0 to test both diffusionally and non-diffusionally limited cases (see section 3.3).
Dependency on $V$

Figure 8 presents the comparison of the different parameterizations at $T_o = 213$ (left panel, $T$ between 208.6 and 209.4 K) and 233 K (right panel, $T$ between 228.8 and 229.2 K), and $a_d = 0.1$ (black) and 1.0 (blue). At $T_o = 233$ K, all parameterizations agree fairly well when $a_d = 0.1$ 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, although the difference becomes significant only for $V > 3 \text{ m s}^{-1}$. At these conditions the adjusted parameterization follows well the parcel model results whereas the theoretical parameterization slightly underpredicts $N_c$ at low $V$. Runs made using $a_d = 1$ (blue) showed a good agreement between KL2002, the adjusted and theoretical parameterizations, and the numerical results. This is expected as equation (28) bears the same dependency on $V$ and $p_i^o$, reported by KL2002 in their “fast growth” solution (i.e., $N_c \propto V^{3/2}$) and emphasized by more recent works [Gierens, 2003; Ren and Mackenzie, 2005]. At high $f_c$ (i.e., low $T$, low $a_d$, and high $V$) the exponential term in (30) dampens the effect of $V$ (also due to the dependency of $D_{c,s_{max}}$ on $V$) and $N_c$ becomes almost linear on $V$. Results at $a_d = 1$ lie below those of LP2005 and SB2000, who used lower $a_d$ values for their numerical simulations (LP2005 used $a_d = 0.1$ and SB2000 used $a_d = 0.36$ [Lin, et al., 2002]). At $T_o = 213$ K, and $a_d = 0.1$ (left, black), the parameterizations agree only for $V$ below 0.3 m s$^{-1}$ whereas for large $V$ they diverge, being $N_c$ calculated using KL2002, the largest over the whole $V$ interval. At very high $V$ ($>3 \text{ m s}^{-1}$) the adjusted parameterization underpredicts $N_c$ with respect to the parcel model results which is a result of the exponential term introduced in (30). As with $T_o = 233$ K, KL2002, and the adjusted and
theoretical parameterizations agree well with the numerical results when $\alpha_d = 1$, and $T_o=213$ K (left, blue).

Dependency on $N_o$

Figure 9 presents $N_c$ as a function of $N_o$ for $V=0.2$ m s$^{-1}$ (left) and $V=1.0$ m s$^{-1}$ (right) and $T_o=213$ (black) and 233 K (blue); for these simulations $D_{g,dry}$ 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$^{-1}$, the adjusted parameterization underpredicts with respect to the numerical results, for $N_o$ below 20 cm$^{-3}$ whereas LP2005 overpredicts; in both cases the difference with the parcel model results is about $\pm 50\%$, 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 a larger $N_c$ than the parcel model, however the difference becomes much smaller at large $N_o$. In the same interval of $N_o$, SB2000 predicts $N_c$ close to the average of the parcel model results at $T_o=213$ K; when $T_o=233$ K, SB2000 predicts $N_c$ close to the parcel model results at large $N_o$. The theoretical parameterization shows the opposite tendency and tends to agree better with the parcel model results at low $N_o$. In most of the cases the parcel model results can be reasonable well fitted in the form $N_c = aN_o^b$ where $a$ and $b$ are functions of $T$, $V$, $D_{g,dry}$ and $\alpha_d$ (also proposed in LP2005). The dependency of $N_c$ on $N_o$ generally increases when $T$ and $\alpha_d$ decrease, and $V$ 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 in good agreement with experimental and numerical studies that usually report an
increase in $N_c$ by a factor between 2 and 4 for a 10-fold increase in $N_o$ [i.e., Heymsfield and Sabin, 1989; Jensen and Toon, 1994; Seifert, et al., 2004].

