Atmos. Chem. Phys. Discuss., 11, 29601–29646, 2011 www.atmos-chem-phys-discuss.net/11/29601/2011/ doi:10.5194/acpd-11-29601-2011 © Author(s) 2011. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

# On the ice nucleation spectrum

## D. Barahona

Global Modeling and Assimilation Office, NASA Goddard Space Flight Center, Greenbelt, Maryland, USA

I.M. Systems Group Inc., Rockville, Maryland, USA

Received: 5 October 2011 - Accepted: 22 October 2011 - Published: 2 November 2011

Correspondence to: D. Barahona (donifan.o.barahona@nasa.gov)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Discussion Pap	AC 11, 29601–4	<b>ACPD</b> 11, 29601–29646, 2011									
oer	On the ice spec	nucleation trum									
Discu	D. Baı	D. Barahona									
ission P	Title	Title Page									
aper	Abstract	Introduction									
_	Conclusions	References									
Discu	Tables	Figures									
oissr	14	►I.									
n Pa	•	•									
per	Back	Close									
—	Full Scre	een / Esc									
Discuss	Printer-frier	ndly Version									
sion	Interactive	Discussion									
Paper	œ	<b>()</b> BY									

## Abstract

This work presents a novel formulation of the ice nucleation spectrum, i.e. the function relating the ice crystal concentration to cloud formation conditions and aerosol properties. The new formulation relies on a statistical view of the ice nucleation process and explicitly accounts for the dependency of the ice crystal concentration on temperature, supersaturation, cooling rate, and particle size, and, in the case of heterogeneous ice nucleation, on the distributions of particle area and surface composition. The new formulation is used to generate ice nucleation parameterizations for the homogeneous freezing of cloud droplets and the heterogeneous deposition ice nucleation on dust and soot ice nuclei. For homogeneous freezing, it was found that by increasing the

- and soot ice nuclei. For homogeneous freezing, it was found that by increasing the dispersion in the droplet volume distribution the fraction of supercooled droplets in the population increases. For heterogeneous ice nucleation it was found that ice nucleation on efficient ice nuclei (IN) shows features consistent with the singular hypothesis (characterized by a lack of temporal dependency of the ice nucleation spectrum) whereas
- <sup>15</sup> less efficient IN tend to display stochastic behavior. Analysis of empirical nucleation spectra suggested that inferring the aerosol heterogeneous ice nucleation properties from measurements of the onset supersaturation and temperature may carry significant error as the variability in ice nucleation properties within the aerosol population is not accounted for. This work provides a simple and rigorous ice nucleation framework were theoretical predictions, laboratory measurements and field campaign data can be
- reconciled, and that is suitable for application in atmospheric modeling studies.

## 1 Introduction

Aerosol emissions impact the formation of ice and mixed-phase clouds by modifying the background concentration of ice-forming particles (e.g. Rosenfeld and Woodley,

25 2000; DeMott et al., 2003a; Pratt et al., 2009; Prenni et al., 2009; Lohmann and Feichter, 2005; IPCC, 2007; Barahona et al., 2010; Hoose et al., 2010). Satellite retrievals suggest that cloud condensation nuclei (CCN) emissions may decrease the



average size of cloud droplets and "delay" homogeneous ice nucleation in convective clouds (Rosenfeld and Woodley, 2000; Ramanathan et al., 2001). Ice nuclei (IN) emissions may lead to enhanced competition between homogeneous and heterogeneous ice nucleation reducing the ice crystal concentration in cirrus clouds (Barahona et al.,

- <sup>5</sup> 2010; Kärcher et al., 2006; DeMott et al., 1994). IN emissions can also increase the cloud glaciation temperature in mixed-phase clouds leading to enhanced precipitation (Lohmann, 2002; Lohmann and Diehl, 2006; Diehl et al., 2007). Accounting for these effects in atmospheric modeling studies requires a link between the ice crystal number concentration, cloud formation conditions (i.e. saturation ratio with respect to ice,  $S_i$ ,
- and temperature, *T*) and the aerosol physicochemical properties. Such relation is usually termed the "ice nucleation spectrum",  $N_c(S_i, T,...)$  (Barahona and Nenes, 2009; Meyers et al., 1992; Pruppacher and Klett, 1997). Laboratory and field campaign data have been used extensively to generate expressions for  $N_c(S_i, T,...)$  (e.g. DeMott et al., 2010; Meyers et al., 1992; Phillips et al., 2008; Murray et al., 2011; Welti et al., 2009; Möhler et al., 2006; Vali, 1994), however theoretical prediction of  $N_c(S_i, T,...)$  remains
- a challenge.

Classical nucleation theory (CNT) is often used to calculate the nucleation rate coefficient, J, which when integrated over the appropriate time scale gives  $N_c(S_i, T, ...)$  (e.g. Khvorostyanov and Curry, 2004; Liu and Penner, 2005; Hoose et al., 2010; Chen et al.,

- 20 2008; Pruppacher and Klett, 1997; Barahona and Nenes, 2009). CNT-based models are usually associated with the so-called "stochastic hypothesis" (Pruppacher and Klett, 1997), where all particles in the aerosol population are assumed to have the same ice nucleation probability. Application of this approach to the homogeneous freezing of liquid droplets has shown agreement with experimental results (e.g. Khvorostyanov).
- <sup>25</sup> and Sassen, 1998; Liu and Penner, 2005; Koop et al., 2000). However, for heterogeneous ice nucleation it provides only a rough approximation to the ice nucleation properties of ambient aerosol (Marcolli et al., 2007; Murray et al., 2011; Lüönd et al., 2010) and often requires empirical constraints to reproduce observations (Eidhammer et al., 2009; Phillips et al., 2008; DeMott et al., 2010).



The assumptions behind CNT however do not require that all particles in an aerosol population should have the same heterogeneous ice nucleation probability, just that all surfaces of the same composition and structure do (Kashchiev, 2000). In fact, due to the heterogeneity of ambient particles, some variation in the particle surface prop-<sup>5</sup> erties within an aerosol population may be expected. This has been recognized in recent studies. For example, Marcolli et al. (2007) found good agreement between theoretical predictions and laboratory results when the heterogeneous nucleation rate coefficient,  $J_{het}$ , was averaged over a distribution of contact angles. Along this line various mechanistic models have been proposed, considering besides a contact angle distribution, the dependency of  $N_c(S_i, T, ...)$  on active site area and the external mixing of IN (Niedermeier et al., 2011; Broadley et al., 2011; Lüönd et al., 2010; Marcolli

et al., 2007). These models however rely on idealized pictures of the particle surface structure limiting their applicability to ambient aerosol.

- A different approach, usually referred to as the "singular hypothesis" (Vali, 2008, 1994; Pruppacher and Klett, 1997, and references therein), relies on the hypothetical existence of active sites on the surface of IN where ice nucleation occurs instantaneously at some characteristic *T* and *S*<sub>i</sub> (Pruppacher and Klett, 1997). The lack of temporal dependency of  $N_c(S_i, T,...)$  found in several studies (Möhler et al., 2006; Broadley et al., 2011; Connolly et al., 2009; Vali, 2008) supports this view. However a theory de-
- <sup>20</sup> scribing the nature of the active sites that allows the prediction of their characteristic *T* and *S*<sub>i</sub> is yet to be formulated and *N*<sub>c</sub>(*S*<sub>i</sub>, *T*,...) is generally fitted to limited experimental results. Vali (2008; 1994) proposed a hybrid singular-stochastic approach for immersion freezing where the IN follow singular behavior but there is scatter in the observed freezing point due to fluctuations in the ice-embryo size. This model however does not
- specify how the main freezing point and the width of the dispersion around it should be determined. Using a CNT-based model over an idealized particle Niedermeier et al. (2011) were able to reconcile singular and stochastic behavior.

In this work a novel formulation of the ice nucleation spectrum is presented. The new formulation relies on a statistical view of the ice nucleation process and explicitly



considers the effects of supersaturation, temperature, cooling rate, and aerosol size and surface area, on the ice crystal number concentration. This is achieved by introducing the concepts of ice nucleation coefficient and ice nucleation probability dispersion. The new formulation is applied to generate parameterizations of  $N_c(S_i, T,...)$  for

the homogeneous freezing of cloud droplets and the heterogeneous nucleation of ice on dust and soot IN in the deposition mode.

#### 2 General theory

In this section the concepts of ice nucleation coefficient and ice nucleation probability dispersion are introduced and used to develop a general relation for the aerosol ice nucleation fraction,  $f_{\rm f}$  (i.e. the number fraction of the aerosol where ice is nucleated). Nucleation theory is then used to link  $f_{\rm f}$  to measurable quantities such as T and  $S_{\rm i}$  and to derive the homogeneous and heterogeneous ice nucleation spectra.

We start by introducing the ice nucleation coefficient,  $\varphi$ , heuristically related to  $f_{\rm f}$  by

 $f_{\rm f,uniform} = 1 - e^{-\varphi}$ 

<sup>15</sup> where the subscript "uniform" indicates that all particles in the aerosol population have the same composition and size, and in the case of heterogeneous ice nucleation, the same surface composition and structure. For the latter, Eq. (1) also requires a constant surface composition on each particle.

The conditions for which Eq. (1) is defined are highly idealized. Ice nucleation is <sup>20</sup> influenced by variation in the particle composition, surface area and structure. This indicates that  $\varphi$  must be associated with a probability distribution,  $n(\varphi)$ , so that,

$$f_{\rm f} = 1 - \int_0^\infty n(\varphi) e^{-\varphi} \mathrm{d}\varphi$$

Making  $\xi = \frac{\varphi}{\bar{\varphi}}$ , where  $\bar{\varphi}$  is a "characteristic" nucleation coefficient (e.g. measured at the mean aerosol properties), Eq. (2) can be written as,



(1)

(2)

29605

$$f_{\rm f} = 1 - \int_0^\infty n(\xi) e^{-\xi \bar{\varphi}} \mathrm{d}\xi$$

where  $n(\xi)$  is termed the "Nucleation Probability Dispersion Function" (NPDF). It can be noticed immediately from Eq. (3) that

 $f_{\rm f} = 1 - \mathcal{N}(\bar{\varphi})$ 

- <sup>5</sup> where  $\mathcal{N}(\bar{\varphi})$  is the Laplace transform of  $n(\xi)$ .  $\mathcal{N}(\bar{\varphi})$  and  $n(\xi)$  are equivalent representations of the NPDF (Medhi, 1994). Thus  $f_{\rm f}$  contains all the information on the underlying distribution of nucleation coefficients (and vice-versa), hence of nucleation probability, in the aerosol population.
- $\mathcal{N}(\bar{\varphi})$  for gamma, sectional and lognormal NPDFs is shown in Table 1. For the Lognormal distribution  $\mathcal{N}(\bar{\varphi})$  is approximated using  $\mathcal{N}(\bar{\varphi}) \propto \int_{0}^{1/\bar{\varphi}} n(\xi) d\xi$  (Rossberg, 2008) which is accurate to within 5% for  $\sigma_{\varphi} > 3$ , when compared against the direct numerical solution of Eq. (3) (not shown). Complex materials may exhibit multimodal NPDFs for which  $n(\xi)$  must be adequated accordingly (Sect. 3.2.4). In the general case of a sectional NPDF calculation of  $\mathcal{N}(\bar{\varphi})$  involves a discrete approximation to the Laplace transform (Shortle et al., 2003).

