**Atmospheric
Chemistry
and Physics
Discussions**

Heterogeneous ice nucleation: bridging stochastic and singular freezing behavior

D. Niedermeier[1], R. A. Shaw[2], S. Hartmann[1], H. Wex[1], T. Clauss[1], J. Voigtländer[1], and F. Stratmann[1]

[1]Leibniz Institute for Tropospheric Research, 04318 Leipzig, Germany
[2]Dept. of Physics, Michigan Technological University, Houghton, Michigan 49931, USA

Correspondence to: D. Niedermeier (niederm@tropos.de)

ACPD

11, 3161–3180, 2011

Bridging stochastic and singular freezing behavior

D. Niedermeier et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|
◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

Heterogeneous ice nucleation, a primary pathway for ice formation in the atmosphere, has been described alternately as being stochastic, in direct analogy with homogeneous nucleation, or singular, with ice nuclei initiating freezing at deterministic temper-
5 atures. We present an idealized model that bridges these stochastic and singular descriptions of heterogeneous ice nucleation. This "soccer ball" model treats statistically similar particles as being covered with surface sites (patches of finite area) characterized by different nucleation barriers, but with each surface site following the stochastic nature of ice embryo formation. The model provides a phenomenological explanation
10 for seemingly contradictory experimental results obtained in our research groups. We suggest that ice nucleation is fundamentally a stochastic process but that for realistic atmospheric particle populations this process can be masked by the heterogeneity of surface properties. Full evaluation of the model will require experiments with well characterized ice nucleating particles and the ability to vary both temperature and waiting
15 time for freezing.

1 Introduction

Much of the dispersed water in atmospheric clouds is in a metastable, supercooled state, and often freezing is stimulated by relatively rare aerosol particles known as heterogeneous ice nuclei. Heterogeneous ice nucleation directly influences cloud physi-
20 cal processes, precipitation formation, global radiation balances, and therefore Earth's climate (Cantrell and Heymsfield, 2005; Pruppacher and Klett, 1997, and references therein). It is important to understand the heterogeneous freezing process at a fundamental level in order to describe this process in a physically-based way that will behave robustly in weather and climate models.
25 There is longstanding debate as to whether heterogenous ice nucleation is a stochastic process or whether nucleation takes place on specific particle surface

sites at characteristic (deterministic) freezing temperatures, known as the singular hypothesis. The debate is more than academic since it lies at the foundation of how we represent ice nucleation in complex atmospheric simulations for weather and climate. The two different points of view on heterogeneous ice nucleation first emerged in the 1950's. The first, known as stochastic hypothesis, was developed by Bigg (1953a,b, 1955), Carte (1956, 1959) and Dufour and Defay (1963). They stated that the efficiency of the random nucleation process is increased due to the presence of insoluble particles (also called ice nuclei (IN)) without disturbing the stochastic nature of ice embryo formation (Pruppacher and Klett, 1997). For example, when considering immersion freezing, a population of droplets with each containing one immersed, insoluble particle (particles are assumed to be similar concerning size, chemical composition etc.) exhibits equal chance of freezing at a given temperature within a given time period (Vali, 2008), i.e., ice nucleation is time-dependent. Newer experimental observations (e.g., Durant and Shaw, 2005; Seeley and Seidler, 2001a,b; Shaw et al., 2005; Zobrist et al., 2007) support this stochastic view of ice nucleation.

The other approach, called the singular hypothesis, was developed by Levine (1950) and Langham and Mason (1958), among others. This hypothesis assumes that ice embryos form on specific sites on the IN surface at a characteristic (i.e., deterministic) temperature T_c (Langham and Mason, 1958; Pruppacher and Klett, 1997; Vali, 1994, 2008). These "active" sites are considered to be preferred sites, presumably as a result of the particle-ice interfacial free energy being minimal (Fletcher, 1969; Vali, 2008). But the exact nature of these sites is unknown. Presumably, they are (i) sites with a geometric arrangement of the atoms/molecules similar to that of the ice lattice (hexagonal arrangement of hydroxyl groups at ice active surface), (ii) sites featuring hydrogen bonds of specific strength and polarity (e.g., hydrogen-bonding groups like –OH, –NH$_2$ or =O) or (iii) sites consisting of steps, etch pits, edges, etc., that could enhance the ice nucleation process (Pruppacher and Klett, 1997). However, the site with the lowest energy barrier and therefore highest characteristic temperature determines the freezing/nucleation temperature. Being cooled to this T_c, IN with these active sites

will initiate ice nucleation instantaneously. If the temperature is constant afterwards, no additional nucleation events will occur, i.e., the ice nucleation process is assumed to be time-independent. Recent observations, such as those of Möhler et al. (2006) and Connolly et al. (2009), show negligible time dependence of the ice particle for-
5 mation rate and are therefore interpreted as consistent with singular hypothesis. The viewpoint was further established by Vali and Stansbury (1966) and Vali (1994, 2008), who performed experiments of repeated freezing and melting cycles of water droplets containing different kinds of particles and observed freezing temperatures with small fluctuations. These findings were interpreted as reflecting the existence of characteris-
10 tic freezing temperatures for active sites on the immersed particles, for which stochastic effects only slightly modify the characteristic freezing temperatures (modified singular hypothesis).

