Atmos. Chem. Phys., 11, 8767–8775, 2011
www.atmos-chem-phys.net/11/8767/2011/
doi:10.5194/acp-11-8767-2011

Atmospheric Chemistry and Physics

Heterogeneous ice nucleation: exploring the transition from stochastic to 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

Received: 12 November 2010 – Published in Atmos. Chem. Phys. Discuss.: 28 January 2011
Revised: 24 June 2011 – Accepted: 19 August 2011 – Published: 30 August 2011

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 temperatures. We present an idealized, conceptual model to explore the transition between stochastic and singular ice nucleation. This "soccer ball" model treats 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 for seemingly contradictory experimental results obtained in our research groups. Even with ice nucleation treated fundamentally as a stochastic process this process can be masked by the heterogeneity of surface properties, as might be typical for realistic atmospheric particle populations. Full evaluation of the model findings will require experiments with well characterized ice nucleating particles and the ability to vary both temperature and waiting 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 physical 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.

There is longstanding debate as to whether heterogenous ice nucleation is a stochastic process or whether nucleation takes place at specific particle surface sites at 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 and extreme points of view on heterogeneous ice nucleation first emerged in the 1950's. The first, known as stochastic hypothesis, is exemplified by the work of 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 nucleus are assumed to be similar concerning size, chemical composition, etc., i.e., having featureless surfaces) 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 specific (i.e., deterministic) temperature T_s (Langham and Mason, 1958; Pruppacher and Klett, 1997; Vali, 1994, 2008). These "active" sites are considered to be preferred locations, presumably as a result of the particle-ice interfacial free energy

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

being minimal (Fletcher, 1969; Vali, 2008). The exact nature of these sites is unknown, but presumably the site with the lowest energy barrier and therefore highest T_s determines the freezing/nucleation temperature for the whole particle. Being cooled to this T_s, 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 non-random and time-independent: "time is not an important factor and no new nucleation can occur if environmental conditions remain the same" (Chen et al., 2008). Recent observations, such as those of Möhler et al. (2006) and Connolly et al. (2009), show negligible time dependence of the ice particle formation rate and therefore have been interpreted as consistent with singular hypothesis.

Various combinations of these two extremes have been postulated, originally by Vali and Stansbury (1966), and can be broadly regarded as falling within the "modified singular hypothesis" (Vali, 1994; Marcolli et al., 2007; Vali, 2008; Lüönd et al., 2010). The experiments of Vali and Stansbury (1966) and Vali (1994, 2008) consisted of repeated freezing and melting cycles of water droplets containing different kinds of particles, and freezing temperatures with small fluctuations were observed. These findings were interpreted as reflecting the existence of characteristic freezing temperatures for active sites on the immersed particles, about which stochastic effects lead to slight variability in the freezing temperatures. The concept can be expressed as particles possessing active sites, each with a distribution of nucleation rates, and with nucleation rate being a steep function of temperature (see comment by Gabor Vali[1] and Fig. 1 within his comment).

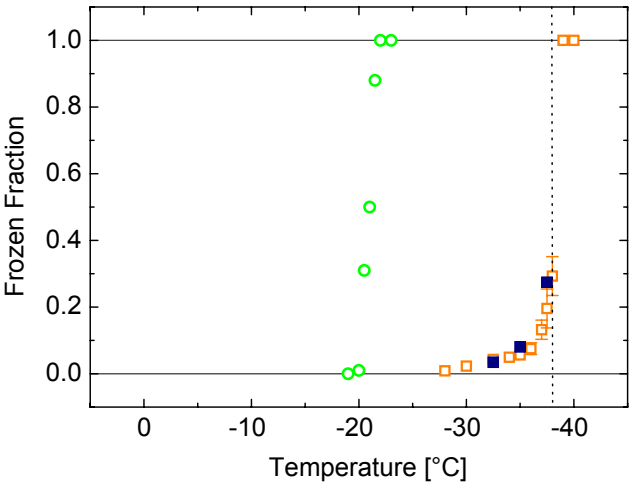

Fig. 1. Green open circles: freezing results of Shaw et al. (2005) investigating tens to hundreds of freezing and melting cycles of an individual water droplet (∼30 µl) containing a single silicate-glass rich trachyandesitic volcanic ash particle (diameter between ∼100–300 µm). Orange open squares: IN 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 the dashed line) meaning that the frozen fraction turns to 1 due to homogeneous ice nucleation. Black squares: similar to previously shown results but with increased nucleation time (10 s).