The ice nucleation spectrum is calculated directly from  $f_{\rm f}$ ,

$$N_{\rm c}(S_{\rm i}, T, \ldots) = N_{\rm a} f_{\rm f}[\bar{\varphi}(S_{\rm i}, T, \ldots)]$$

where  $N_a$  is the aerosol number concentration. The differential ice nucleation spectrum is obtained by taking the total derivative of Eq. (5),

$${}_{20} \quad n_{\rm c}(S_{\rm i},T,\mu_{\rm i}) = -N_{\rm a}\frac{\partial\mathcal{N}(\bar{\varphi})}{\partial\bar{\varphi}} \left[\frac{\partial\bar{\varphi}}{\partial S_{\rm i}}{\rm d}S_{\rm i} + \frac{\partial\bar{\varphi}}{\partial T}{\rm d}T + \sum\frac{\partial\bar{\varphi}}{\partial\mu_{\rm i}}{\rm d}\mu_{\rm i}\right] \tag{6}$$

where  $\mu_i$  denotes the *i*-th moment of the distribution of aerosol number concentration.



(3)

(4)

(5)

29606

## **2.1** Definition of $\bar{\varphi}$ and $n(\xi)$

Equation (4) holds regardless of the ice nucleation mechanism (homogeneous or heterogeneous), or, the interpretation of heterogeneous ice nucleation, e.g. singular vs. stochastic. Its application however requires linking  $\bar{\varphi}$  to  $S_i$ , T and the aerosol properties; this is accomplished below.

#### 2.1.1 Homogeneous nucleation

The homogeneous freezing of cloud droplets and deliquesced aerosol is generally modeled using the the homogeneous nucleation rate coefficient,  $J_{hom}$ . Comparison of Eq. (1) against Eq. (7.66) of Pruppacher and Klett (1997) suggests that

10 
$$\varphi = v_p \int_0^t J_{\text{hom}} dt$$

5

15

where  $v_p$  is the particle volume. Equation (7) can also be written as

 $\varphi \approx v_{\rm p} J_{\rm hom} \tau_{\rm nuc}$ 

where  $\tau_{nuc}$  is the timescale of nucleation (Sect. 3.1.1). Homogeneous nucleation is a stochastic process (Pruppacher and Klett, 1997) where  $J_{hom}$  is the same in all droplets that have the same composition. Variability in  $\varphi$  therefore originates only from dispersion in  $v_p$ . Thus, the homogeneous NPDF is determined by the droplet number volume distribution (Sect. 3.1).

#### 2.1.2 Heterogeneous nucleation

The probability that ice nucleates heterogeneously on the surface of an aerosol particle is usually expressed in terms of the heterogeneous nucleation rate coefficient,  $J_{het}$ , or alternatively, in terms of the surface density of active sites,  $\rho_{as}$ .  $J_{het}$  and  $\rho_{as}$  are locally defined and can vary over the surface of each particle as well as among particles in

(7)

(8)

the aerosol population (Niedermeier et al., 2011; Zobrist et al., 2007; Broadley et al., 2011). Using the common definitions of  $J_{\rm het}$  and  $\rho_{\rm as}$  (Pruppacher and Klett, 1997) we can write

$$\varphi = s_{\rm p} \int_0^t J_{\rm het} dt = s_{\rm p} \rho_{\rm as}$$

- <sup>5</sup> where it is assumed that the same experimental conditions (i.e. *T*, *S*<sub>i</sub> and particle residence time) are maintained in determining *J*<sub>het</sub> and *ρ*<sub>as</sub>. In this work the particle surface area, *s*<sub>p</sub>, is used as the characteristic length associated with *J*<sub>het</sub> and *ρ*<sub>as</sub>. The active site surface area (Pruppacher and Klett, 1997; Zobrist et al., 2007) is however also suitable to define *φ*.
- The NPDF can be obtained from Eqs. (3) and (9). If ice nucleation is described in terms of  $\rho_{\rm as}$  then,

$$\xi = s_{\rm p} \rho_{\rm as} / \overline{s_{\rm p} \rho_{\rm as}} \tag{10}$$

and

 $n(\xi) \propto n(s_{\rm p}\rho_{\rm as})$ 

If  $J_{het}$  is employed, then using  $\int_0^t J_{het} dt \approx J_{het} \tau_{nuc}$ , we obtain,

$$\xi = s_{\rm p} J_{\rm het} / \overline{s_{\rm p} J_{\rm het}} \tag{12}$$

and

$$n(\xi) \propto n(s_{\rm p}J_{\rm het})$$

Equation (13) can also be related to the contact angle distribution (Sect. 3.2).

<sup>20</sup> If  $J_{het}$  and  $\rho_{as}$  are constant over the surface of all particles in the aerosol population, then dispersion in  $\varphi$  originates only from variation in the particle surface area and the NPDF is determined by the number area distribution.



(9)

(11)

(13)

## 3 Application

## 3.1 Homogeneous freezing of cloud droplets

Aerosol emissions impact the cloud droplet size distribution altering the cloud glaciation temperature and the cold generation of precipitation (Rosenfeld and Woodley, 2000;

<sup>5</sup> Ramanathan et al., 2001). It is therefore important to determine how the droplet volume distribution and the cooling rate play a role in determining  $f_{\rm f}$  in cloud droplets. Austin et al. (1995) suggested that the droplet volume distribution can be adequately represented by,

$$n(\xi) = \frac{(1+\nu)^{1+\nu}}{\Gamma(1+\nu)} \xi^{\nu} e^{-(1+\nu)\xi}$$
(14)

where  $\xi = \frac{v_p}{\bar{v}_p}$  and *v* is related to the relative variance of the droplet volume distribution  $(\text{varr} = [7(v+1)]^{-1}$ , Austin et al., 1995). Making  $\alpha = \beta = (v+1)$  and using Table 1 with  $\bar{\varphi} = \bar{v}_p J_{\text{hom}} \tau_{\text{nuc}}$ , we obtain

$$\mathcal{N}(\bar{\varphi}) = \left(\frac{\bar{\nu}_{p}J_{\text{hom}}\tau_{\text{nuc}}}{(1+\nu)} + 1\right)^{-(1+\nu)}$$

#### 3.1.1 Nucleation time scale

<sup>15</sup> During an experiment at constant  $S_i$  and T,  $\tau_{nuc}$  is related to the residence time of the particles before ice nucleation is observed,  $\Delta t_{exp}$ . Equation (7) is then easily integrated to give

$$\bar{\rho} = \bar{v}_{\rm p} J_{\rm hom} \Delta t_{\rm exp}$$

(

In atmospheric models it is however more difficult to define  $\tau_{nuc}$  as it depends on T, S<sub>i</sub>,

the predominant nucleation mechanism and the cooling rate,  $\gamma$ . In general  $\tau_{nuc}$  differs from the model's time step (Barahona and Nenes, 2008).



(15)

(16)

To develop an expression for  $\tau_{nuc}$  it is advantageous to write  $\int_0^t J_{het} dt$  in terms of  $\partial T/\partial t$  and  $\partial S_w/\partial t$ , being  $S_w$  the saturation ratio with respect to water, i.e.

$$\int_{0}^{t} J_{\text{het}} dt = \int_{T_{0}}^{T} \frac{J_{\text{hom}}}{\frac{\partial T}{\partial t}} dT + \int_{S_{\text{w}}^{\text{isat}}}^{S_{\text{w}}} \frac{J_{\text{hom}}}{\frac{\partial S_{\text{w}}}{\partial t}} dS_{\text{w}}$$
(17)

where  $T_0 = 273$  K,  $S_w^{\text{isat}} = p_{s,i}/p_{s,w}$  is the value of  $S_w$  at  $S_i = 1$ , and  $p_{s,w}$  and  $p_{s,i}$  are the liquid water and ice saturation vapor pressures at T, respectively (Murphy and Koop, 2005).

5

15

Taking into account that for the droplet population  $S_w \approx 1$  and  $dS_w \approx 0$ , Eq. (17) can be simplified to

$$\int_{0}^{t} J_{\text{hom}} dt = \int_{T_{0}}^{T} \frac{J_{\text{hom}}}{\frac{\partial T}{\partial t}} dT$$
(18)

<sup>10</sup> Over the small *T* interval in which ice nucleation occurs (typically about 2 K, Fig. 2)  $\frac{d\ln J_{\text{hom}}}{dT} \approx k_{\text{hom}}$  being  $k_{\text{hom}}$  a constant (Barahona and Nenes, 2008). Using this, Eq. (18) can be written in the form,

$$\int_{0}^{t} J_{\text{hom}} dt = \frac{J_{\text{hom}}}{\gamma} \int_{\varepsilon}^{0} e^{-k_{\text{hom}}\varepsilon} d\varepsilon$$
(19)

where  $\epsilon$  is a temperature perturbation from T to  $T - \epsilon$  and  $\gamma$  is the cooling rate. Solving the integral in Eq. (19) we obtain,

$$\int_{0}^{t} J_{\text{hom}} dt = \frac{J_{\text{hom}}}{k_{\text{hom}} \gamma}$$
(20)

where it has been assumed that  $J_{\text{hom}}(T) \gg J_{\text{hom}}(T - \epsilon)$ . Using the chain rule,  $k_{\text{hom}} = \left[\frac{d\ln J_{\text{hom}}}{dS_{\text{w}}}\frac{dS_{\text{w}}}{dT}\right]_{S_{\text{w}}=1}$  where  $J_{\text{hom}}$  is given by the parameterization of Koop et al. (2000). From Murphy and Koop (2005),  $\left[\frac{dS_{\text{w}}}{dT}\right]_{S_{\text{w}}=1} = 6132.9/T^2$  K. Using this into Eq. (20) 29610 Discussion Paper ACPD 11, 29601-29646, 2011 On the ice nucleation spectrum **Discussion** Paper D. Barahona **Title Page** Abstract Introduction Conclusions References **Discussion** Paper Tables Figures Back Full Screen / Esc **Discussion Paper Printer-friendly Version** Interactive Discussion

it can be readily seen that  $\tau_{nuc} = (k_{hom}\gamma)^{-1} = \left(\frac{6132.9\gamma}{T^2} \frac{d\ln J_{hom}}{dS_w}\right)^{-1}$ . Collecting terms into Eq. (15) we obtain the final expression for homogeneous ice nucleation in cloud droplets,

$$\mathcal{N}(\bar{\varphi}) = \left[\frac{\bar{\nu}_{p}J_{\text{hom}}\left(\frac{6132.9\gamma}{T^{2}}\frac{\text{dln}J_{\text{hom}}}{\text{d}S_{w}}\right)^{-1}}{(1+\nu)} + 1\right]^{-(1+\nu)}$$
(21)

#### **5 3.2 Heterogeneous ice nucleation in the deposition mode**

Deposition ice nucleation is thought to significantly impact the formation of cirrus (Barahona et al., 2010; Hoose et al., 2010; Möhler et al., 2006). Weakly wettable species like soot may also nucleate ice in this mode at warmer T potentially impacting the formation mixed-phase clouds (Seisel et al., 2005). Currently only CNT provides sufficient detail to allow the calculation of  $J_{het}$  over a wide range of conditions and is therefore used here to derive  $\bar{\phi}$  for deposition ice nucleation.

#### 3.2.1 Ice nucleation rate coefficient

Within the framework of CNT,  $J_{het}$  is given by (Pruppacher and Klett, 1997; Kashchiev, 2000),

<sup>15</sup> 
$$J_{\text{het}} = Z_{\text{het}} c_{1,s} \beta_{\text{h}} \exp\left(-\frac{\Delta g_{\text{g}}}{kT}\right)$$

where  $Z_{het}$  is the Zeldovich factor,  $c_{1,s}$  is the surface concentration of water molecules,  $\beta_h$  is the rate at which water molecules are incorporated into the critical ice cluster, and and *k* is the Boltzmann constant. The remaining term in Eq. (22) is the energy of formation of the ice germ, given by (Pruppacher and Klett, 1997)

$$_{20} \quad \Delta g_{\rm g} = f \frac{4\pi}{3} \sigma_{\rm i/v} r_{\rm g}^2$$

J

10



(22)

(23)

where  $\sigma_{i/v}$  is the surface tension of ice (106 mJ m<sup>-2</sup> (Pruppacher and Klett, 1997)), and  $r_{\rm q}$  is the ice germ size given by,

$$r_{\rm g} = \frac{2v_{\rm w}\sigma_{\rm i/v}}{kT\ln S_{\rm i}}$$

5

where  $v_w$  is the volume of a water molecule (Zobrist et al., 2007).