2 Apparent conflict between stochastic and singular descriptions

The apparent conflict between these descriptions of nucleation is drawn into sharp fo-
15 cus by considering results from two ice nucleation experiments conducted by several of the authors. These are but two of a number of similar experiments carried out in various groups, but they are sufficiently controlled so as to allow interpretation with a simple model. First, Shaw et al. (2005) and Durant and Shaw (2005) measured the freezing temperature of a water drop containing a single mineral (volcanic ash) particle (Fig. 1).
20 By repeating the measurement tens or hundreds of times a distribution of freezing temperatures was obtained. This result, the appearance of random fluctuations in freezing temperature for an identical particle, unambiguously contradicts the singular description, for which a single particle is characterized by a single, threshold freezing temperature. Also the modified singular hypothesis can not convincingly explain these
25 freezing results. Second, Niedermeier et al. (2010) measured the freezing temper-ature of large numbers of water droplets each containing a size-selected, monodis-perse mineral particle (Arizona Test Dust, ATD). They found that ATD nucleated ice

Bridging stochastic and singular freezing behavior

D. Niedermeier et al.

over a broad temperature range and the determined freezing temperature distributions can be parameterized using both, stochastic and singular descriptions. When similar measurements were made under nearly identical thermodynamic conditions but with increased nucleation time (the time interval within which supercooled droplets can freeze), however, the freezing temperature distributions remained essentially unchanged. This apparently contradicts the stochastic description, for which an increase in measurement time should lead to an increase in the freezing probability. Both experiments involve "complex" particles with no simple, well defined composition or simple crystalline structure. The experiments are distinguished fundamentally, however, in the two approaches to forming a statistical ensemble of freezing temperatures: by repeating a measurement of one system many times versus measuring many similar systems independently. The single-particle ensemble exhibits clear stochastic behavior, while the multi-particle ensemble apparently exhibits singular behavior.

3   Description of the soccer-ball model

To reconcile the seeming contradiction and more generally to better understand the competing ideas and that somewhat bewildering range of interpretations and applications of stochastic and singular ice nucleation we have developed a model extending the mixed-stochastic-singular concept of Marcolli et al. (2007) and Lüönd et al. (2010), who found that their measurements were best described using the singular hypothesis while keeping the stochastic concept of a nucleation rate. Our model, which is for convenience placed in the context of immersion freezing but could just as easily be adapted to deposition nucleation, is fundamentally based on the stochastic view of nucleation: That is, nucleation is viewed as always occurring as a result of random fluctuations of water molecules leading, eventually, to a critical ice embryo able to grow spontaneously. The model, being highly idealized, has the following essential features:

1. We consider a large number N_0 (statistical ensemble) of spherical "ice nucleus" particles of identical size, each particle immersed in a water droplet. The

population of particle-containing water droplets is assumed to be exposed to uniform thermodynamic conditions for a certain length of time. The fraction of frozen droplets at a given time and temperature therefore can be directly related to the probability of freezing on a particle of the specified size, composition, etc.

2. The properties of individual particles are not necessarily identical, but the probability exists for particles to feature similar properties. To that end, the surface of each particle is imagined to be divided into a number n_{site} of surface sites, with each site having well-defined properties (e.g., interfacial free energy). The word site is used to denote a surface two-dimensional "patch" of finite extent and the image of a spherical particle covered by a finite number of patches leads to the colloquial name "soccer ball" model. For simplicity, n_{site} is identical on all particles and the sites are assumed to be of the same size, $s_{site} = S_p/n_{site}$, where S_p is the particle surface area. Hence each surface site is associated with a given area depending on the number of sites per particle. Since individual sites are homogeneous concerning their properties ice embryo formation will occur randomly at some point on a given site.