Dependency on $D_{g, \text{dry}}$

Figure 10 presents $N_c$ as a function of $D_{g, \text{dry}}$ for $T_o=213$ (left) and $T_o=233$ (right), and $\alpha_d = 0.1$ (black) and $\alpha_d = 1$ (blue); for these simulations $V=1.0 \text{ m s}^{-1}$ and $N_o = 200 \text{ cm}^{-3}$. To apply KL2002, $D_{g, \text{dry}}$ was converted into the volume-weighted mean diameter in equilibrium with $S_{i,\text{max}}$; however $N_c$ results in Figure 10 are plotted using the original $D_{g, \text{dry}}$. In all conditions of Figure 10 parcel model results suggest an approximated linear dependency of $N_c$ with $D_{g, \text{dry}}$, which is also found by the combination of equations (29) and (32). This 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)), which was also observed in LP2005. This result is opposite to the tendency predicted by KL2002 ($N_c \propto \bar{D}_a^{-1}$), and also (although much more slightly) by the theoretical parameterization. In the latter, the effect of increased $P_f$ is not accounted for due 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 $D_{g, \text{dry}} = 80 \text{ nm}$, and $\alpha_d = 0.1$. SB2000 predicted $N_c$ agrees with the parcel model results at $D_{g, \text{dry}} = 40 \text{ nm}$ and $T_o=213$, and at $D_{g, \text{dry}} = 120 \text{ nm}$ and $T_o=233$, when $\alpha_d = 0.1$. If a linear fit is adjusted to the cases shown in Figure 10 then its slope will decrease from 0.32 at $T_o=213$ and $\alpha_d = 0.1$ to 0.015 at $T_o=233$ and $\alpha_d = 1$, which indicates again that these effects would be more important at low $T$ and high $V$. In all cases of Figure 10 the adjusted parameterization reproduces closely 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 vary between 40-100 nm (and between 100-500 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

To address the need for improved physics of ice cloud formation in large scale models, we have developed a parameterization for cirrus clouds 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, in a given ice saturation profile, connecting their size to their freezing probability. Using this approach, an expression for the crystal size distribution is derived, the integration of which yields the number concentration of crystals, and compared against the solution of a detailed parcel model. The numerical solution of the parcel model was accomplished by using a Lagrangian particle tracking scheme. In this method the evolution of the ice crystal size distribution is described by the superposition and growth of monodisperse crystal populations generated by the freezing of single classes (of same size and composition) of supercooled droplets.
The parameterized ice crystal size distribution captured well the characteristics of the ice crystal population and represents a robust approximation to calculate $N_c$. Its integration to find $N_c$ was carried out either using complete theoretical arguments or their combination with parcel model results. When compared against the predictions of the numerical parcel model over a broad set of conditions, the theoretically based parameterization for $N_c$ reproduced the results of the parcel model within a factor of two and with an average relative error of about -15%. Adjustments in the ice crystal growth rate (using numerical simulations) further reduced the relative error to $1 \pm 28\%$, which is remarkable given the simplicity of the final expression obtained for $N_c$, the broad set of conditions tested, and the complexity of the parcel model equations.

Due to its analytical nature the proposed parameterization presented in this work offers explicitly relation between variables, that as analyzed in the last section goes beyond scaling factors, and it is not constrained to a single set of parameters (i.e., $\alpha_d$, aerosol characteristics) which is desirable due to the large uncertainty associated with them. As shown in Figure 7 the accuracy with which the parameterization reproduces the parcel model results, is independent of these parameters. In this regards, only the KL2002 parameterization shares this advantages, however the presented parameterization offers explicitly the relation between the different variables that determine the freezing time scale of the particles, and explicitly considers the effect of the aerosol number on $N_c$.

This work offers a new, alternative approach to the description of cirrus formation and its representation in large scale models. The results given are applicable for cirrus formation
on predominantly homogenous freezing conditions. Still, in a number of cases heterogeneous freezing and competition between multiple particle types significantly affect the cloud formation process. Both the numerical model and the parameterization can be readily extended to include these effects, which will be the focus of future work.

6 Acknowledgments

This study was supported by NASA MAP, NASA EOS-IDS-CACTUS, and a NASA New Investigator Award. We would also like to thank Dr. B.Kahn for his comments on the manuscript.