The compatibility parameter, f, in Eq. (23) accounts for the reduction in the work of ice formation caused by the heterogeneous surface (Kashchiev, 2000). It is given by

$$f = \frac{1}{4}(2 + \cos\theta)(1 - \cos\theta)^2$$

where  $\theta$  is the local contact angle between the solid surface and the ice germ (Pruppacher and Klett, 1997). In writing Eq. (25) it is assumed that the substrate has a planar geometry. Given the complex geometry of atmospheric particles (e.g. Dymarska et al., 2006; Zimmermann et al., 2008) it is not clear whether assuming a spherical substrate (or any other simple geometry) would represent a better approximation to *f* than Eq. (25). Therefore curvature effects are not considered. Extensions of Eq. (24) to include active sites and elastic strain have been proposed (Fletcher, 1969; Khvorostyanov and Curry, 2004; Pruppacher and Klett, 1997). The NPDF allows a finite probability of  $\theta < 1$  therefore accounting for active sites. Misfit strain can reduce  $J_{het}$  (Khvorostyanov and Curry, 2004; Pruppacher and Klett, 1997) however current parameterizations depend on largely unconstrained parameters and such effects are not considered.

- <sup>20</sup> Despite the simplicity of Eq. (22) calculation of  $J_{het}$  is subject to uncertainty. The form of  $Z_{het}$ ,  $c_{1,s}$ , and  $\beta_h$  depends on whether the water molecules are incorporated directly into the ice germ from the vapor phase or they first adsorb onto the particle surface and then diffuse to the ice germ. The value of  $c_{1,s}$  is also strongly influenced by the formation of water monolayers on the particle surface (Määttänen et al., 2005; Seisel et al., 2005). Määttänen et al. (2005) has shown that these factors may introduce up to
- a factor of two uncertainty in  $f_{\rm f}$ .

(24)

(25)

Assuming direct water vapor deposition onto the ice germ and a steady-state monomer concentration on the particle surface (which typically results in a conservative estimate of  $J_{het}$ ) gives (Määttänen et al., 2005),

$$J_{\text{het}} = \frac{\alpha_{\text{c}}}{\sqrt{f}} \frac{p_{\text{v}}^2 v_{\text{w}}}{m_{\text{w}} k T v_{\text{s}}} \sqrt{\frac{\sigma_{\text{i/v}}}{k T}} \exp\left(\frac{\Delta g_{\text{d}}}{k T}\right) \exp\left(\frac{-\Delta g_{\text{g}}}{k T}\right)$$
(26)

<sup>5</sup> where  $\Delta g_d$  is the desorption energy of water molecules from the surface,  $p_v$  the water vapor pressure,  $v_s$  the molecular frequency of vibration (10<sup>13</sup> s<sup>-1</sup>), and  $m_w$  the mass of a water molecule (2.99 × 10<sup>-26</sup> kg) (Pruppacher and Klett, 1997).

Equation (26) resembles Eq. (11) of Chen et al. (2008), however in Eq. (26) *f* is raised to the -1/2 power instead of 1/2. The latter may result from neglecting the effect of the solid surface on  $r_g$  (Vehkamäki et al., 2007) and leads to unphysical behavior implying that  $J_{het} \rightarrow 0$  when  $f \rightarrow 0$  (i.e. ice nucleation would more difficult on easily wettable materials). To assure physical consistency it is also necessary that  $\exp\left(\frac{\Delta g_d}{kT}\right) > 1$ as large values of  $\Delta g_d$  lead to low desorption rates increasing  $c_{1,s}$  (hence  $J_{het}$ ). The mass accommodation coefficient,  $\alpha_c$ , has been introduced into Eq. (26) to account for the low sticking efficiency of the water vapor molecules onto the particle surface (it is assumed that  $\alpha_c = 1.0$  for the ice surface) (Pruppacher and Klett, 1997; Seisel et al., 2005). Equation (26) can be written in the form

$$J_{\rm het} = A \exp\left(-\frac{\Delta g_{\rm g}}{kT}\right)$$

where  $A = \frac{\alpha_c}{\sqrt{f}} \frac{p_v^2 v_w}{m_w k T v_s} \sqrt{\frac{\sigma_{i/v}}{kT}} \exp\left(\frac{\Delta g_d}{kT}\right)$ . Typical values of A range between 10<sup>23</sup> and 10<sup>26</sup> m<sup>-2</sup> s<sup>-1</sup>.



(27)

#### 3.2.2 Nucleation time scale

For ice nucleation in the deposition mode the relative variation in  $S_w$  is significantly larger than the relative variation in T (Barahona and Nenes, 2009), i.e.  $\frac{1}{S_w} \frac{dS_w}{dt} \gg \frac{1}{T} \frac{dT}{dt}$ . Equation (17) can then be approximated as,

$$\int_{0}^{t} J_{\text{het}} dt = \int_{S_{\text{w}}^{\text{isat}}}^{S_{\text{w}}} \frac{J_{\text{het}}}{\frac{\partial S_{\text{w}}}{\partial t}} dS_{\text{w}}$$
(28)

Using  $\frac{\partial S_w}{\partial t} \approx \alpha_s u$  (Barahona and Nenes, 2009), where u is the vertical velocity and  $\alpha_s = \frac{g\Delta H_s m_w}{c_p kT^2} - \frac{gm_a}{kT}$ , where g is the acceleration of gravity,  $\Delta H_s$  the latent heat of sublimation of ice (Pruppacher and Klett, 1997), and  $c_p$  and  $m_a$  are the heat capacity and molecular mass of air, respectively, Eq. (28) becomes,

10 
$$\int_{0}^{t} J_{\text{het}} dt = \frac{1}{\alpha_{s} u} \int_{S_{w}^{\text{isat}}}^{S_{w}} J_{\text{het}} dS_{w}$$

5

Integration of Eq. (29) is accomplished by separating  $J_{het}$  into its  $S_w$  and T dependencies (Khvorostyanov and Curry, 2004). Using Eq. (24), assuming  $\ln(S_w) \approx S_w - 1$ , and rearranging we obtain,

$$r_{\rm g} \approx \frac{r_{\rm g}^{\circ}}{1 + \frac{S_{\rm w} - 1}{\ln(\rho_{\rm s,i}/\rho_{\rm s,w})}}$$

where  $r_g^{\circ} = r_g |_{S_w=1}$ . Expanding the denominator of Eq. (30) into a power series of  $\frac{S_w-1}{\ln(\rho_{s,i}/\rho_{s,w})}$  (Khvorostyanov and Curry, 2004) and introducing the result into Eq. (23) gives,

$$\Delta g_{\rm g} \approx \frac{4\pi}{3} (r_{\rm g}^{\circ})^2 \sigma_{\rm i/v} \left( 1 - \frac{2(S_{\rm w} - 1)}{\ln(\rho_{\rm s,i}/\rho_{\rm s,w})} \right)$$
29614

Discussion Paper ACPD 11, 29601-29646, 2011 On the ice nucleation spectrum D. Barahona **Discussion** Paper **Title Page** Abstract Introduction Conclusions References **Discussion** Paper Tables Figures Back Full Screen / Esc **Discussion** Paper **Printer-friendly Version** Interactive Discussion

(29)

(30)

(31)

which after substitution into Eq. (22) gives,

$$J_{\rm het} \approx J_{\rm het}^{\circ} \exp\left(f n_{\rm g}^{\circ}(S_{\rm w}-1)\right)$$

where  $J_{het}^{\circ} = J_{het}|_{S_w=1}$ , and  $n_g^{\circ} = \frac{4\pi}{3} \frac{r_g^{\circ}}{v_w}$  is the number of water molecules in the ice germ at water saturation. Substituting Eq. (32) into Eqs. (9) and (29), and solving for the integral gives,

$$\varphi = s_{\rm p} J_{\rm het} \left( \frac{1}{\alpha_{\rm s} u f n_{\rm g}^{\circ}} \right) = s_{\rm p} J_{\rm het} \tau_{\rm nuc}$$

where  $\tau_{\rm nuc} = (\alpha_{\rm s} u f n_{\rm g}^{\circ})^{-1}$ 

5

10

#### 3.2.3 The nature of $n(\xi)$ in deposition ice nucleation

The NPDF can be related to the distribution of  $\theta$ , as follows. Using Eqs. (23) and (26) into Eq. (13) we obtain,

 $n(\xi) = n\left(\frac{s_{\rm p}}{\bar{s}_{\rm p}}e^{-\Delta g_{\rm g}(f(\theta) - f(\bar{\theta}))}\right)$ 

Expanding  $f(\theta)$  into its Taylor series and rearranging gives,

$$n(\xi) = n\left(\frac{S_{\mathsf{p}}}{\bar{S}_{\mathsf{p}}}e^{-\Delta g_{\mathsf{g}}\frac{\mathrm{d} f(\bar{\theta})}{\mathrm{d} \theta}(\theta-\bar{\theta})}\right)$$

which can be written as

<sup>15</sup> 
$$n(\xi) = n\left(\frac{s_{\rm p}}{\bar{s}_{\rm p}}e^{c\theta/\bar{\theta}}\right)$$

(32)

(33)

(34)

(35)

(36)

Discussion Paper **ACPD** 11, 29601-29646, 2011 On the ice nucleation spectrum D. Barahona Discussion Paper **Title Page** Abstract Introduction Conclusions References **Discussion** Paper **Figures** Back Full Screen / Esc **Discussion** Paper **Printer-friendly Version** Interactive Discussion

where  $c = -\Delta g_g \frac{df(\bar{\theta})}{\bar{\theta}d\theta}$ . If all particles in the population have the same surface area, the NPDF reduces to

$$n(\xi) = n\left(e^{c\theta/\bar{\theta}}\right)$$

Equation (37) suggests that  $n(\xi)$  for heterogeneous ice nucleation follows a lognormal distribution. If the particle surface composition is randomly determined then  $\theta$  follows a normal distribution and  $e^{\theta}$  distributes lognormally (Rossberg, 2008). At the limit of constant  $\theta$  the number area distribution (which is usually lognormally distributed, Seinfeld and Pandis, 1998) determines  $n(\xi)$  (Eq. 13). These two limits of variability in  $\varphi$  suggest a lognormal NPDF.

#### **3.2.4** Final form for deposition ice nucleation

Combining the expressions of Table 1 with Eqs. (4) and (33), a concise expression for  $\mathcal{N}(\bar{\varphi})$  can be written in the form,

$$\mathcal{N}(\bar{\varphi}) = \frac{1}{2} \operatorname{erfc}\left[\frac{\ln\left(\frac{\bar{s}_{p}J_{\text{het}}}{\sigma_{s}uf\,n_{g}^{\circ}}\right)}{\sqrt{\pi}\sigma_{\varphi}}\right]$$

where *f* and  $J_{het}$  are calculated at the mean aerosol properties. Equation (38) shows that given  $S_i$ , *T* and *u*,  $f_f$  depends only on the mean contact angle,  $\bar{\theta}$ , the mean particle surface area,  $\bar{s}_p$ , and the ice nucleation dispersion coefficient,  $\sigma_{\varphi}$ . Complex aerosol mixtures may exhibit multimodal NPDFs. Equation (38) is readily extended to such cases by making,

$$\mathcal{N}(\bar{\varphi}) = \frac{1}{2} \sum_{i=1}^{M} w_i \operatorname{erfc}\left[\frac{\ln\left(\frac{\bar{s}_p J_{\text{het},i}}{\alpha_s u f_i n_g^\circ}\right)}{\sqrt{\pi} \sigma_{\varphi,i}}\right]$$

(37)

(38)

(39)

29617

where  $w_i$  is the weight of the *i*-th lognormal mode in  $n(\xi)$ , and M is the total number of modes.