3. Each surface site, i, is characterized by a fixed, but randomly chosen water contact angle θ_i. For simplicity, the contact angle distribution function $P(\theta)$ is assumed to be the integral over the Gaussian (error function) characterized through mean μ_θ and standard deviation σ_θ. The contact angle distribution is discretized in 1800 bins between 0 and π and through uniformly distributed random numbers $n \in [0,1]$ each site is associated with a specific contact angle, shown in the right panel of Fig. 2 through θ_i.

It is a separate question whether such an ensemble view reasonably captures the features of natural aerosol systems, and we leave detailed evaluation of that question for future work. Several comments will illustrate important features of the model. Concerning point 2, we note that the site size s_{site} is independent of the critical ice embryo size. It is implicitly assumed that the sites are sufficiently large such that

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

classical nucleation theory applies at any given site (e.g., surface sites are not allowed to be smaller than approximately $10\,\text{nm}^2$, the area covered by a critical ice embryo at $-29\,°\text{C}$ according to classical nucleation theory (Marcolli et al., 2007)). Consequently the number of surface sites is limited, too. Finally, it should be clear that $n_{\text{site}} = 1$ indicates a particle with completely homogeneous surface properties. Concerning point 3, the contact angles are drawn from a contact angle distribution function $P(\theta)$ that holds for the ensemble of particles, and therefore contact angles can vary between surface sites and consequently between particles, too. This results in the important feature that the population of particles can be thought of as "externally mixed" with respect to ice nucleating properties. Only when n_{site} is very large (mathematically going towards infinity) might it be safe to assume that a similar distribution of contact angles will exist on each and every particle, thereby representing what could be considered an "internally mixed" population.

The soccer ball model is formulated to yield several limits:

(A) When $n_{\text{site}} = 1$ and $\sigma_\theta = 0$, the population is completely uniform.

(B) When $n_{\text{site}} = 1$ and $\sigma_\theta > 0$, we have an externally mixed population.

(C) When $n_{\text{site}} \to \infty$ and $\sigma_\theta > 0$, we obtain an internally mixed population.

In the atmosphere we might expect that particle populations are between the internally- and externally-mixed limits, or in other words, conditions between limits (B) and (C), implying $n_{\text{site}} > 1$ and $\sigma_\theta > 0$. So we expect that particles have a somewhat nonuniform surface composition or morphology (more than one site), and that the properties, and therefore also the probability of the surface sites to initiate nucleation at a given temperature, vary between particles.

Using classical nucleation theory the freezing probability P_{freeze} of a supercooled droplet containing one immersed particle from the population is given through:

$$P_{freeze}(T,\theta) = 1 - \prod_{i=1}^{n_{site}} e^{-j_{het}(T,\theta_i)s_{site}t} \qquad (1)$$

where t is the observation time and $j_{het}(T,\theta_i) = \frac{kTn_s}{h}\exp\left(-\left(\frac{\Delta F(T)+\Delta G(T)f(\theta_i)}{kT}\right)\right)$ is the

5 heterogeneous ice nucleation rate coefficient. Here, h and k are the Planck and Boltzmann constants, T is the absolute temperature and n_s is the number density of water molecules at the ice nucleus/water interface. $\Delta F(T)$ is the activation energy for diffusion of water molecules across the liquid water/ice boundary and $\Delta G(T)$ represents the Gibbs free energy for critical ice embryo formation. The reduction of the

10 free energy barrier due to the IN can be represented through the spherical-cap factor $f(\theta_i) = \frac{1}{4}(2+\cos\theta_i)(1-\cos\theta_i)^2$, based on the contact angle. The model calculations given here use the n_s, $\Delta F(T)$, and $\Delta G(T)$ values/parameterizations given by Zobrist et al. (2007).

Finally, the frozen fraction f_{ice} of the supercooled droplets can be calculated through

15 $$f_{ice}(T) = \frac{N_f(T)}{N_0} = 1 - \frac{N_u(T)}{N_0} = \frac{1}{N_0}\sum_{k=1}^{N_0} P_{freeze,k}(T) \qquad (2)$$

with N_u and N_f being the number of unfrozen and frozen droplets, respectively.

4 Model results and discussion

The time behavior of the freezing process resulting from this model is illustrated in Fig. 3 and 4. First, in Fig. 3 we consider limit (A), i.e, a uniform particle population

20 consisting of 1000 particles is assumed, with all particles featuring the same contact angle. Plotted is the logarithm of the unfrozen fraction $\ln\frac{N_u}{N_0}$ as function of time t for various contact angles at $T = -20°C$. Each curve is a straight line, reflecting the purely

stochastic behavior of the freezing process. As can be deduced from Eq. (1), the slopes of these lines correspond to the reciprocal of the mean nucleation time ($\tau = \frac{1}{j_{\text{het}}(T,\theta_i)s_{\text{site}}}$), which is a function of both temperature and contact angle.