2 Apparent conflict between stochastic and singular descriptions

The apparent conflict between these descriptions of nucleation is drawn into sharp focus 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 clear interpretation in the context of the stochastic vs. singular controversy. 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, exposed to a constant cooling rate (Fig. 1). By repeating the measurement tens or hundreds of times a distribution of freezing temperatures was obtained, corresponding directly to inherent randomness of the freezing process. 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, deterministic threshold freezing temperature. Second, Niedermeier et al. (2010) measured the freezing temperature of large numbers of water droplets each containing a size-selected, monodisperse mineral particle (Arizona Test Dust, ATD). They found that ATD nucleated ice over a broad temperature range and the determined freezing temperature distributions could be parameterized using either stochastic or singular descriptions. Subsequently, an attempt to distinguish experimentally between singular and stochastic behavior was made (not shown in Niedermeier et al., 2010). Experiments were repeated under nearly identical thermodynamic conditions but with increased nucleation time (the time interval within which supercooled droplets can freeze), but the freezing behavior remained essentially unchanged (Fig. 1). This apparently contradicts the stochastic description, for which an increase in nucleation 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

[1] http://www.atmos-chem-phys-discuss.net/11/C315/2011/acpd-11-C315-2011-supplement.pdf

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 explore the seeming contradiction and more generally to better understand the competing ideas and the somewhat bewildering range of interpretations and applications of stochastic and singular ice nucleation, we introduce a conceptual model describing the freezing behavior of an idealized population of ice nucleating particles. The model serves to illustrate how a smooth transition between purely stochastic and nearly-singular behavior occurs as IN surface properties are changed. The work extends the concept of Marcolli et al. (2007) and Lüönd et al. (2010), who found that their measurements were best described using the active site approach while keeping the stochastic concept of a nucleation rate. Our conceptual 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.

We explore the stochastic-singular transition in the context of a highly idealized model, possessing 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. If the population of particle-containing water droplets is assumed to be exposed to uniform thermodynamic conditions, the fraction of frozen droplets at a given time and temperature 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 are drawn from a probability distribution. 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, $s_{\mathrm{site}} = S_{\mathrm{p}}/n_{\mathrm{site}}$, 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 each individual site has homogeneous properties, ice embryo formation can occur randomly at some point on the given site or patch. In other words, ice formation on any given site can be considered to be described by classical nucleation theory.

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. Our purpose here is to illustrate how the conceptual model bridges continuously from purely stochastic to nearly-singular behavior. Several important features of the model should be discussed. 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 classical nucleation theory applies at any given site (e.g., surface sites are not allowed to be smaller than the area covered by a critical ice embryo (approximately $10\,\mathrm{nm}^2$ at $-29^\circ\mathrm{C}$ according to classical nucleation theory, Marcolli et al., 2007). Consequently the number of surface sites is limited, too. For $n_{\mathrm{site}} = 1$ the particle surface is completely homogeneous in its surface properties (one contact angle per IN similar to the contact angle approach of Marcolli et al. (2007) and the α-pdf-model of Lüönd et al., 2010), i.e., the particle surface is featureless, and ice embryo formation can occur everywhere on the nucleus with uniform probability (purely stochastic view). With increasing number of patches or sites (a) the size of each patch/site decreases (at least to the limiting size of an ice embryo) and (b) the variety of surface properties between the patches/sites increases with broadening contact angle distribution (similar to active site approach of Marcolli et al. (2007) and Lüönd et al. (2010), however, with contact angles for the sites/patches being collected from a Gaussian distribution and different site/patch size.). Finally, 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 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.