## 4 Results and discussion

# 4.1 General behavior of $\mathcal{N}(\bar{\phi})$

- The probability of observing a nucleation event in an aerosol population increases with φ, i.e. f<sub>f</sub> is always a monotonic function of φ. Figure 1 shows f<sub>f</sub> for lognormal, gamma, and sectional NPDFs. The width of each NPDF (e.g. σ<sub>φ</sub>, α, and the standard deviation, σ, respectively) has been varied over a wide interval and the distribution mean set to ξ = 1 (Eq. 3). To illustrate the discrete transform approximation method (Table 1, Shortle et al., 2003), the sectional distribution in Fig. 1 (top panels) has been derived from a normal distribution using 20 bins. This method produces a continuous, smooth increasing f<sub>f</sub>, however using only 20 bins results in smaller sensitivity to σ than the analytical transform to n(ξ) (not shown).
- The form and width of the NPDF strongly influences  $f_{\rm f}$ . As a consequence of the support of the normal distribution between  $-\infty$  and  $\infty$ , nucleation spectra derived from the normal NPDF tend to shift right as  $\sigma$  decreases. Indeed, if  $\varphi$  is normally distributed then a finite probability of  $\varphi < 0$  exist, leading to unphysical behavior. As the gamma and lognormal NPDFs have support only on the positive real axis, values of  $\varphi < 0$  are not accessible to  $\mathcal{N}(\bar{\varphi})$ . Thus, the inflection point in the  $f_{\rm f}$  curve (Fig. 1) for these NPDFs is always around  $\bar{\varphi} = 1$ , defining characteristic values for  $J_{\rm het}$  (or  $J_{\rm hom}$ )
- and  $\rho_{as}$ . A similar conclusion was reached by Khvorostyanov and Curry (2004) using the empirical constraint of  $\bar{s}_p J_{het} \approx 1 \text{ s}^{-1}$ . The theory presented here generalizes this picture and suggests that the characteristic  $J_{het}$  (at  $\bar{\phi} = 1$ ) is found at  $f_f \approx 0.5$  instead of the typical  $f_f \approx 0.01$  used in experimental studies.
- The lognormal and gamma distributions display distinctive behavior to the variation in the width of the NPDF. For the gamma distribution the slope of  $f_{\rm f}$  remains almost



constant for  $\alpha > 0.5$  but decreases steeply for  $\alpha < 0.5$ , which is explained by the larger probability of finding small  $\varphi$  at lower  $\alpha$  (Fig. 1, left panels). For the lognormal distribution a larger  $\sigma_{\varphi}$  leads to a larger probability of both, small and large  $\varphi$ . The former limits the value of  $f_f$  as  $\bar{\varphi} \to \infty$  whereas the latter increases  $f_f$  at low  $\bar{\varphi}$ . These features may explain the low  $f_f$  typically observed in ambient aerosol (e.g. Eidhammer et al., 2009; Phillips et al., 2008) and the diversity of ice nucleation thresholds observed in experimental studies. This is further analyzed in Sect. 4.3.2.

## 4.2 Homogeneous nucleation

5

Figure 2 shows the sensitivity of the nucleation spectra for homogeneous freezing to  $D_{\rm p}$ ,  $\gamma$  and varr (Eq. 15). Although Eq. (21) is written in terms of  $\bar{v}_{\rm p}$ , the equivalent droplet size,  $D_{\rm p}$ , is most often used in experimental studies; they are simply related by

 $D_{\rm p} = \left(\frac{6\bar{\nu}_{\rm p}}{\pi}\right)^{1/3}$ . As  $\bar{\varphi}$  scales with  $\gamma$  and  $D_{\rm p}$  their variation tends to "shift"  $f_{\rm f}$  along the *T* axis. Decreasing  $D_{\rm p}$  from 40 µm to 10 µm decreases  $T_{\rm onset}$  (defined at  $f_{\rm f} \approx 0.01$ ) from 236 K to 233 K. Variation in  $\gamma$  has the opposite effect although with a weaker impact: a factor of 10<sup>3</sup> increase in  $\gamma$  only results in about 3 K lower  $T_{\rm onset}$  (explained by the decrease in  $\tau_{\rm nuc}$  as  $\gamma$  increases, Eq. 19). This indicates that temporal effects may have a limited role in ice crystal production by homogeneous freezing in ambient clouds.

Homogeneous freezing may be strongly impacted by dispersion in the droplet size distribution. For varr < 0.4 the slope of  $f_{\rm f}$  remains almost constant and nearly all deviate for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly all deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly deviates for the slope of  $f_{\rm f}$  remains almost constant and nearly deviates for the

- <sup>20</sup> droplets freeze within 2–3K of  $T_{onset}$ . However as varr increases beyond 0.4,  $f_f$ "stretches" over a wider T interval so that at varr = 0.7 some droplets freeze at T as low as 228 K. This is explained by the decrease in  $\alpha$  as varr increases (i.e. varr  $\propto \frac{1}{\alpha}$ ) resulting in a larger fraction of small droplets in the population (Sect. 4.1). This previously unidentified behavior of homogeneous freezing may have important implications for the development of apprentice abude as acread aminging and entrainment tend
- <sup>25</sup> for the development of convective clouds as aerosol emissions and entrainment tend to broaden the droplet size distribution (Pruppacher and Klett, 1997).



### 4.3 Heterogeneous ice nucleation in the deposition mode

## 4.3.1 General features

Figure 3 shows representative profiles of  $f_{\rm f}$  for heterogeneous ice nucleation in the deposition mode. In general  $f_{\rm f}$  is primarily a function of  $S_{\rm i}$  and  $\bar{\theta}$ , and to a lower extent, of T,  $\bar{s}_{\rm p}$ , u and  $\sigma_{\varphi}$ . For  $\bar{\theta} < 10^{\circ}$ ,  $f_{\rm f}$  tends to be very steep and almost insensitive to T,  $\bar{s}_{\rm p}$ , u and  $\sigma_{\varphi}$ . Therefore a single, constant  $S_{\rm i,onset}$  can be assigned to aerosol populations with low  $\bar{\theta}$ . This indicates that highly efficient IN would tend to follow "singular" behavior. Less efficient IN (with high  $\bar{\theta}$ ) are however strongly influenced by T,  $\bar{s}_{\rm p}$  and u. The sensitivity of  $f_{\rm f}$  to u suggests that temporal effects may be significant. In this regime  $f_{\rm f}$  is also impacted by  $\sigma_{\varphi}$  therefore variation in the NPDF caused by repeated freezing cycles and by variation in the particle surface structure and composition may affect  $S_{\rm i,onset}$ . These characteristics imply that inefficient IN behave "stochastically". Thus within the context of the theory presented here, stochastic and singular behavior can be understood as two limits of variability in the NPDF.

<sup>15</sup> For the highest  $\bar{\theta}$  used in Fig. 3 (23°) decreasing *T* from 250 K to 210 K leads to an increase of 0.15 in  $S_{i,onset}$  (defined at  $f_f \approx 0.01$ ). This is explained by the increase in  $r_g$  and  $\Delta g_g$  as *T* decreases, lowering  $J_{het}$  (Eq. 22). Increasing *u* from 10<sup>-3</sup> to 10 m s<sup>-1</sup> increases the  $S_{i,onset}$  by about 0.1 at  $\theta = 23^\circ$  (Fig. 3, bottom left panels). This is explained by the decrease in  $\tau_{nuc}$  as *u* increases (Eq. 33) so that higher  $J_{het}$  is required to reach  $\bar{\varphi} = 1$ . Although the sensitivity of  $S_{i,onset}$  to *u* is significant, achieving a large variation in *u* in experimental studies may be technically challenging and temporal

large variation in *u* in experimental studies may be technically challenging and temporal effects on deposition ice nucleation may be difficult to observe.

 $S_{i,onset}$  increases by about 0.08 when  $\bar{s_p}$  increases from 0.1 µm<sup>2</sup> to 100 µm<sup>2</sup>. Although this is consistent with existing studies (Kanji et al., 2008; Welti et al., 2009) direct comparison against experimental results is difficult as the number area distribution is usually not reported. The range of  $\bar{s_p}$  considered in Fig. 3 is however typically observed in ambient aerosol (Eastwood et al., 2008; Dymarska et al., 2006; Kanji et al., 2008) and the effect of  $\bar{s_p}$  on  $f_f$  may be readily observable in the laboratory.

Increasing  $\sigma_{\varphi}$  tends to decrease  $S_{i,onset}$  as larger  $\sigma_{\varphi}$  leads to larger probability of finding high  $\varphi$  (Sect. 4.1). This effect is evident for  $\bar{\theta} > 10^{\circ}$  and indicates that the relation between  $S_{i,onset}$  and  $\bar{\theta}$  (Fig. 4) can be strongly impacted by  $\sigma_{\varphi}$ . When  $\sigma_{\varphi} \to 0$  (i.e. a very narrow NPDF, Eq. 1)  $\bar{\theta}$  and  $S_{i,onset}$  are related by an exponential function, weakly dependent on T,  $\bar{s_p}$  and u. This is consistent with experimental studies (Wang and Knopf, 2011), however hardly surprising. The correlation between  $\bar{\theta}$  and  $S_{i,onset}$  is implicit in Eq. (22) and therefore independent of empirical data. Moreover, it does not imply a physical dependency of  $\bar{\theta}$  on  $S_i$ . In fact, for  $\sigma_{\varphi} > 1$ , different combinations of T,  $\bar{s_p}$  and u result in a family of relations between  $\bar{\theta}$  and  $S_{i,onset}$  (Fig. 4). Figure 3, however suggest that by measuring  $S_{i,onset}$  at  $f_f = 0.5$ , instead of  $f_f = 0.01$ , the effect of  $\sigma_{\varphi}$  on  $S_{i,onset}$  can be minimized.

#### 4.3.2 Parameterization of the ice nucleation spectra of dust and soot

Among the different IN species present in the atmosphere, soot and dust have been identified to play a significant role in the formation of cirrus and mixed-phase clouds (e.g. DeMott et al., 2003a,b; Gayet et al., 2004). The theory presented in Sects. 2 and 3 can be used to analyze empirical ice nucleation spectra and generate parameterizations for usage in atmospheric models, as follows.

#### Dust

15

Several authors have studied the ice nucleation properties of dust (e.g. Eastwood et al., 2008; Zimmermann et al., 2008, and references therein). Although most studies focus on measuring  $S_{i,onset}$ , the works of Möhler et al. (2006, M06) and Welti et al. (2009, W09) have reported empirical expressions for the ice nucleation spectra of dust in the deposition mode. M06 studied the ice nucleation properties of Arizona Test Dust (ATD), Saharan Dust (SD) and Arizona Dust (AD) using the AIDA cloud chamber (Möhler et al.,

<sup>25</sup> 2003) and reported exponential fits to  $f_{\rm f}$ . W09 studied the ice nucleation properties of several size-selected dust species using the Zurich Ice Nucleation Chamber (ZINC,



Stetzer et al., 2008) and reported sigmoidal fits to  $f_{\rm f}$  for Kaolinite (KAO) and Montmorrinolite (MONT).