Second, we consider the effect of variable surface properties over the particle population, by allowing for a broader contact angle distribution; i.e., we allow $\sigma_\theta > 0$ in $P(\theta)$ (Fig. 4). We do so for different numbers of particle surface sites by setting n_{site} to 1, 10 and 100, i.e., moving from limiting case (B) towards case (C). All populations are assumed to feature the same mean contact angle. Here model results are presented exemplarily with fixed $\mu_\theta = 1.0$ rad. The model results are presented for different absolute temperatures for reasons shown later.

For $\sigma_\theta = 0.001$ rad (Fig. 4a), we still observe a straight line for all three n_{site} values. That means freezing appears as purely stochastic, despite the small variability of the contact angles and consequently in the mean nucleation time τ across the particle population.

For $\sigma_\theta = 0.01$ rad (Fig. 4b), the curve slopes start to change. For $n_{\text{site}} = 1$, a decrease in the slope, i.e., a weaker time dependence of the nucleation process with increasing time can be observed. However, with increasing number of sites on the particle surfaces this effect weakens, returning to an almost constant slope for $n_{\text{site}} = 100$.

Considering even wider ranges of contact angles $\sigma_\theta = 0.1$ rad (Fig. 4c) and $\sigma_\theta = 0.5$ rad (Fig. 4d), the flattening out of the frozen fraction versus time curves becomes even more pronounced. For $\sigma_\theta = 0.5$ rad, after an initial jump, the frozen droplet fraction stays more or less constant, i.e., the freezing process appears to be of a purely singular nature. Increasing n_{site} generally leads to steeper slopes, i.e., pushes the freezing behavior back towards a more apparently stochastic nature.

In summary, Fig. 4 displays the transition from a stochastic to an apparently singular behavior of the heterogeneous ice nucleation process, with this transition being due to a wider distribution of contact angles, and consequently mean nucleation times, or more generally speaking, ice nucleation related surface properties across the particle population. It should be noted that the results presented above were determined

assuming all particles to be of the same size. Considering different particle sizes inside the particle population would lead to an even wider distribution of surface properties, pushing the nucleation statistics even more towards apparently singular behavior.

Since experimental studies often focus on the determination of freezing temperatures, and modeling in terms of freezing temperature is a common practice, it is beneficial to also discuss the model results in that context. Therefore in Fig. 5, the fractions of frozen droplets are plotted as function of temperature. Here, a nucleation time of 1 s was chosen for the calculation of the frozen fraction. The freezing temperature T_f now is defined as the temperature at which 50% of the droplets are frozen. Within one panel, we consider different values of σ_θ, i.e., spreads in the contact angle distribution function, while each panel represents a different number of surface sites n_{site} on the particles. For $n_{site} = 1$, the mean freezing temperature T_f is identical for all σ_θ values ($T_f \approx -21°C$). However, with increasing σ_θ the temperature range in which droplets freeze (increase of the frozen fraction from 0 to 1) becomes broader. For example, for $\sigma_\theta = 0.001$ droplets freeze within a narrow temperature interval of about 3 K, while for $\sigma_\theta = 0.5$ rad freezing occurs over a temperature range of about 40 K.

Now, increasing the number of surface sites (moving from left to right in Fig. 5) two effects can be observed: For example, for $\sigma_\theta = 0.1$ rad (red line), the curve becomes steeper, and the freezing temperature shifts to larger values. The explanation for the curves becoming steeper is simply the "recovery" of the stochastic behavior with increasing n_{site} as discussed above. The shift of freezing temperature to larger values is remarkable and needs further consideration. It is a fact that with increasing spread in the contact angle distribution function, and with increasing n_{site}, the probability that contact angles significantly smaller than the mean occur on various members of the particle population increases. Keeping in mind, that the smallest contact angle and therefore lowest energy barrier for ice embryo formation determines the highest freezing probability, this implies that more and more droplets will freeze at temperatures higher than that corresponding to the mean contact angle. Ultimately, this will result in the shift of the freezing temperature T_f.

Generally, freezing temperatures found in atmospheric observations are higher than those determined in the laboratory using relatively pure clay mineral particle species like Kaolinite, Montmorillonite, etc. (e.g., Lüönd et al., 2010; Salam et al., 2006; Zimmermann et al., 2007; Zuberi et al., 2002) and using size selected particles (e.g., Archuleta et al., 2005; Lüönd et al., 2010; Niedermeier et al., 2010). In the view of the results presented in Fig. 5, we can speculate that atmospheric IN feature a variability in size, composition, and surface properties much larger than that of the IN investigated in the laboratory, and consequently higher freezing temperatures. This has to be considered as a hypothesis and needs further investigation.