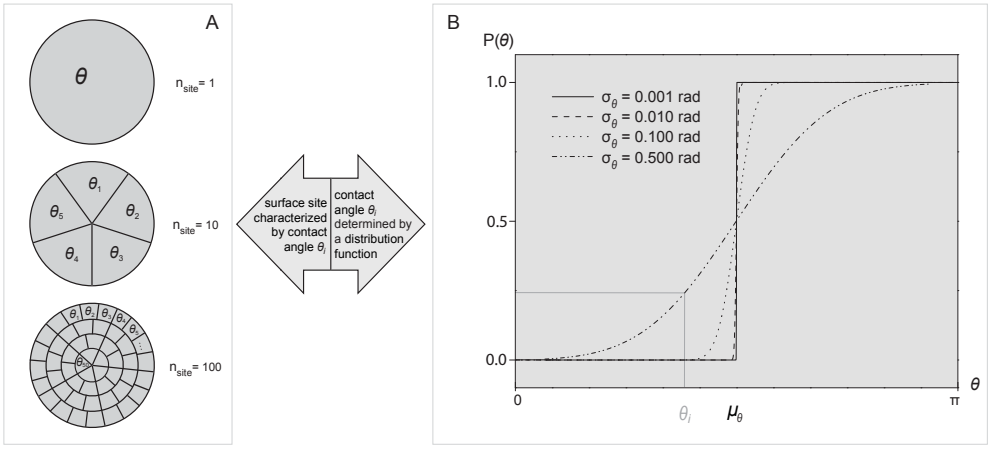

Fig. 2. Surface of each particle is divided into a number n_{site} of surface sites. For model calculations $n_{\mathrm{site}} = 1,\ 10,\ 100$ is used. Each surface site is associated with a certain energy barrier, represented through contact angle θ. Contact angles are drawn from distribution function $P(\theta)$ (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.

The soccer ball model is formulated to yield several limits:

(a) When $\sigma_\theta = 0$, the population is completely uniform.

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

(c) When $n_{\mathrm{site}} \to \infty$ 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 $n_{\mathrm{site}} > 1$ 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 obtained by assuming independence of the probability of freezing on any given patch, such that:

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

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

$$f_{\mathrm{ice}}(T,t) = \frac{N_{\mathrm{f}}(T,t)}{N_0} = 1 - \frac{N_{\mathrm{u}}(T,t)}{N_0} = \frac{1}{N_0}\sum_{\mathrm{k}=1}^{N_0} P_{\mathrm{freeze,k}}(T,t) \quad (2)$$

with N_{u} and N_{f} being the number of unfrozen and frozen droplets, respectively. N_0 is the particle/droplet number.

4 Model results and discussion

The time behavior of the freezing process resulting from this model is illustrated in Figs. 3 and 4. First, in Fig. 3 we consider limit (A), i.e, a uniform particle population consisting of 1000 particles is assumed, with all particles featuring the same contact angle. Plotted is the logarithm of the unfrozen fraction $\ln\frac{N_{\mathrm{u}}}{N_0}$ as function of time t for various contact angles at $T = -20\,^{\circ}$C. Each curve is a straight line, reflecting the purely stochastic behavior of the freezing process and the resulting exponential distribution of freezing times. As can be

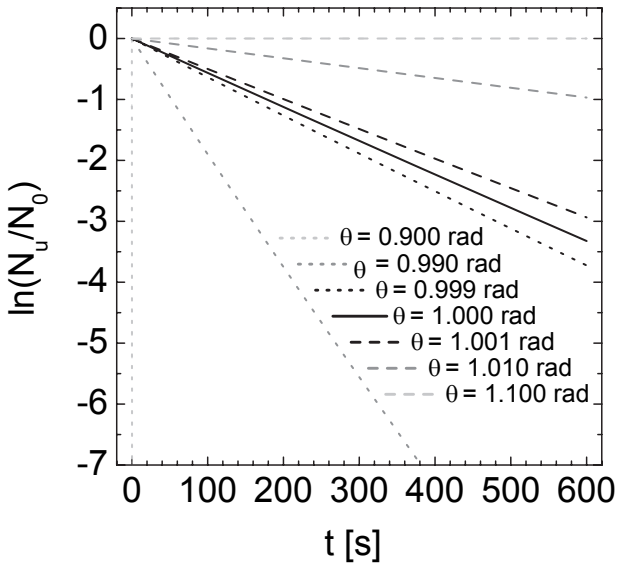

Fig. 3. Logarithm of the unfrozen fraction ($\ln \frac{N_u}{N_0}$) versus the nucleation time t representing limit case (A) ($n_{site} = 1$ and $\sigma_\theta = 0$ rad) for different contact angles at $T = -20\,^\circ$C.

deduced from Eq. (1), the slopes of these lines correspond to the reciprocal of the mean nucleation time ($\tau = \frac{1}{j_{het}(T,\theta_i) s_{site}}$), which is a function of both temperature and contact angle as discussed above.