The expressions reported by M06 and W09 are used to derive the parameters of  $\mathcal{N}(\bar{\varphi})$  for the different dust species. Basically,  $\bar{\theta}$  (associated with  $\bar{\varphi}$ ) and  $\sigma_{\varphi}$  in Eqs. (38) and (39) are found for each of the  $f_{\rm f}$  curves reported by M06 and W09 (Table 2). From Seisel et al. (2005),  $\Delta g_{\rm d} = 6.5 \times 10^{-20}$  J and  $\alpha_{\rm c} = 6.3 \times 10^{-2}$ . To reduce the parameter space it is assumed that  $\sigma_{\varphi}$  is the same for all modes. To minimize the effect of condensation, only experiments with  $S_{\rm w} < 0.9$  are used. For M06 it is assumed that  $\Delta t_{\rm exp} = \left(\frac{\mathrm{ds}}{\mathrm{dt}}\right)^{-1}$  where  $\frac{\mathrm{ds}}{\mathrm{dt}}$  is the measured rate of change of  $S_{\rm i}$  (Möhler et al., 2006). For the W09 data it is assumed that  $\Delta t_{\rm exp} = 12$  s. M09 reported the value of  $\bar{s}_{\rm p}$  used in their experiments however W09 reported the mean equivalent aerosol size. For the latter,  $\bar{s}_{\rm p}$  is estimated assuming spherical particles and a lognormal size distribution with geometric mean dispersion of 2.5 (cf. Welti et al., 2009, Fig. 3). The resulting values for  $\theta_i$ ,  $\sigma_{\varphi}$  and  $w_i$  are listed in Table 2. Since the number area distribution was not measured in neither M09 nor W09, area dispersion and surface composition effects are assumed to be combined into  $\sigma_{\varphi}$ .

The NPDF of KAO and MONT is well represented using bimodal lognormal distributions. Since ATD and SD are mixtures of different materials, three lognormal modes are required to represent their NPDFs (Table 2). It is however remarkable that such <sup>20</sup> complexity can be described using a few parameters. Consistent with W09, the spectra derived for the KAO sample with  $D_{eq} = 800$  nm tends to reach higher  $f_f$  than for  $D_{eq} = 200$  nm (Fig. 5). This is however not the case for MONT, which may be a consequence of the slightly lower  $\sigma_{\varphi}$  in MONT than in KAO (Table 3) i.e. high  $f_f$  is already reached in the MONT sample with  $D_{eq} = 200$  nm. However, measurement of the num-<sup>25</sup> ber area distribution is required to better constraint  $\sigma_{\varphi}$  and understand such behavior.

The average  $w_i$ ,  $\sigma_{\varphi}$  and  $\bar{\theta}_i$  of each mode for the different dust species of Table 2 is presented in Table 3. All dust species exhibit modes in the NPDF centered around  $\bar{\theta}_i \approx 15^\circ$  and  $\bar{\theta}_i \approx 20^\circ$  (although they are centered at slightly lower  $\bar{\theta}_i$  in ATD, Table 3). ATD and SD exhibit a third mode at  $\bar{\theta} \approx 10^\circ$ . The standard deviation of  $\bar{\theta}_i$  among all



dust species is typically between 10% and 20% of the average  $\bar{\theta}_i$ . This consistency suggests that the NPDF of very different dust species may be parameterized using a linear combination of a few lognormal modes. In principle  $w_i$  for each mode would be linked to the dust source. Such information is however not readily available in most models. A "generic dust" parameterization is therefore formulated by averaging  $w_1$  and  $w_2$  between ATD and SD (with  $w_3 = 1 - w_1 - w_2$ ). The NPDF of dust is assumed to follow a three-modal lognormal distribution with  $\bar{\theta}_i$  and  $\sigma_{\varphi}$  averaged among all the species of Table 3. The parameterization is summarized in Table 4 and shown in Fig. 8.

#### Soot

A parameterization for the ice nucleation spectrum of soot can also be derived from 10 experimental data. Few studies however focus on ice nucleation on soot particles (Dymarska et al., 2006; Möhler et al., 2005; DeMott et al., 1999; Gorbunov et al., 2001). Crawford et al. (2011, C11) studied the nucleation properties of soot derived from the combustion of propane. It was found that ice nucleated in the deposition mode on uncoated soot with organic carbon content below 30% (OC30). Crawford et al. 15 (2011) reported values of  $S_i$  at  $f_f = 0.1\%$  and  $f_f = 1\%$ , which are used to constraint Eq. (38). The mean particle area,  $\bar{s}_{p}$ , is estimated using bulk surface area and density of  $32 \text{ m}^2 \text{ g}^{-1}$  and 1600 Kg m<sup>-3</sup>, respectively (Popovitcheva et al., 2000), and assuming a lognormal size distribution with geometric mean diameter of 250 nm and geometric dispersion equal to 2 (Crawford et al., 2011). From Seisel et al. (2005),  $\Delta g_{d} = 4.4 \times$ 20  $10^{-20}$  J and  $\alpha_c = 4.7 \times 10^{-2}$ . From the C11 data,  $\Delta t_{exp} = 80$  s, corresponding to a cooling rate of about  $2 \text{ K min}^{-1}$ .

Figure 7 shows the derived nucleation spectra for OC30 soot.  $\bar{\theta}$  ranges between 32° and 36° and  $\sigma_{\varphi}$  between 22 and 32. The latter is slightly larger than the dust average  $\sigma_{\varphi}$ . Due to the fractal characteristics of soot (Dymarska et al., 2006; Gorbunov et al., 2001), it is possible that surface area dispersion plays a more significant role in determining the NPDF than for dust. The limiting  $f_{\rm f}$  (at  $S_{\rm i} = 1.7$ ) is about 25%, in good



agreement with the C11 data. The average  $\bar{\theta}$  and  $\sigma_{\varphi}$  among the spectra of Table 2 (OC30 cases) are used to parameterize  $f_{\rm f}$  (Table 4). The resulting parameterization is shown in Fig. 8; as it is based on limited data its usage is recommended only for exploratory studies.

#### **5 5 Summary and conclusions**

A novel formulation of the ice nucleation spectrum for homogeneous and heterogeneous ice nucleation was developed. This was accomplished by introducing the concepts of ice nucleation coefficient and ice nucleation probability dispersion. It was shown that the NDPF and the aerosol ice nucleation spectra are simply related by Laplace transformation. The new formulation accounts for the dependency of  $N_{c}(S_{i}, T,...)$  on particle size,  $T, S_{i}, u$ , and, in the case of heterogeneous ice nucleation, on the distribution of particle area and surface composition. It was applied to the homogeneous freezing of cloud droplets and the heterogeneous ice nucleation on IN in the deposition mode. For the latter, parameterizations of deposition ice nucleation 15 on dust and soot for usage in atmospheric models were developed.

It was shown that the NPDF for the homogeneous freezing of cloud droplets is determined by the droplet volume distribution and well represented by a gamma distribution. Analysis of  $N_c(S_i, T,...)$  for this case showed that variation in  $D_p$  and  $\gamma$  may result in about 2–3 K variation in  $T_{onset}$ . Dispersion in the droplet volume distribution however does not impact  $T_{onset}$  but "stretches"  $f_f$  over a wider T interval so that some droplets in the population may freeze at T as low as 228 K. This effect is significant for varr > 0.4 (Eq. 14) and may have important implications for the cold generation of precipitation as CCN emissions and entrainment tend to broaden the droplet size distribution.

The theory presented here suggests that the NPDF for heterogeneous ice nucleation on simple materials follows a lognormal distribution whereas the NPDF of complex materials can be adequately represented by a sum of lognormal modes. It was also found that NPDFs with support over the whole real axis, like the normal distribution, may



introduce unphysical behavior and wrongly imply that values of  $\theta < 0$  are accessible to  $\mathcal{N}(\bar{\phi})$ . For the lognormal and gamma distributions it was found that  $\bar{\phi} = 1$  defines the characteristic ice nucleation properties of the aerosol population. Although this was shown for deposition ice nucleation, it is likely that immersion and condensation freezing display the same behavior as Eq. (26) is common to different heterogeneous nucleation modes.

5

10

15

Singular and stochastic behavior were reproduced using the new formulation of  $N_{\rm c}(S_{\rm i}, T,...)$ . In deposition ice nucleation  $S_{\rm i}$ ,  $\bar{\theta}$ , u, T,  $\bar{s}_{\rm p}$ , and  $\sigma_{\varphi}$  play a role defining  $f_{\rm f}$ , however highly efficient IN ( $\theta < 10^{\circ}$ ) are only sensitive to variation in  $S_{\rm i}$ , and  $\bar{\theta}$ . This is however not the case for less efficient IN for which temporal effects (expressed through the dependency of  $f_{\rm f}$  on u) and variability in surface characteristics (expressed through the dependency of  $f_{\rm f}$  on  $\sigma_{\varphi}$ ) impact  $f_{\rm f}$ . Thus, ice nucleation on IN with high  $\bar{\theta}$  shows features commonly referred to as stochastic while highly efficient IN (low  $\bar{\theta}$ ) tend to display singular behavior. This implies that ice nucleation on materials with multimodal NPDF would likely exhibit both, singular and stochastic characteristics.

Comparison of the derived  $N_c(S_i, T,...)$  against empirical data (Möhler et al., 2006; Welti et al., 2009) showed that the NPDF of simple dust species like Kaolinite and Montmorrinolite can be accurately represented by bimodal NPDFs whereas complex mixtures like Arizona Test Dust and Saharan Dust are well represented by three-modal NPDFs. It is however remarkable that for all of the dust species studied these modes are consistently located around  $\bar{\theta}_1 \approx 10^\circ$ ,  $\bar{\theta}_2 \approx 15^\circ$ , and  $\bar{\theta}_3 \approx 20^\circ$ , suggesting that the NPDF of dust from different sources can be represented by a linear combination of few lognormal modes. This feature was used to generate a parameterization of deposition ice nucleation on "generic dust". Further measurements of  $N_c(S_i, T,...)$  covering the

full range of  $f_f$  (i.e.  $f_f = [0-1]$ ) are required to elucidate the fundamental reasons behind such behavior.

The nucleation spectrum of soot was also investigated. It was found that deposition ice nucleation on low organic content soot is well represented using a single-mode log-normal NPDF with  $\bar{\theta} = 34.2^{\circ}$ . The limiting  $f_{\rm f}$  of 25% found by Crawford et al. (2011)



was in good agreement with the predictions of Eq. (38). A parameterization was proposed for usage in atmospheric models, however further experimental measurements are required to better represent the ice nucleation properties of soot.

- The theory presented here suggests that inferring the aerosol ice nucleation properties from measurement of  $S_{i,onset}$  at  $f_f \approx 0.01$  may carry significant error. First, Fig. 3 shows that  $S_{i,onset}$  is strongly impacted by  $\sigma_{\varphi}$  so that it may vary between samples of the same material or between freezing cycles. Second,  $S_{i,onset}$  represents the ice nucleation properties associated with the most efficient mode in the NPDF, which maybe the less abundant (Table 2). Finally  $S_{i,onset}$  does not provide information on  $\sigma_{\varphi}$  which
- <sup>10</sup> may impact the inferred  $\bar{\theta}$  (Fig. 4). These effects can be minimized by measuring  $S_{i,onset}$ at  $f_f \approx 0.5$  (corresponding to  $\bar{\phi} \approx 1$ ); ideally, it would be best to determine the entire  $f_f$ curve. For this, it is also important to measure the aerosol number area distribution instead of the number size distribution as it is the former, not the latter, what determines  $\bar{\phi}$  and  $\sigma_{\phi}$ , hence  $N_c(S_i, T,...)$ .
- Although this work focuses on heterogeneous nucleation in the deposition mode, it is readily suited for other nucleation modes. Heterogeneous freezing in the immersion and condensation modes share many features with deposition ice nucleation. Still, water adsorption on the particle surface (e.g. Seisel et al., 2005; Kumar et al., 2009), the effect of the solute on the interfacial tension, and the droplet size distribution may play a role in defining  $f_{\rm f}$ . This is detailed in a companion study.