APPENDIX

List of Symbols

\( \alpha, \beta \) Parameters defined in equation (14)
\( \alpha_d \) Water vapor to ice deposition coefficient
\( c_p \) Heat capacity of air
\( \Delta H_s \) Heat of sublimation of water
\( D_{c,S_{\text{max}}} \) Diameter of the largest ice particle at \( S_{i,\text{max}} \)
\( D_c \) Volume sphere-equivalent diameter of an ice particle
\( D_{g, \text{dry}} \) Geometric mean diameter of the dry aerosol size distribution
\( D_o \) Diameter of a liquid aerosol particle
\( D_v \) Bulk water vapor diffusion coefficient
$f_c$ Fraction of frozen particles at $S_{i,max}$

g Acceleration of gravity

$\Gamma(D_c, D_o)$ Growth function defined in equation (20)

$\bar{\Gamma}$ Effective growth parameter defined in equation (25)

$\Gamma_1, \Gamma_2$ Parameters defined in equation (6).

$J$ Nucleation rate coefficient

$k(T)$ Constant defined in equation (18)

$k_a$ Thermal conductivity of air

$\mu$ Parameter defined in equation (20)

$M_w, M_a$ Molar masses of water and air, respectively

$n_c(D_c, D_o)$ Ice crystal number distribution function originated at $D_o$

$n_c(D_c)$ Ice crystal number distribution function

$n_a(D_o)$ Liquid aerosol size distribution function

$\bar{n}_a(D_o)$ Average liquid aerosol size distribution function during freezing

$N_c|_{S_{i,max}}$ Ice crystal number concentration at $S_{i,max}$

$N_c$ Ice crystal number concentration

$N_o$ Aerosol number concentration

$p$ Ambient pressure

$p_i^o$ Ice saturation vapor pressure

$P_f, P_f(D_o, t)$ Cumulative probability of freezing

$\rho_i, \rho_a$ Ice and air densities, respectively
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>$\sigma_g$</td>
<td>Geometric dispersion of the liquid aerosol size distribution</td>
</tr>
<tr>
<td>$\sigma_{g,\text{dry}}$</td>
<td>Geometric dispersion of the dry aerosol size distribution</td>
</tr>
<tr>
<td>$S_l$</td>
<td>Water vapor saturation ratio with respect to ice</td>
</tr>
<tr>
<td>$S_{l,\text{eq}}$</td>
<td>Equilibrium ice saturation ratio</td>
</tr>
<tr>
<td>$S_{l,\text{max}}$</td>
<td>Maximum ice saturation ratio</td>
</tr>
<tr>
<td>$S_o$</td>
<td>Ice saturation ratio at the beginning of freezing</td>
</tr>
<tr>
<td>$S_{o,\text{'}t}$</td>
<td>Ice saturation ratio at which an ice crystal was formed</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$t_o$</td>
<td>Time of freezing</td>
</tr>
<tr>
<td>$V$</td>
<td>Updraft velocity</td>
</tr>
<tr>
<td>$v_o$</td>
<td>Volume of a liquid droplet of size $D_o$</td>
</tr>
<tr>
<td>$w_i$</td>
<td>Ice mass mixing ratio</td>
</tr>
<tr>
<td>$\psi(D_o, t)$</td>
<td>Ice nucleation function</td>
</tr>
</tbody>
</table>
7 References


Gershenzon, M., P. Davidovits, L. R. Williams, Q. Shin, J. T. Jayne, C. H. Kolb, and D. R. Worsnop (2004), Uptake of H$_2^{17}$O(g) and D$_2$O(q) by aqueous sulfuric acid droplets, *J. Phys. Chem. A*, 108, 1567-1573.


IPCC (2007), *Climate change 2007: the physical basis. Contribution of working group I to the fourth assessment report of the Intergovernmental Panel on Climate*


Penner, J. E., D. H. Lister, D. J. Griggs, D. J. Dokken, and M. McFarland (1999), *Aviation and the global atmosphere - A special report of IPCC working groups I*
and III. Intergovernmental Panel on Climate Change., 365 pp., Cambridge University Press.


Table 1. Cloud formation conditions used in evaluation.

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

**Figure 1.** Lagrangian particle-tracking scheme for a hypothetical population of two liquid droplets during three successive time steps. Circles represent supercooled liquid droplets, and hexagons ice crystals. Black arrows indicate growth and aging whereas red arrows onset of freezing. Transition of light to darker shady indicates temporal evolution.