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, as an example, model results are presented with fixed $\mu_\theta = 1.0$ rad. The model results are presented for different absolute temperatures for reasons discussed later.

For $\sigma_\theta = 0.001$ rad (Fig. 4a), we still observe a straight line (i.e., exponential pdf) 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 $n_{site} = 1$, 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 $n_{site} = 100$.

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. Similar behavior was observed by Yankofsky et al. (1981) in an investigation of freezing times of cells from INA bacteria. 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 practically useful, it is beneficial to also discuss the model results in that context. Therefore in Fig. 5, the fractions of frozen droplets are plotted as a 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 ($T_f \approx -21\,^\circ$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 $\sigma_\theta = 0.001$ rad 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. The former is similar to the observations of Shaw et al. (2005) illustrated in Fig. 1, not surprisingly since a vanishingly small σ_θ is equivalent to an identical particle being frozen repeatedly.

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 that the particles will exhibit sites with a similar range of contact angles as n_{site} increases. This behavior can also simply be interpreted as the "recovery" of the stochastic behavior as discussed above. The noticeable shift of freezing temperature to larger values also 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. With increasing σ_θ the smallest contact angle and therefore lowest energy barrier for

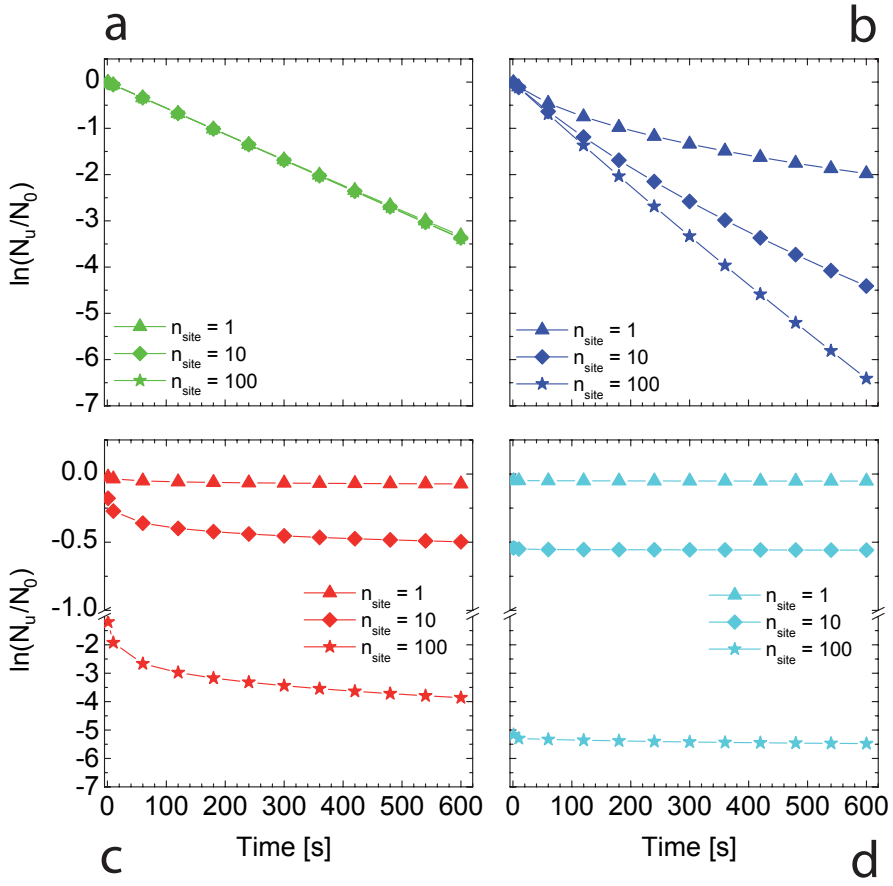

Fig. 4. Logarithm of the unfrozen fraction ($\ln \frac{N_u}{N_0}$) versus the nucleation time t for different fixed absolute temperatures T showing the effect of variable surface properties across the particle populations for different n_{site} values. Different colors represent different σ_θ values, different symbols represent different n_{site} values: **(a)** $\sigma_\theta = 0.001$ rad and $T = -20\,^\circ$C, **(b)** $\sigma_\theta = 0.01$ rad and $T = -20\,^\circ$C, **(c)** $\sigma_\theta = 0.1$ rad and $T = -15^\circ$C and **(d)** $\sigma_\theta = 0.5$ rad and $T = -1\,^\circ$C.

