Exploring the Mechanisms of Ice Nucleation on Kaolinite: From Deposition Nucleation to Condensation Freezing

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ABSTRACT

To identify the temperature and humidity conditions at which different ice nucleation mechanisms are active, the authors conducted experiments on 200-, 400-, and 800-nm size-selected kaolinite particles, exposing them to temperatures between 218 and 258 K and relative humidities with respect to ice (RH$_i$) between 100% and 180%, including the typical conditions for cirrus and mixed-phase-cloud formation. Measurements of the ice active particle fraction as a function of temperature and relative humidity with respect to ice are reported. The authors find enhanced activated fractions when water saturation is reached at mixed-phase-cloud temperatures between 235 and 241 K and a distinct increase in the activated fraction below 235 K at conditions below water saturation. To provide a functional description of the observed ice nucleation mechanisms, the experimental results are analyzed by two different particle-surface models within the framework of classical nucleation theory. Describing the ice nucleation activity of kaolinite particles by assuming deposition nucleation to be the governing mechanism below water saturation was found to be inadequate to represent the experimental data in the whole temperature range investigated. The observed increase in the activated fraction below water saturation and temperatures below 235 K corroborate the assumption that an appreciable amount of adsorbed or capillary condensed water is present on kaolinite particles, which favors ice nucleation.

1. Introduction

Ice crystals that form in the atmosphere influence cloud and precipitation formation. Ice can nucleate homogeneously from the liquid water phase or heterogeneously on the surface of aerosol particles serving as ice nuclei (IN). From the analysis of ice crystal residuals found in mixed-phase clouds (e.g., Ebert et al. 2011) and cirrus clouds (DeMott et al. 2003; Twohy and Poellot 2005), it was shown that mineral dust aerosols are the prevalent IN. The number of active IN present at cloud-forming conditions affects the optical thickness, the maximum supercooling, and the lifetime of clouds and might thereby influence events like winter storms (Schaefer 1949) or tornadoes (Rosenfeld and Bell 2011). On a larger time scale, ice formation in clouds impacts climate by altering the flux of radiation through the atmosphere (Baker 1997). A better understanding of the microscopic mechanisms leading to ice formation and their functional description in numerical models increases the predictability of the effect of heterogeneous ice nucleation on cloud properties and precipitation formation in the present and a future climate.

Heterogeneous ice formation on the substrate of dust aerosols is initiated by the nucleation of an ice embryo, often thought of as a spherical cap, on which the macroscopic ice crystal can grow. Depending on the ambient conditions, heterogeneous ice nucleation can occur through four different modes: immersion,
condensation, or contact freezing or deposition nucleation (Vali 1985).

Immersion freezing occurs when an aerosol particle first serves as a cloud condensation nucleus (CCN) (i.e., water is condensing on the particle surface and a cloud droplet forms). The cloud droplet is subsequently supercooled to a temperature where ice nucleation is catalyzed on the particle–water interface and causes the droplet to freeze. Immersion freezing is an important mechanism for ice formation in mixed-phase clouds (Ansmann et al. 2008; Hoose et al. 2010; de Boer et al. 2011; Murray et al. 2012) and has been implied to dominate heterogeneous cirrus cloud formation via freezing of solution droplets containing IN (Kärcher and Lohmann 2003; Wiacek et al. 2010).

Ice formation is attributed to condensation freezing when water condenses on an IN at supercooled temperatures \( T < 273 \text{ K} \) and ice nucleation spontaneously occurs without further cooling of the condensed water. When a liquid water layer forms on the IN surface, four processes that favor ice formation could take place (which will be referred to as condensation I, II, III, and IV). First (I), nucleation during the process of water condensation at the growth boundary of condensing water clusters where water molecules have higher degrees of freedom or entropy than in the bulk (Fukuta 1975). Second (II), a subcritical ice cluster formed from the vapor phase could be incorporated into a growing water cap as proposed by Cooper (1974). This process favors ice nucleation by allowing an ice cluster, subcritical in the vapor phase, to become stable in the water phase where the critical radius is smaller (i.e., fewer water molecules are required to form a critical ice germ). The mechanism is illustrated in Fig. 1. Third (III) is nucleation in capillary condensed water. Ice embryo formation in small confinements is facilitated owing to the reduced chemical potential of capillary-held water caused by the capillary pressure (Fukuta 1966). Fourth (IV), mechanistically equivalent to ice nucleation by immersion freezing, a critical embryo forms at the interface of the condensed water and the particle substrate. Condensation freezing has often been implied to occur exclusively above water-saturated conditions (e.g., Al-Naimi and Saunders 1985). However, condensation freezing below water saturation related to the presence of capillary condensed water (Fukuta 1966) or soluble material on the IN (Fletcher 1968; Archuleta et al. 2005) have been implied as possible mechanisms. Fukuta (1966) discussed the possibility of water condensation in capillary structures on the surface of particles and the effect of capillary-held water on ice nucleation. Recently, Marcolli (2013) proposed such a mechanism to be a more probable pathway of ice formation below water saturation than deposition nucleation. Field et al. (2006) and Phillips et al. (2008) attributed a jump in IN activity of desert dust and ambient aerosol with increasing relative humidity toward water saturation to the onset of a condensation freezing mechanism below water saturation. Field et al. (2006) attribute an increase in the ice activated particle fraction, which they observed exclusively below 233 K to the onset of heterogeneous nucleation within a solution droplet forming from the soluble material on the desert dust samples that were investigated. Also, Phillips et al. (2008) suggest an increase in dilution of solute associated with aerosol to allow freezing to occur at increasingly higher temperatures toward higher relative humidity. As in the supercooled part of the atmosphere, typically relative humidities below water saturation are measured (Gettelman et al. 2006); condensation freezing (I–III) below water saturation might be more prominent than droplet formation on insoluble aerosols followed by freezing. Only in the center of cumulus clouds do relative humidities exceed water saturation by up to 7% (Pruppacher and Klett 1997) or, in the wake of freezing droplets, much higher water supersaturation up to 30% is theoretically possible (Dye and Hobbs 1968). Experimental support for the calculations by Dye and Hobbs (1968) was reported by Jung et al. (2012), who observed the formation of a condensate halo on a substrate around freezing droplets that where supercooled to 258.6 K. Conditions for efficient condensation freezing (IV) above water saturation might be preferably encountered there.