Let us finally return to the seemingly contradictory laboratory results, and here specifically the results published by Shaw et al. (2005) and Niedermeier et al. (2010). The most plausible explanation in light of the model presented here, is that the variability of the surface properties across the population of ATD particles investigated by Niedermeier et al. (2010) is responsible for the broad temperature range over which droplets freeze and for the apparent missing time dependence for freezing. Since in the study of Shaw et al. (2005) a single particle was used repeatedly, the variability of the surface properties is eliminated so that the results reflect only the purely stochastic freezing nature. The soccer-ball model successfully reconciles these contrasting results, but of course the results taken alone do not verify the model. Evaluation of the basic, fundamental features of the model (i.e., inherent stochastic nature of ice nucleation operating over a finite number of patches) challenges current experimental methods because it requires determining the freezing probability versus both time and temperature. For example, fitting the frozen fractions of the ATD particles presented in Niedermeier et al. (2010) alone leads to a non-unique result because in that case the system is under-determined: different combinations of the three parameters n_{site}, μ_θ and σ_θ can successfully fit the observed freezing probabilities. The different parameter choices, however, lead to very different time dependencies for the frozen fraction, which could be observed in an appropriately designed experiment. This implies that, in a hypothetical set of experiments aimed at fully characterizing the ice-nucleating

properties of a population of particles, both temperature and nucleation time have to be varied, and particles with a size distribution as narrow and surface properties as uniform as possible need to be considered.

5 Conclusions

Finally, the central conclusion of this work is: The emergence of singular, or nearly singular behavior can be explained without appeal to active sites possessing characteristic (i.e., deterministic) freezing temperatures. Rather, an idealized population of statistically similar but individually different particles, characterized by a relatively wide distribution of surface free energies, and subject to purely stochastic freezing behavior, can manifest seemingly singular behavior: weak time dependence of freezing probability, and wide freezing temperature distributions. In this regard, the detailed implementation of the model (i.e., specific choice of Gaussian distribution for contact angles) is not so important as its essential elements: statistically similar particles covered by surface patches following a classical, stochastic nucleation behavior. If this general approach survives subsequent experimental scrutiny, it may provide a useful means for representing ice nucleation in computational models.

Now we can speculate, what does this model imply for future heterogeneous ice nucleation research? We suggest that, on the one hand, investigations concerning chemical composition and surface properties of atmospheric particles have to be enhanced. On the other hand, to clearly show the stochastic nature of heterogeneous ice nucleation experiments should be performed using IN with a size distribution as narrow and surface properties as uniform as possible. In these investigations, the actual measurement time scales have to be carefully considered, because depending on the time available for the nucleation process, it may appear as being of stochastic or singular nature. Ultimately, when parameterizing heterogeneous ice nucleation, depending on the heterogeneity of the considered IN, it might be a satisfactory approximation to assume a singular behavior. We anticipate that may be true for realistic atmospheric

IN populations, but again, relevant time scales would need to be carefully considered since those in the atmosphere are typically much greater than in the laboratory. A basic conclusion of the model is that what looks singular on one time scale, may exhibit stochastic time dependence on other, i.e. shorter or longer time scales.

References

Archuleta, C. M., DeMott, P. J., and Kreidenweis, S. M.: Ice nucleation by surrogates for atmospheric mineral dust and mineral dust/sulfate particles at cirrus temperatures, Atmos. Chem. Phys., 5, 2617–2634, doi:10.5194/acp-5-2617-2005, 2005. 3171

Bigg, E.: The supercooling of water, Proc. Phys. Soc. B, 66(8), 688–694, 1953a. 3163

Bigg, E.: The formation of atmospheric ice crystals by the freezing of droplets, Q. J. Roy. Meteor. Soc., 79(342), 510–519, 1953b. 3163

Bigg, E.: Ice-crystal counts and the freezing of water drops, Q. J. Roy. Meteor. Soc., 81(349), 478–479, 1955. 3163

Cantrell, W. and Heymsfield, A.: Production of ice in tropospheric clouds – a review, B. Am. Meteorol. Soc., 86(6), 795–807, 2005. 3162

Carte, A.: The freezing of water droplets, Proc. Phys. Soc. B, 69(10), 1028–1037, 1956. 3163

Carte, A.: Probability of freezing, Proc. Phys. Soc. B, 73(2), p. 324, 1959. 3163

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. 3164

Dufour, L. and Defay, R.: Thermodynamics of Clouds, Academic Press, New York, 1963. 3163