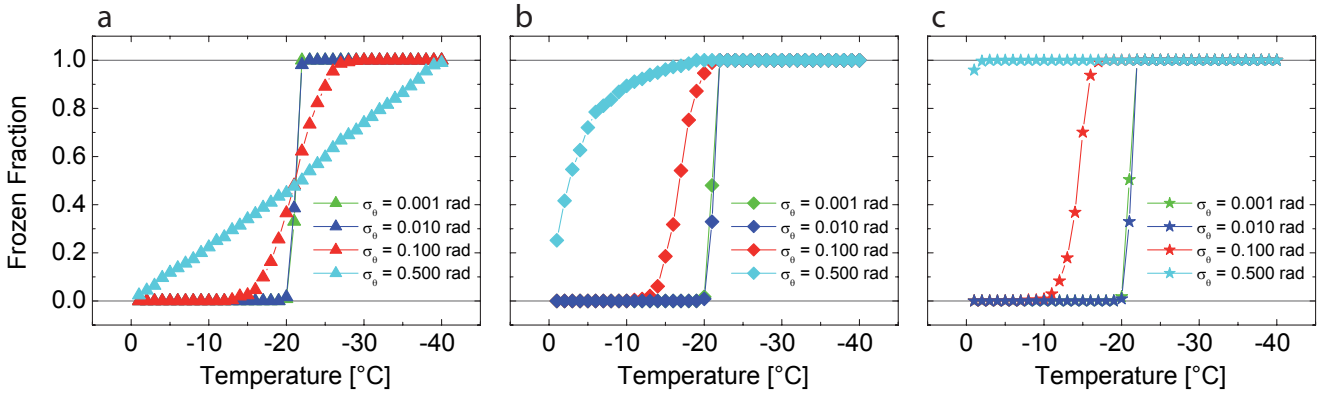

Fig. 5. Calculated fractions of frozen droplets are plotted as function of temperature for a nucleation time of 1 s. Again, different colors represent different σ_θ values, different symbols represent different n_{site} values. **(a)** $n_{site} = 1$, **(b)** $n_{site} = 10$ and **(c)** $n_{site} = 100$. 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.

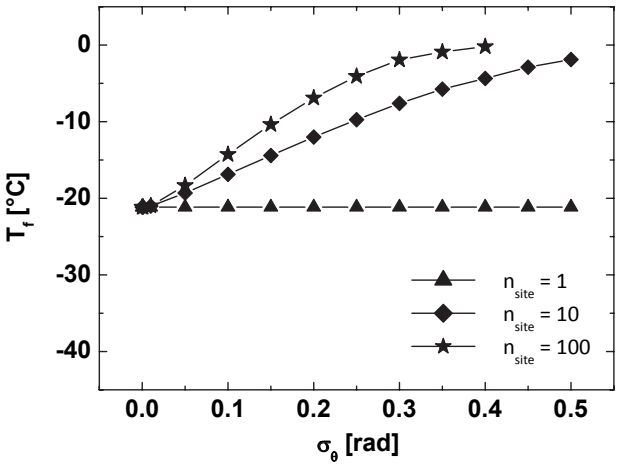

Fig. 6. The mean freezing temperature T_f, i.e., the temperature where 50 % of the supercooled droplets are frozen, as function of σ_θ for $\mu_\theta = 1.0$ rad and nucleation time of 1 s.

ice embryo formation determines the highest freezing probability, implying that more and more droplets will freeze at temperatures higher than that corresponding to the mean contact angle. Ultimately, this will result in a shift of the freezing temperature T_f which is additionally presented in Fig. 6 showing T_f as function of σ_θ.