In the general sense, the NPDF represents the combined distribution of ice nucleation efficiency and the area over which that efficiency maintains. The NPDF is therefore fundamentally different from the contact angle and the active site distributions. In fact, they can be recovered from the NPDF when either the contact angle or the active site area is constant in the aerosol population. However only the NPDF is related to  $N_c(S_i, T,...)$  by Laplace transformation and contains all the information on the ice nucleation spectrum. Thus, compared to existing approaches the formulation of  $N_c(S_i, T,...)$ presented here expresses the greatest degree of variability using the fewest parameters, and unlike fits to experimental results, assigns precise physical meaning to such



parameters. This work provides a physically-based method to reconcile theory, laboratory measurements and field campaign data, within a unified ice nucleation framework suitable for atmospheric modeling studies.

## Appendix A

# List of symbols

- Parameter of the gamma distribution α
- $\frac{g\Delta H_{\rm s}m_{\rm w}}{c_{\rm p}kT^2} \frac{gm_{\rm a}}{kT}$  $\alpha_{\rm s}$
- Water vapor mass accommodation coefficient  $\alpha_{\rm c}$
- Parameter of the gamma distribution β
- Rate at which water molecules are incorporated into the critical ice cluster  $\beta_{\rm h}$
- Cooling rate γ
- Desorption energy of the water molecules from the particle's surface  $\Delta g_{\rm d}$
- Energy of formation of the ice germ  $\Delta g_{a}$
- $\Delta H_{s}$ Latent heat of sublimation of ice
- $\Delta t_{\mathrm{exp}}$ Experimental nucleation time scale
- Temperature perturbation  $\epsilon$
- Local contact angle between the solid surface and the ice germ θ
- $\bar{\theta}$ Mean contact angle
- *i*-th moment of the distribution of aerosol number concentration  $\mu_i$
- 1 7varr ν  $\frac{\varphi}{\bar{\varphi}}$
- ξ
- Surface density of active sites  $\rho_{as}$
- Ice nucleation dispersion coefficient  $\sigma_{\varphi}$
- Surface tension of ice  $\sigma_{i/v}$

Discussion Paper	ACPD 11, 29601–29646, 2011 On the ice nucleation spectrum							
Discu	D. Bar	ahona						
ission P	Title	Page						
aper	Abstract	Introduction						
	Conclusions	References						
Disc	Tables	Figures						
ussio		▶1						
n Pa	•	Þ						
per	Back	Close						
—	Full Scre	en / Esc						
Discussio	Printer-frier	dly Version						
n Paper	œ	<b>D</b> BY						

$ au_{\sf nuc}$	Timescale of nucleation	Dis		
arphi	Ice nucleation coefficient	CUS	AC	PD
$ar{arphi}$	Characteristic ice nucleation coefficient	0.0	11 29601-2	29646 2011
A	$\frac{\alpha_c}{\sqrt{f}} \frac{p_v^2 v_w}{m_w k T v_s} \sqrt{\frac{\sigma_{i/v}}{k T}} \exp\left(\frac{\Delta g_d}{k T}\right)$	n Pap		
C <sub>1,s</sub>	Surface concentration of water molecules	)er	On the ice	nucleation
Cp	Heat capacity of air		spec	trum
$D_{\rm p}$	Equivalent droplet size			
f	Compatibility parameter	Dis	D. Bar	ahona
f <sub>f</sub>	Ice nucleation fraction	CUS		
g	Acceleration of gravity	Sic		
$J_{ m het}$	Heterogeneous ice nucleation coefficient	л Г	Title	Page
$J_{\rm hom}$	Homogeneous ice nucleation coefficient	ap	Abstract	Introduction
k	Boltzmann constant	₽		
m <sub>a</sub>	Molecular mass of air		Conclusions	References
m <sub>w</sub>	Mass of a water molecule		Tables	Figuros
Μ	Total number of lognormal modes in the NPDF	)isc	Tables	riguies
N <sub>a</sub>	Aerosol number concentration	SUS		
$N_{\rm c}(S_{\rm i},T,\ldots)$	Ice Nucleation Spectrum	Sior		►I
$n_{\rm c}(S_{\rm i},T,\mu_i)$	Differential ice nucleation spectrum	P	•	•
n <sub>g</sub>	Number of water molecules in the ice germ at liquid water saturation	ape		
n(̈φ)	Probability distribution function of $arphi$	1	Back	Close
n(ξ)	Nucleation Probability Dispersion Function (NPDF)	—	Full Scre	en / Esc
$\mathcal{N}(ar{arphi})$	Laplace transform of $n(\xi)$			
$ ho_{ m s,w}$ , $ ho_{ m s,i}$	Liquid water and ice saturation vapor pressures at $T$ , respectively	SCL	Printer-frier	dlv Version
$\rho_{v}$	Water vapor pressure	ISS!		-
r <sub>g</sub>	Ice germ size	ON	Interactive	Discussion
r <sub>g</sub>	Value of $r_{\rm g}$ at $S_{\rm w}$ = 1	Pa		
$\mathcal{S}_{i}$	Saturation ratio with respect to ice	per	<u></u>	<b>O</b>

$S_{w}$	Saturation ratio with respect to liquid water	Disc		
$S_{\rm w}^{\rm lsat}$	$p_{s,i}/p_{s,w}$	SUS	AC	PD
$s_{p}$	Particle surface area	0	11, 29601-2	29646, 2011
ť	Time	P	,	
Т	Temperature	ape		
$T_0$	273 K	1	On the ice	nucleation
u	Vertical wind velocity	—	spec	trum
varr	Variance of the droplet volume distribution		D Bar	ahona
V <sub>p</sub>	Droplet volume	isc	D. Dai	anona
V <sub>s</sub>	Molecular frequency of vibration	SSN		
V <sub>w</sub>	Volume of a water molecule	ion	Title	Page
Wi	Weight of the <i>i</i> -th lognormal mode in the NPDF	P		
Zhet	Zeldovich factor	aper	Abstract	Introduction
Acknowle	edgements. This work was supported by the NASA Modeling, Analysis and Predic-	_	Conclusions	References
tion progr	am under WBS 802678.02.17.01.07. The author also thanks Athanasios Nenes and		Tablaa	Eiguroo
Ricardo N	Iorales for their helpful comments and discussion.	Disc	Tables	Figures
Referen	295	SUS		
		sion	14	•1
Austin, P	, Wang, Y., Kujala, V., and Pincus, R.: Precipitation in Stratocumulus Clouds:	Pa	•	•
Observ	rational and Modeling Results, J. Atmos. Sci., 52, 2329-2352, doi:10.1175/1520-	lpei	Pook	Close
0469(1	995)052<2329:PISCOA>2.0.CO;2, 1995. 29609		Dack	CIOSE
moden	L, D. and Neries, A.: Parameterization of cirrus formation in large scale models. Ho-		Full Scre	en / Esc
29609.	29610			
Barahona	I, D. and Nenes, A.: Parameterizing the competition between homogeneous and het-	Scu	Printer-frier	dly Version
erogen	eous freezing in ice cloud formation - polydisperse ice nuclei, Atmos. Chem. Phys.,	SS:		<b>D</b> 1 1
9, 5933	3-5948, doi:10.5194/acp-9-5933-2009, 2009. 29603, 29614	on F	Interactive	Discussion
Barahona	i, D., Rodriguez, J., and Nenes, A.: Sensitivity of the global distribution of cir-	ap		
rus ice	crystal concentration to heterogeneous freezing, J. Geophys. Res., 15, D23213,	er	$\sim$	BY

5 Austin.

10

rus Ice crystal concentration to heterogeneous freezing, J. Geophys. Res., 15, D23213, 15 doi:10.1029/2010JD014273, 2010. 29602, 29603, 29611



- Broadley, S. L., Murray, B. J., Herbert, R. J., Atkinson, J. D., Dobbie, S., Condliffe, E., and Neve, L.: Immersion mode heterogeneous ice nucleation by an illite rich powder representative of atmospheric mineral dust, Atmos. Chem. Phys. Discuss., 11, 22801–22856, doi:10.5194/acpd-11-22801-2011, 2011. 29604, 29608
- <sup>5</sup> Chen, J.-P., Hazra, A., and Levin, Z.: Parameterizing ice nucleation rates using contact angle and activation energy derived from laboratory data, Atmos. Chem. Phys., 8, 7431–7449, doi:10.5194/acp-8-7431-2008, 2008. 29603, 29613
  - Connolly, P. J., Möhler, O., Field, P. R., Saathoff, H., Burgess, R., Choularton, T., and Gallagher,
     M.: Studies of heterogeneous freezing by three different desert dust samples, Atmos. Chem.
     Phys., 9, 2805–2824, doi:10.5194/acp-9-2805-2009, 2009. 29604
- Phys., 9, 2805–2824, doi:10.5194/acp-9-2805-2009, 2009. 29604
   Crawford, I., Möhler, O., Schnaiter, M., Saathoff, H., Liu, D., McMeeking, G., Flynn, M., Bower, K. N., Connolly, P. J., Gallagher, M. W., and Coe, H.: Studies of propane flame soot acting as heterogeneous ice nuclei in conjunction with single particle soot photometer measurements, Atmos. Chem. Phys. Discuss., 11, 11007–11038, doi:10.5194/acpd-11-11007-2011, 2011.

15 29622, 29624, 29636

20

DeMott, P., Meyers, M., and Cotton, R.: Parameterization and impact of ice initiation processes relevant to numerical model simulations of cirrus clouds, J. Atmos. Sci., 51, 77–90, 1994. 29603

DeMott, P., Chen, Y., Kreidenweis, S., Rogers, D., and Sherman, D.: Ice formation by black carbon particles, Geophys. Res. Lett., 26, 2429–2432, 1999. 29622

DeMott, P., Cziczo, D., Prenni, A., Murphy, D., Kreidenweis, S., Thompson, D., Borys, R., and Rogers, D.: Measurements of the concentration and composition of nuclei for cirrus formation, P. Natl. Acad. Sci. USA, 100, 14655–14660, 2003a. 29602, 29620

DeMott, P., Sassen, K., Poellot, M., Baumgardner, D., Rogers, D., Brooks, S., Prenni, A., and

- Kreidenweis, S.: African dust aerosols as atmospheric ice nuclei, Geophys. Res. Lett., 30, 1732, doi:10.1029/2003GL017410, 2003b. 29620
  - DeMott, P. J., Prenni, A. J., Liu, X., Kreidenweis, S. M., Petters, M. D., Twohy, C. H., Richardson, M. S., Eidhammer, T., and Rogers, D. C.: Predicting global atmospheric ice nuclei distributions and their impacts on climate, P. Natl. Acad. Sci., 107, 11217–11222, doi:10.1077/mres.00101010107
- <sup>30</sup> doi:10.1073/pnas.0910818107, 2010. 29603
  - Diehl, K., Simmel, M., and Wurzler, S.: Effects of drop freezing on microphysics of an ascending cloud parcel under biomass burning conditions, Atmos. Environ., 41, 303–314, 2007. 29603
    Dymarska, M., Murray, B., Sun, L., Eastwood, M., Knopf, D., and Bertram, A.: Deposition ice



nucleation on soot at temperatures relevant for the lower troposphere, J. Geophys. Res., 111, D04204; doi:10.1029/2005JD006627, 2006. 29612, 29619, 29622