Durant, A. J. and Shaw, R. A.: Evaporation freezing by contact nucleation inside-out, Geophys. Res. Lett., 32, L20814, doi:10.1029/2005GL024175, 2005. 3163, 3164

Fletcher, N. H.: Active sites and ice crystal nucleation, J. Atmos. Sci., 26(6), 1266–1271, 1969. 3163

Langham, E. J. and Mason, B. J.: The heterogeneous and homogeneous nucleation of supercooled water, P. R. Soc. London, A 247, 493–505, 1958. 3163

Levine, J.: Statistical Explanation of Spontaneous Freezing of Water Droplets, NACA Tech. Notes, No. 2234, 1950. 3163

Lüönd, F., Stetzer, O., Welti, A., and Lohmann, U.: Experimental study on the ice nucleation

Bridging stochastic and singular freezing behavior

D. Niedermeier et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

◄◄   ►►

◄   ►

Back   Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

ability of size-selected kaolinite particles in the immersion mode, J. Geophys. Res., 115, D14201, doi:10.1029/2009JD012959, 2010. 3165, 3171

Marcolli, C., Gedamke, S., Peter, T., and Zobrist, B.: Efficiency of immersion mode ice nucleation on surrogates of mineral dust, Atmos. Chem. Phys., 7, 5081–5091, doi:10.5194/acp-7-5081-2007, 2007. 3165, 3167

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. 3164

Niedermeier, D., Hartmann, S., Shaw, R. A., Covert, D., Mentel, T. F., Schneider, J., Poulain, L., Reitz, P., Spindler, C., Clauss, T., Kiselev, A., Hallbauer, E., Wex, H., Mildenberger, K., and Stratmann, F.: Heterogeneous freezing of droplets with immersed mineral dust particles – measurements and parameterization, Atmos. Chem. Phys., 10, 3601–3614, doi:10.5194/acp-10-3601-2010, 2010. 3164, 3171, 3176

Pruppacher, H. R. and Klett, J. D.: Microphysics of Clouds and Precipitation, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1997. 3162, 3163

Salam, A., Lohmann, U., Crenna, B., Lesins, G., Klages, P., Rogers, D., Irani, R., MacGillivray, A., and Coffin, M.: Ice nucleation studies of mineral dust particles with a new continuous flow diffusion chamber, Aerosol Sci. Technol., 40(2), 134–143, 2006. 3171

Seeley, L. and Seidler, G.: Preactivation in the nucleation of ice by Langmuir films of aliphatic alcohols, J. Chem. Phys., 114, 10464–10470, 2001a. 3163

Seeley, L. and Seidler, G.: Two-dimensional nucleation of ice from supercooled water, Phys. Rev. Lett., 87(5), 055702, doi:10.1103/PhysRevLett.87.055702, 2001b. 3163

Shaw, R. A., Durant, A. J., and Mi, Y.: Heterogeneous surface crystallization observed in undercooled water, J. Phys. Chem. B, 109, 9865–9868, 2005. 3163, 3164, 3171, 3176

Vali, G.: Freezing rate due to heterogneous nucleation, J. Atmos. Sci., 51(13), 1843–1856, 1994. 3163, 3164

Vali, G.: Repeatability and randomness in heterogeneous freezing nucleation, Atmos. Chem. Phys., 8, 5017–5031, doi:10.5194/acp-8-5017-2008, 2008. 3163, 3164

Vali, G. and Stansbury, E.: Time-dependent characteristics of the heterogeneous nucleation of ice, Can. J. Phys., 44(3), 477–502, 1966. 3164

Zimmermann, F., Ebert, M., Worringen, A., Schütz, L., and Weinbruch, S.: Environmental scanning electron microscopy (ESEM) as a new technique to determine the ice nucleation capa-

Bridging stochastic and singular freezing behavior

D. Niedermeier et al.

bility of individual atmospheric aerosol particles, Atmos. Environ., 41(37), 8219–8227, 2007. 3171

Zobrist, B., Koop, T., Luo, B. P., Marcolli, C., and Peter, T.: Heterogeneous ice nucleation rate coefficient of water droplets coated by a nonadecanol monolayer, J. Phys. Chem. C, 111(5), 2149–2155, 2007. 3163, 3168

Zuberi, B., Bertram, A. K., Cassa, C. A., Molina, L. T., and Molina, M. J.: Heterogeneous nucleation of ice in $(NH_4)_2SO_4-H_2O$ particles with mineral dust immersions, Geophys. Res. Lett., 29(10), 1504, doi:10.1029/2001GL014289, 2002. 3171