**Figure 2.** Sketch of the parameterization concept. Circles represent supercooled liquid droplets, and hexagons ice crystals.

**Figure 3.** $S_i$, $N_c$, and ice water content (IWC) profiles obtained from the numerical solution of the parcel model. Cases considered are those of Lin et al. [2002]. Solid lines indicates $T_o = 233$ K and dashed lines $T_o = 213$ K. $V$=0.04 m s$^{-1}$ (upper), 0.2 m s$^{-1}$ (middle), and 1 m s$^{-1}$ (lower).

**Figure 4.** Parameterization algorithm.

**Figure 5.** $S_i$ (red, left axes) and $N_c$ (blue, right axes) evolution calculated by the parcel model. $T$ and $V$ conditions shown are 233 K and 1 m s$^{-1}$ (top right), 203 K and 1 m s$^{-1}$ (top left), 233 K and 0.04 m s$^{-1}$ (bottom right), 203 K and 0.04 m s$^{-1}$ (bottom left). Dashed lines represent the time at which $S_{i,max}$ is reached and dotted lines $S_i$ evolution under “free growth”.

**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. $D_{c,s,max}$ was calculated using either equation (31) (right) or (32) (left).
Gray scale represents the value of $\alpha_d$ used in the calculations; dashed lines represent the ± 50 % difference.

**Figure 8.** Ice crystal number concentration as a function of the updraft velocity, calculated using the parcel model (symbols), KL2002 (dashed line), LP2005 (dashed-dotted line), SB2000 (dotted line), and the theoretical (stars), and adjusted (solid line) parameterizations. Results are shown for $T=233$ K, $p=34000$ Pa (right) and $T=213$ K, $p=17000$ Pa (left), and $\alpha_d = 0.1$ (black) and $\alpha_d = 1.0$ (blue). $N_o=200$ cm$^{-3}$, and $D_{g,dry} = 40$ nm.

**Figure 9.** Ice crystal number concentration as a function of the aerosol number concentration. Symbols as in Figure 8. Results are shown for $V= 0.2$ m s$^{-1}$ (left) and 1 m s$^{-1}$, and $T=233$ K, $p=38812$ Pa (blue) and $T=213$ K, $p=27350$ Pa (black). $\alpha_d = 0.1$, and $D_{g,dry} = 40$ nm.

**Figure 10.** Ice crystal number concentration as a function of the aerosol mean dry diameter. Symbols as in Figure 8. Results are shown for $T=233$ K, $p=34000$ Pa (right) and $T=213$ K, $p=17000$ Pa (left), and $\alpha_d = 0.1$ (black) and $\alpha_d = 1.0$ (blue). $N_o=200$ cm$^{-3}$, and $V= 1$ m s$^{-1}$. 
FIGURE 1
FIGURE 2
**FIGURE 3**

- Parcel ice saturation
- \( S_{i,\text{max}} \)
- \( S_o' \)
- \( S_o \)
- Ice germ
- "free growth"
- "growth tracing-back"
- \( t_0 \)
- \( t \)
Input: $p$, $T$, $V$, $\alpha_d$ and aerosol characteristics.

Calculate $D_{c,\varepsilon_{\text{max}}}$, $\Gamma$

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

$$f_c = \frac{\rho_e}{\rho_i} \frac{[k(T)]^{1/2}}{\beta N_e} \left[ \frac{2 \alpha V S_{\varepsilon_{\text{max}}}}{\pi \Gamma(S_{\varepsilon_{\text{max}}}-1)} \right]^{3/2} \exp \left[ -\frac{\alpha V k(T) S_{\varepsilon_{\text{max}}}}{2 \Gamma(S_{\varepsilon_{\text{max}}}-1) D_c^2} \right]$$

Output: $N_c = N_0 e^{-f_c} (1 - e^{-f_c})$

Re-calculate $J(S_{\varepsilon_{\text{max}}}) = \frac{f_c \alpha V S_{\varepsilon_{\text{max}}}}{\Gamma(u_e) \varepsilon_{\text{max}} \sigma_e}$

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

FIGURE 4
FIGURE 5
FIGURE 6
FIGURE 7
FIGURE 8
FIGURE 9
FIGURE 10