- Eastwood, M., Cremel, S., Gehrke, C., Girard, E., and Bertram, A.: Ice nucleation on mineral dust particles: Onset conditions, nucleation rates and contact angles, J. Geophys. Res., 113, D22203, doi:10.1029/2008JD10639, 2008. 29619, 29620
- 5 Eidhammer, T., DeMott, P., and Kreidenweis, S.: A comparison of heterogeneous ice nucleation parameterizations using a parcel model framework, J. Geophys. Res., 114, D06202, doi:10.1029/2008JD011095, 2009. 29603, 29618

Fletcher, H.: Active sites and ice crystal nucleation, J. Atmos. Sci., 26, 1266–1271, 1969. 29612

- Gayet, J., Ovarlez, J., Shcherbakov, V., Ström, J., Schumann, U., Minikin, A., Auriol, F., Petzold, A., and Monier, M.: Cirrus cloud microphysical and optical properties at southern and northern midlatitudes during the INCA experiment, J. Geophys. Res., 109, D20206. doi:10.1029/2004JD004803.2004.29620
- Gorbunov, B., Baklanov, A., Kakutkina, N., Windsor, H. L., and Toumi, R.: Ice nucleation on soot 15 particles, J. Aerosol Sci., 32, 199–215, doi:10.1016/S0021-8502(00)00077-X, 2001. 29622 Hoose, C., Kristjansson, J., Chen, J.-C., and Hazra, A.: A classical-theory-based parameterization of heterogeneous ice nucleation by mineral dust, soot, and biological particles in a global climate model, J. Atmos. Sci., 67, 2483-2503, doi:10.1175/2010JAS3425.1, 2010. 29602, 29603, 29611
- 20

10

- IPCC: Climate change 2007: the physical basis. Contribution of working group I to the fourth assessment report of the Intergovernmental Panel on Climate Change., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA., 2007. 29602

Kanji, Z., Florea, O., and Abbatt, J.: Ice formation via deposition nucleation on mineral dust and

- organics: dependence of onset relative humidity on total particulate surface area, Environ. 25 Res. Lett., 3, 025004, doi:10.1088/1748-9326/3/2/025004, 2008. 29619
  - Kärcher, B., Hendricks, J., and Lohmann, U.: Physically based parameterization of cirrus cloud formation for use in global atmospheric models, J. Geophys. Res., 111, D01205. doi:10.1029/2005JD006219.2006.29603
- <sup>30</sup> Kashchiev, D.: Nucleation: basic theory with applications, Butterworth Heinemann, 2000. 29604, 29611, 29612
  - Khvorostyanov, V. and Curry, J.: The theory of ice nucleation by heterogeneous freezing of deliguescent mixed CCN. Part I: critical radius, energy and nucleation rate, J. Atmos. Sci.,



61, 2676–2691, 2004. 29603, 29612, 29614, 29617

5

10

15

20

Khvorostyanov, V. and Sassen, K.: Toward the theory of homogeneous nucleation and its parameterization for cloud models, Geophys. Res. Lett., 25, 3155–3158, 1998. 29603

Koop, T., Luo, B., Tslas, A., and Peter, T.: Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, Nature, 406, 611–614, 2000. 29603, 29610

Kumar, P., Sokolik, I. N., and Nenes, A.: Parameterization of cloud droplet formation for global and regional models: including adsorption activation from insoluble CCN, Atmos. Chem. Phys., 9, 2517–2532, doi:10.5194/acp-9-2517-2009, 2009. 29625

Liu, X. and Penner, J.: Ice nucleation parameterization for global models, Meteorol. Z., 14, 499–514, 2005. 29603

Lohmann, U.: A glaciation indirect aerosol effect caused by soot aerosols, Geophys. Res. Lett, 29, 1052, doi:10.1029/2001GL014357, 2002. 29603

Lohmann, U. and Diehl, K.: Sensitivity studies of the importance of dust ice nuclei for the indirect aerosol effect of stratiform mixed-phase clouds, J. Atmos. Sci., 63, 968–982, 2006. 29603

Lohmann, U. and Feichter, J.: Global indirect aerosol effects: a review, Atmos. Chem. Phys., 5, 715–737, doi:10.5194/acp-5-715-2005, 2005. 29602

Lüönd, F., Stetzer, O., Welti, A., and Lohmann, U.: Experimental study on the ice nucleation ability of size-selected kaolinite particles in the immersion mode, J. Geophys. Res., 115, D14201, doi:10.1029/2009JD012959, 2010. 29603, 29604

Määttänen, A., Vehkamäki, H., Lauri, A., Merikallio, S., Kauhanen, J., Savijärvi, H., and Kulmala, M.: Nucleation studies in the Martian atmosphere, J. Geophys. Res., 110, E02002, doi:10.1029/2004JE002308, 2005. 29612, 29613

Marcolli, C., Gedamke, S., Peter, T., and Zobrist, B.: Efficiency of immersion mode ice nucle-

 ation on surrogates of mineral dust, Atmos. Chem. Phys., 7, 5081–5091, doi:10.5194/acp-7-5081-2007, 2007. 29603, 29604

Medhi, J.: Stochastic processes, J. Wiley, 1994. 29606

- Meyers, M., DeMott, P., and Cotton, R.: New primary ice-nucleation parameterization in an explicit cloud model, J. Appl. Meteorol., 31, 708–721, 1992. 29603
- Möhler, O., Stetzer, O., Schaefers, S., Linke, C., Schnaiter, M., Tiede, R., Saathoff, H., Krämer, M., Mangold, A., Budz, P., Zink, P., Schreiner, J., Mauersberger, K., Haag, W., Kärcher, B., and Schurath, U.: Experimental investigation of homogeneous freezing of sulphuric acid particles in the aerosol chamber AIDA, Atmos. Chem. Phys., 3, 211–223, doi:10.5194/acp-



3-211-2003, 2003. 29620

20

30

- Möhler, O., Linke, C., Saathoff, H., Schnaiter, M., Wagner, R., Mangold, A., Krämer, M., and Schurath, U.: Ice nucleation on flame soot aerosol of different organic carbon content, Meteorol. Z., 14, 477–484, doi:10.1127/0941-2948/2005/0055, 2005. 29622
- <sup>5</sup> Möhler, O., Field, P. R., Connolly, P., Benz, S., Saathoff, H., Schnaiter, M., Wagner, R., Cotton, R., Krämer, M., Mangold, A., and Heymsfield, A. J.: Efficiency of the deposition mode ice nucleation on mineral dust particles, Atmos. Chem. Phys., 6, 3007–3021, doi:10.5194/acp-6-3007-2006, 2006. 29603, 29604, 29611, 29620, 29621, 29624, 29636

Murphy, D. and Koop, T.: Review of the vapour pressures of ice and supercooled water for atmospheric applications, Q. J. Roy. Meteorol. Soc., 131, 1539–1565, 2005. 29610

Murray, B. J., Broadley, S. L., Wilson, T. W., Atkinson, J. D., and Wills, R. H.: Heterogeneous freezing of water droplets containing kaolinite particles, Atmos. Chem. Phys., 11, 4191–4207, doi:10.5194/acp-11-4191-2011, 2011. 29603

Niedermeier, D., Shaw, R. A., Hartmann, S., Wex, H., Clauss, T., Voigtländer, J., and Strat-

- mann, F.: Heterogeneous ice nucleation: bridging stochastic and singular freezing behavior, Atmos. Chem. Phys. Discuss., 11, 3161–3180, doi:10.5194/acpd-11-3161-2011, 2011. 29604, 29608
  - Phillips, V., DeMott, P., and Andronache, C.: An empirical parameterization of heterogeneous ice nucleation for multiple chemical species of aerosol, J. Atmos. Sci., 65, 2757–2783, doi:10.1175/2007JAS2546.1, 2008. 29603, 29618
  - Popovitcheva, O. B., Persiantseva, N. M., Trukhin, M. E., Rulev, G. B., Shonija, N. K., Buriko, Y. Y., Starik, A. M., Demirdjian, B., Ferry, D., and Suzanne, J.: Experimental characterization of aircraft combustor soot: Microstructure, surface area, porosity and water adsorption, Phys. Chem. Chem. Phys., 2, 4421–4426, doi:10.1039/B004345L, 2000. 29622
- Pratt, K., DeMott, P., French, J., Wang, Z., Westphal, D., Heymsfield, A., Twohy, C., Prenni, A., and Prather, K.: In situ detection of biological particles in cloud ice-crystals, Nature Geosci., 2, 398–401, 2009. 29602
  - Prenni, A., Petters, M., Kreidenweis, S., Heald, C., Martin, S., Artaxo, P., Garland, R., Wollny,
    A., and Pöschl, U.: Relative roles of biogenic emissions and Saharan dust as ice nuclei in the Amazon basin, Nature Geosci., 2, 402–405, 2009. 29602
  - Pruppacher, H. and Klett, J.: Microphysics of clouds and precipitation, Kluwer Academic Publishers, Boston, MA, 2nd edn., 1997. 29603, 29604, 29607, 29608, 29611, 29612, 29613, 29614, 29618



29633

- Ramanathan, V., Crutzen, P., Kiehl, J., and Rosenfeld, D.: Aerosols, climate, and the hydrological cycle, Science, 294, 2119–2124, 2001. 29603, 29609
- Rosenfeld, D. and Woodley, W. L.: Deep convective clouds with sustained supercooled liquid water down to -37.5 C, Nature, 405, 440-442, doi:10.1038/35013030, 2000. 29602, 29603, 29609
- Rossberg, A.: Laplace transforms of probability distributions and their inversions are easy on logarithmic scales, J. App. Prob., 45, 531–541, 2008. 29606, 29616, 29635
- Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics, John Wiley and Sons, New York, NY, USA, 1998. 29616
- Seisel, S., Pashkova, A., Lian, Y., and Zellner, R.: Water uptake on mineral dust and soot: A fundamental view of the hydrophilicity of atmospheric particles?, Faraday Discuss., 130, 437–451, doi:10.1039/B417449F, 2005. 29611, 29612, 29613, 29621, 29622, 29625
  - Shortle, J. F., Fischer, M. J., Gross, D., and Masi, D. M. B.: Using the transform approximation method to analyze queues with heavy-tailed service, J. Probab. Statist. Sci, 1, 17–30, 2003. 29606. 29617
- 15 2

5

Stetzer, O., Baschek, B., Lüönd, F., and Lohmann, U.: The Zurich ice nucleation chamber (ZINC)-A New instrument to investigate atmospheric ice formation, Aerosol. Sci. Technol., 42, 64–74, 2008. 29621

Vali, G.: Freezing rate due to heterogeneous nucleation, J. Atmos. Sci., 51, 1843–1856, 1994.

20

25

- 29603, 29604
- Vali, G.: Repeatability and randomness in heterogeneous freezing nucleation, Atmos. Chem. Phys., 8, 5017–5031, doi:10.5194/acp-8-5017-2008, 2008. 29604
- Vehkamäki, H., Määttänen, A., Lauri, A., Napari, I., and Kulmala, M.: Technical Note: The heterogeneous Zeldovich factor, Atmos. Chem. Phys., 7, 309–313, doi:10.5194/acp-7-309-2007, 2007. 29613
- Wang, B. and Knopf, D. A.: Heterogeneous ice nucleation on particles composed of humic-like substances impacted by O<sub>3</sub>, J. Geophys. Res., 116, D03205, doi:10.1029/2010JD014964, 2011. 29620

Welti, A., Lüönd, F., Stetzer, O., and Lohmann, U.: Influence of particle size on the ice nucle-

- ating ability of mineral dusts, Atmos. Chem. Phys., 9, 6705–6715, doi:10.5194/acp-9-6705-2009, 2009. 29603, 29619, 29620, 29621, 29624, 29636
  - Zimmermann, F., Weinbruch, S., Schütz, L., Hofmann, H., Ebert, M., Kandler, K., and Worringen, A.: Ice nucleation properties of the most abundant mineral dust phases, J. Geophys.