5

Bridging stochastic and singular freezing behavior

D. Niedermeier et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
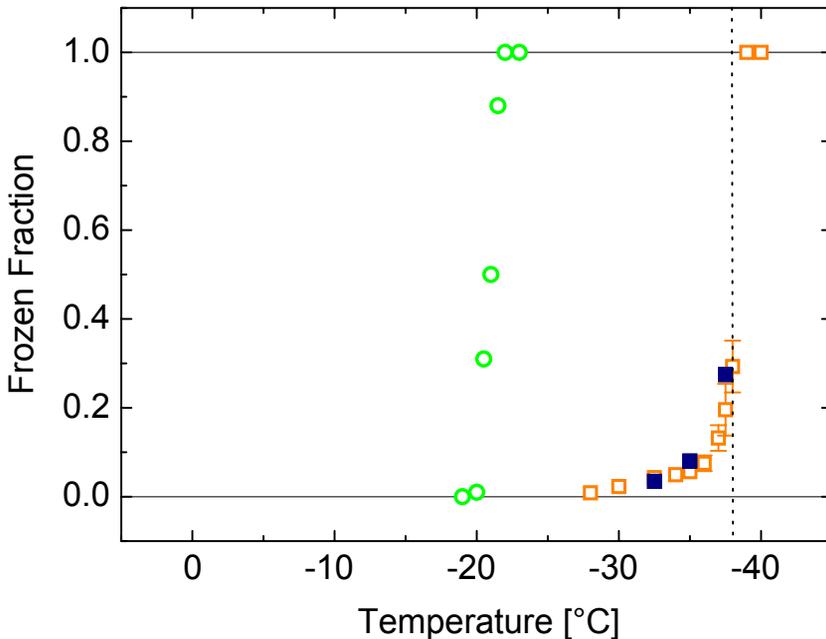
Fig. 1. Green open circles: freezing results of Shaw et al. (2005) investigating tens to hundreds of freezing and melting cycles of an individual water droplet ($\sim 30\,\mu l$) containing a single silicate-glass rich trachyandesitic volcanic ash particle (diameter between ~ 100–$300\,\mu m$). Orange open squares: IN ability of size-segregated monodisperse pure ATD particles investigated by Niedermeier et al. (2010) for nucleation time of about 1.6 s. Data points for $T > -34\,°C$ are not included in Niedermeier et al. (2010). Homogenous freezing becomes dominant for temperatures below $-37.5\,°C$ (indicated by dashed line) meaning that the frozen fraction turns to 1 due to homogeneous ice nucleation. Dark blue squares: similar to previously shown results but with increased nucleation time (10 s).
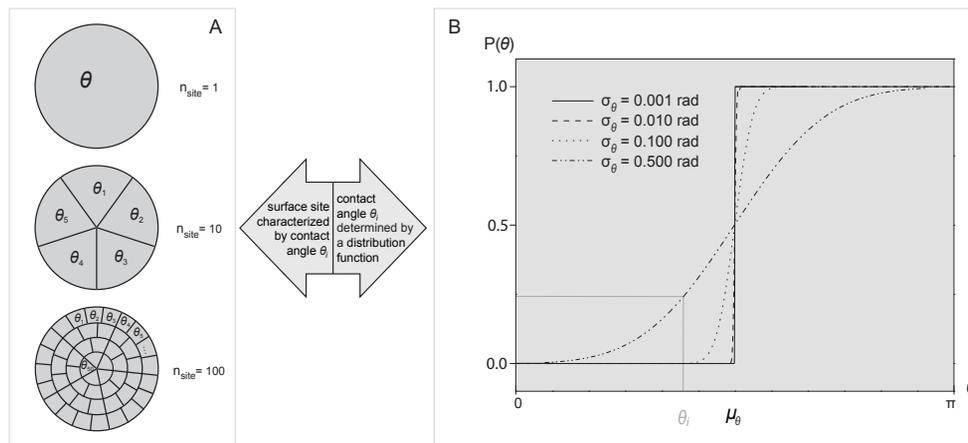
Fig. 2. Surface of each particle is divided into a number n_{site} of surface sites. For model calculations $n_{site} = 1, 10, 100$ is used. Each surface site is associated with a certain energy barrier, represented through contact angle θ. Contact angles are drawn from distribution function $P(\theta)$ (error function) that holds for the ensemble of particles. The contact angle distribution is discretized in 1800 bins between 0 and π and through uniformly distributed random numbers $n \in [0,1]$ each site is associated with a specific contact angle, shown in the right figure through θ_i.
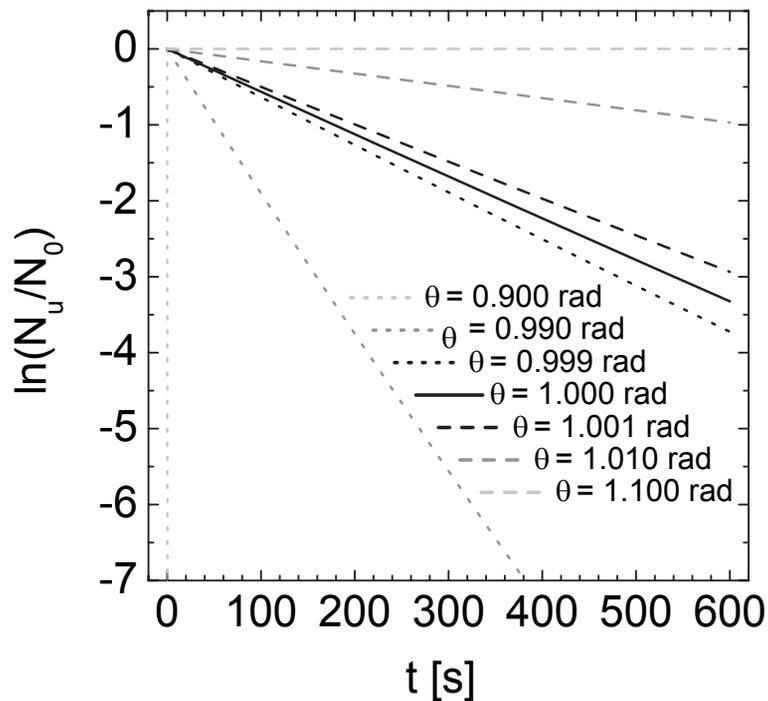
Fig. 3. Logarithm of the unfrozen fraction ($\ln \frac{N_u}{N_0}$) vs. the nucleation time t representing limit case (A) ($n_{site} = 1$ and $\sigma_\theta = 0$ rad) for different contact angles at $T = -20$°C.