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 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 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 soccerball 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, the frozen fraction vs. temperature curves for $\sigma_\theta = 0.001$ rad and 0.010 rad show a similar slope independent of n_{site} (see Fig. 5). But the $\ln \frac{N_u}{N_0}$ vs. time curves show different slopes depending on n_{site} (especially for $\sigma_\theta = 0.010$ rad, see Fig. 4). Furthermore fitting the frozen fractions of the ATD particles presented in Niedermeier et al. (2010) alone leads to an ambiguous result because in that case the system is underdetermined, since the three parameters n_{site}, μ_θ and σ_θ can be combined differently to fit the frozen fraction. The different parameter choices, however, lead to very different time dependencies for the frozen fraction (see Fig. 7), 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 insight gained from this work is: based on classical nucleation theory alone, a population of particles can exhibit behavior over a continuous range, from purely stochastic to nearly singular. The emergence of singular, or nearly singular behavior arises from the existence of sites possessing widely differing nucleation rates (or, in the language of classical nucleation theory, widely differing contact angles), with each individual site exhibiting purely stochastic behavior. Therefore, an idealized population of particles with a statistical distribution of nucleation properties, characterized by a relatively wide distribution of surface free energies, and subject to purely stochastic freezing behavior, can manifest what traditionally has been interpreted as singular behavior: weak time dependence of freezing probability, and wide freezing temperature distributions. Interpreted in this light, the 'lack of time dependence' typical of the singular behavior is only meaningful when the time scale of an experiment or measurement is defined. Fundamentally, in the conceptual model described here, the freezing process is stochastic, so there is always a time dependence. It just may be that the time dependence occurs with a characteristic time scale much less than or much greater than the time scales resolved in a hypothetical experiment. 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.

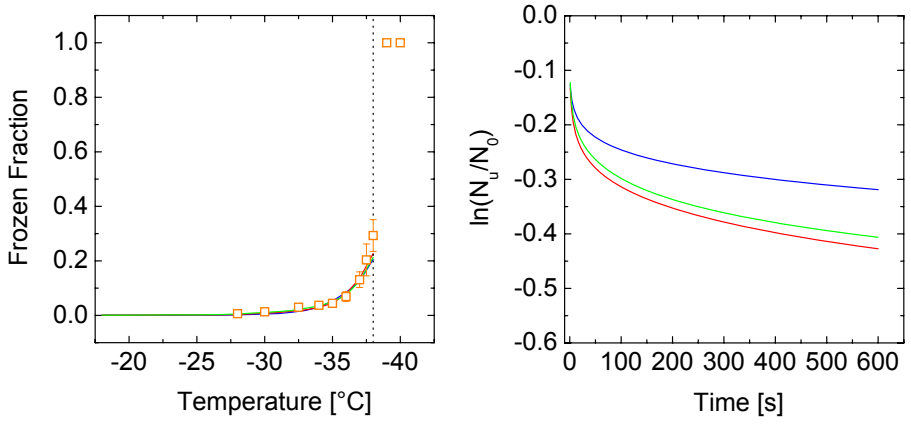

Fig. 7. The solid lines in the left figure show three different fit curves to the immersion freezing behavior ($T > -38\,°C$ indicated by the dashed line) of supercooled droplets each having a single ATD particles immersed (measured with LACIS, Niedermeier et al. (2010)). The different parameter combinations, which lead to different time dependencies (see right figure), feature least square differences between fitted curves and experimental data points which are smaller than 10^{-3}. Black curve: $n_{site} = 1$; $\mu_\theta = 2.13$ rad; $\sigma_\theta = 0.33$ rad; Red curve: $n_{site} = 4$; $\mu_\theta = 2.31$ rad; $\sigma_\theta = 0.34$ rad; Green curve: $n_{site} = 7$; $\mu_\theta = 2.48$ rad; $\sigma_\theta = 0.39$ rad.

Now we can speculate, what does this conceptual 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.

Edited by: P. Spichtinger

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.

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

Bigg, E.: The formation of atmospheric ice crystals by the freezing of droplets, Quart. J. Royal Meteorol. Soc., 79(342), 510–519, 1953b.

Bigg, E.: Ice-crystal counts and the freezing of water drops, Quart. J. Royal Meteorol. Soc., 81(349), 478–479, 1955.

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

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

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

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.

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.

Dufour, L. and Defay, R.: Thermodynamics of clouds, Academic Press, New York, USA, 1963.

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

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

Langham, E. J. and Mason, B. J.: The heterogeneous and homogeneous nucleation of supercooled water, Proc. Roy. Soc., A 247, 493-505, 1958.

Levine, J.: Statistical explanation of spontaneous freezing of water droplets, NACA Tech. Notes, no. 2234, 1950.

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.

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.

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.

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.

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

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.

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

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.

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

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

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

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

Yankofsky, S. A., Levin, Z., Bertold, T., and Sandlerman, N.: Some basic characteristics of bacterial freezing nuclei, J. Appl. Meteorol., 20(9), 1013–1019, 1981.

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

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.

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.