Res., 113, D23204, doi:10.1029/2008JD010655, 2008. 29612, 29620
Zobrist, B., Koop, T., Luo, B., Marcolli, C., and Peter, T.: Heterogeneous ice nucleation rate coefficient of water droplets coated by a nonadecanol monolayer, J. Phys. Chem. C, 111, 2149–2155, 2007. 29608, 29612



**Table 1.**  $\mathcal{N}(\bar{\varphi})$  and  $n(\xi)$  for gamma, lognormal and sectional NPDFs;  $\bar{\varphi}$  is the characteristic ice nucleation coefficient defined in Sect. 2.1,  $\Gamma$  is the gamma function, and  $f_{a,k}$  represents the fraction of the aerosol population with cumulative ice nucleation probability below  $1 - \exp(-\xi_k \bar{\varphi})$ . The lognormal  $\mathcal{N}(\bar{\varphi})$  is approximated using  $\mathcal{N}(\bar{\varphi}) \propto \int_0^{1/\bar{\varphi}} n(\xi) d\xi$  (Rossberg, 2008).

Distribution	n(ξ)	$\mathcal{N}(ar{arphi})$
Gamma	$\frac{\beta^{\alpha}}{\Gamma(\alpha)}\xi^{\alpha-1}e^{-\beta\xi}$	$\left(rac{eta}{ar{arphi}+eta} ight)^{lpha}$
Lognormal	$\frac{e^{-\frac{\ln^2(\xi)}{2\sigma_{\varphi}^2}}}{\sqrt{2\pi}\sigma_{\varphi}\xi}$	$ ext{erfc}\left(rac{ ext{ln}(ar{arphi})}{\sqrt{\pi}\sigma_{arphi}} ight)$
Sectional	$\frac{f_{a,k} - f_{a,k-1}}{\xi_k - \xi_{k-1}}$	$\sum_{i} p_{i} e^{-\bar{\varphi}\xi_{i}} \text{ where } p_{i} = \int_{\xi_{i-1}}^{\xi_{i+1}} n(\xi) d\xi$



**Table 2.** Parameters of the nucleation spectra derived from the data reported by Möhler et al. (2006, M06), Welti et al. (2009, W09), and Crawford et al. (2011, C11);  $\sigma_{\varphi}$  is assumed to be the same in all modes.

Species	Reference	$\bar{s}_{p}$ ( $\mu m^{2}$ )	<i>T</i> (K)	Мо	de 1	Мо	de 2	Мо	de 3	$\sigma_{\omega}$
		F		w <sub>1</sub>	$\bar{\theta}_1(°)$	W <sub>2</sub>	$\bar{\theta}_2(°)$	w <sub>3</sub>	$\bar{\theta}_3(°)$	7
ATD	M05(IN02-148)	0.64	223.3	0.22	8.7	0.34	11.5	0.44	16.9	12.4
ATD	M06(IN02-148)	0.64	223.4	0.21	10.9	0.29	14.4	0.50	18.0	29.8
ATD	M06(IN02-149)	0.64	223.5	0.17	6.7	0.29	10.5	0.54	14.2	15.8
ATD	M06(IN03-05)	0.64	210.8	0.21	10.5	0.30	12.6	0.49	14.7	8.1
ATD	M06(IN03-06)	0.64	210.6	0		0.41	11.7	0.59	13.1	5.9
ATD	M06(IN03-067)	0.64	210.5	0.02	10.2	0.39	11.6	0.59	13.7	9.3
SD	M06(IN04-40)	0.84	224	0		0.16	22.9	0.84	33.6	23.5
SD	M06(IN04-44)	0.84	213.1	0.27	9.8	0.05	14.0	0.68	19.6	30.0
SD	M06(IN03-11)	0.84	210	0.21	11.2	0.27	14.3	0.49	17.7	25.9
MONT	W09(200 nm)	0.25	233	0		0.08	16.1	0.92	21.1	30.0
MONT	W09(200 nm)	0.25	228	0		0.06	13.3	0.94	16.4	15.9
MONT	W09(200 nm)	0.25	223	0		0.10	16.0	0.90	19.8	20.8
MONT	W09(200 nm)	0.25	218	0		0.11	18.5	0.89	23.7	22.0
MONT	W09(400 nm)	1.00	233	0		0.05	13.4	0.95	16.6	25.6
MONT	W09(400 nm)	1.00	228	0		0.10	14.2	0.90	18.5	20.0
MONT	W09(400 nm)	1.00	223	0		0.08	15.8	0.92	20.1	19.9
MONT	W09(400 nm)	1.00	218	0		0.07	15.2	0.92	21.7	25.0
MONT	W09(800 nm)	4.01	233	0		0.13	12.1	0.87	14.5	16.5
MONT	W09(800 nm)	4.01	228	0		0.12	12.8	0.88	15.2	14.3
MONT	W09(800 nm)	4.01	223	0		0.14	15.0	0.86	18.6	16.4
MONT	W09(800 nm)	4.01	218	0		0.04	17.8	0.96	22.6	18.3
KAO	W09(200 nm)	0.25	233	0		0.08	18.4	0.92	22.9	21.8
KAO	W09(200 nm)	0.25	228	0		0.12	16.1	0.88	21.9	21.0
KAO	W09(200 nm)	0.25	223	0		0.15	15.8	0.85	21.8	19.5
KAO	W09(200 nm)	0.25	218	0		0.14	17.2	0.86	22.5	19.6
KAO	W09(400 nm)	1.00	233	0		0.06	15.1	0.94	20.9	29.8
KAO	W09(400 nm)	1.00	228	0		0.16	14.8	0.84	19.5	30.0
KAO	W09(400 nm)	1.00	223	0		0.13	16.0	0.87	20.6	30.0
KAO	W09(400 nm)	1.00	218	0		0.08	17.4	0.92	21.2	19.2
KAO	W09(800 nm)	4.01	233	0		0.15	13.6	0.85	19.1	30.0
KAO	W09(800 nm)	4.01	228	0		0.15	13.4	0.85	17.2	21.2
KAO	W09(800 nm)	4.01	223	0		0.10	14.8	0.90	18.3	17.6
KAO	W09(800 nm)	4.01	218	0		0.1	17.8	0.93	21.8	23.2
OC30	C11(IN11-20)	159.4	225.1	1	32.3					29.7
OC30	C11(IN11-21)	159.4	224.8	1	35.5					32.6
OC30	C11(IN11-22)	159.4	224.5	1	34.6					22.7

**Discussion** Paper ACPD 11, 29601-29646, 2011 On the ice nucleation spectrum **Discussion** Paper D. Barahona **Title Page** Abstract Introduction Conclusions References **Discussion** Paper Tables **Figures** 14 ١ ◀ ► Close Back Full Screen / Esc **Discussion Paper Printer-friendly Version** Interactive Discussion Œ (cc)

29636

Discussion Paper	AC 11, 29601–2 On the ice spec	PD 29646, 2011 nucleation trum							
Discu	D. Barahona								
Ission P	Title	Page							
aper	Abstract	Introduction							
_	Conclusions	References							
Discu	Tables	Figures							
loissr	14	►I.							
n Pap	•	×.							
oer	Back	Close							
_	Full Scre	en / Esc							
Discussi	Printer-frier	ndly Version							
on Pap	Interactive	Discussion							
)er		BY							

**Table 3.** Summary of average parameters (standard deviation) for the nucleation spectra of Table 2.

Species	Mode 1		Mod	Mode 2		lode 3	$\sigma_{arphi}$
	<i>w</i> <sub>1</sub>	$\bar{\theta}_1(°)$	W <sub>2</sub>	$\bar{\theta}_2(°)$	w <sub>3</sub>	$\bar{ heta}_3(\degree)$	,
ATD	0.17(0.08)	9.4(1.7)	0.34(0.05)	12.0(1.3)	0.50	15.1(1.9)	13.6(8.7)
SD	0.24(0.05)	10.5(1.0)	0.16(0.11)	17.1(5.0)	0.60	23.6(8.6)	26.1(5.1)
MONT			0.09(0.03)	15.3(2.0)	0.91	19.1(2.9)	20.4 (4.6)
KAO			0.14(0.07)	16.0(1.8)	0.86	21.4(3.6)	25.5(4.7)
ALL DUST	0.19(0.08)	9.7(1.6)	0.15 (0.10)	15.1(2.6)	0.66	19.3(3.9)	20.8(7.8)
OC30	1	34.2 (1.7)					28.3(5.0)

Discussion Pa	<b>AC</b> 11, 29601–2	<b>PD</b> 29646, 2011							
aper	On the ice spec	On the ice nucleation spectrum							
Discus	D. Bar	ahona							
sion F	Title	Page							
aper	Abstract	Introduction							
_	Conclusions	References							
Disc	Tables	Figures							
Cussio	I	۶I							
n Par	•	•							
ber	Back	Close							
_	Full Scre	en / Esc							
Discussi	Printer-frier	dly Version							
on P	Interactive	Discussion							
aper	œ	BY							

**Table 4.** Suggested parameters for the parameterization of deposition ice nucleation on "generic dust" and soot with low organic carbon content (OC30).

Species	Мо	de 1	Мо	de 2	Мо	de 3	$\sigma_{\omega}$
	w <sub>1</sub>	$\bar{\theta}_1(°)$	<i>W</i> <sub>2</sub>	$\bar{\theta}_2(°)$	W <sub>3</sub>	$\bar{ heta}_3(°)$	,
DUST SOOT	0.20 1	9.9 34.2	0.25	15.1	0.55	19.8	21.4 28.3





Discussion Paper

**ACPD** 

11, 29601-29646, 2011

On the ice nucleation

spectrum

D. Barahona

Fig. 1. Ice nucleation probability dispersion functions (left panels) and corresponding ice nucleation fraction (right panels). Shown are sectional (based on a normal distribution using 20 bins, top panels), gamma (middle panels) and lognormal (bottom panels) distributions.



**Fig. 2.** Homogeneous ice nucleation spectra for the freezing of cloud droplets. Unless otherwise specified  $\gamma = 1 \text{ K min}^{-1}$ ,  $D_p = 20 \text{ }\mu\text{m}$ , and varr = 0.25.





**Fig. 3.** Heterogeneous ice nucleation spectra in the deposition nucleation mode. Lines are grouped by mean contact angle,  $\bar{\theta} = [5^{\circ}, 10^{\circ}, 15^{\circ}, 23^{\circ}]$  (from left to right). Unless otherwise specified  $u = 0.1 \text{ m s}^{-1}$ ,  $\bar{s}_{p} = 5 \text{ } \mu\text{m}^{2}$ ,  $\sigma_{\varphi} = 5$ , and T = 225 K.

















**Fig. 6.** Heterogeneous ice nucleation spectra in deposition mode for Arizona Test Dust (ATD) and Saharan dust (SD).





Fig. 7. Heterogeneous ice nucleation spectra in the deposition mode for OC30 soot.





**Fig. 8.** Parameterization of the heterogeneous ice nucleation spectra for deposition ice nucleation on "generic dust" (DUST) and soot with low organic carbon content (SOOT). The shaded area corresponds to T = [200-250] K, u = [0.01-1] m s<sup>-1</sup>, and  $\bar{s}_p = [0.1-100]$  µm<sup>2</sup>.