Legend:
$\theta = 0.900$ rad
$\theta = 0.990$ rad
$\theta = 0.999$ rad
$\theta = 1.000$ rad
$\theta = 1.001$ rad
$\theta = 1.010$ rad
$\theta = 1.100$ rad

Fig. 4. Logarithm of the unfrozen fraction ($\ln \frac{N_u}{N_0}$) vs. the nucleation time t for different fixed absolute temperatures T showing the effect of variable surface properties across the particle populations for different n_{site} values. Different colors represent different σ_θ values, different symbols represent different n_{site} values: **(a)** $\sigma_\theta = 0.001$ rad and $T = -20°C$, **(b)** $\sigma_\theta = 0.01$ rad and $T = -20°C$, **(c)** $\sigma_\theta = 0.1$ rad and $T = -15°C$ and **(d)** $\sigma_\theta = 0.5$ rad and $T = -1°C$.
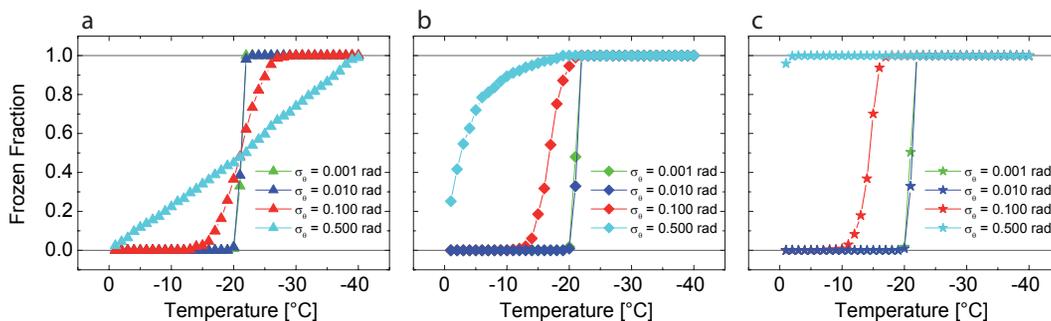
Fig. 5. Calculated fractions of frozen droplets are plotted as function of temperature for a residence time of 1 s. Again, different colors represent different σ_θ values, different symbols represent different n_{site} values. **(a)** $n_{site} = 1$, **(b)** $n_{site} = 10$ and **(c)** $n_{site} = 100$. With increasing number of surface sites on the particles the mean freezing temperatures and curve slopes of the frozen fraction change clearly visible for $\sigma_\theta = 0.1$ rad and 0.5 rad.