Contact freezing refers to the initiation of the ice nucleation process by contact of an interstitial particle with a supercooled water droplet. Freezing might then be initiated by a nucleation process similar to the condensation freezing mechanisms described above.
Deposition nucleation is the formation of critical ice clusters on the particle surface directly from the vapor phase. Two possible mechanisms of ice germ formation in the deposition mode (which will be referred to as type 1 and type 2) have been described by Federer (1968) and in Pruppacher and Klett (1997):

- **Type 1**: A critical ice germ forms on an active site, primarily by surface diffusion of adsorbed water molecules to this site.
- **Type 2**: Critical ice germs grow directly by adsorption of water molecules from the ambient air.

The amount of water molecules necessary to form a stable ice cluster from the vapor phase depends on the properties of the IN substrate, temperature, and relative humidity with respect to ice (RH\text{\textsubscript{i}}). Deposition nucleation can take place as soon as saturation with respect to ice is exceeded.

Which of the above nucleation modes is the most efficient and therefore the dominant process of ice formation in the atmosphere depends on the temperature and saturation history of an ice-forming particle, the particle properties, and the ambient conditions that the particle experiences. We attempt to distinguish the different ice nucleation modes in the temperature–saturation regimes from 218 to 258 K and 100%–180% relative humidity with respect to ice, in which homogeneous, immersion, condensation, and deposition nucleation can compete. By measuring ice formation on kaolinite aerosols with the Zurich Ice Nucleation Chamber (ZINC) described in Stetzer et al. (2008) and comparing the results to classical nucleation theory (CNT) formulated by Volmer and Weber (1926), we relate the occurrence of homogeneous nucleation, condensation, and deposition mode nucleation to temperature–saturation conditions. Additionally, ice nucleation efficiency at water-saturated conditions is compared to previous measurements of immersion freezing on the same kaolinite sample (Lüönd et al. 2010; Welti et al. 2012).

### 2. Methods

#### a. Experimental setup and procedure

A schematic of the experimental setup is shown in Fig. 2. Kaolinite aerosols were generated in a fluidized bed aerosol generator (TSI model 3400A) and forwarded in conductive tubes to a 5-L mixing volume (not shown in Fig. 2) to homogenize the particle concentration before size selection. Particles with a diameter significantly larger than the size used in an experiment were removed by a cascade of cyclones and impactors. A Po-210 radioactive source was used to apply an equilibrium charge distribution on the particles prior to selecting a specific size according to the electrostatic mobility in a differential mobility analyzer (DMA; TSI model 3081). Size-selected particles were introduced into ZINC and sandwiched between two sheath layers of filtered air to keep the aerosol layer in the center of the chamber. The front and back walls of ZINC were coated with thin ice layers whose temperature is controlled by two separate cryostats (LAUDA PROLINE RP890). For the ice nucleation experiments the relative humidity at the sample position was set by increasing the temperature difference between the warm and the cold walls while keeping the temperature in the center between the walls constant. Because of the nonlinear temperature dependence of the saturation vapor pressure, the linear temperature and vapor pressure gradient between the ice-covered walls leads to supersaturated conditions between the two wall plates. For details on operating methods and principles of ZINC, we refer to the work of Stetzer et al. (2008).
The ice nucleation activity of the kaolinite aerosol was observed by measuring the number of ice crystals exiting ZINC with an optical particle counter (OPC; CLiMET C1-3100) and counting the total number of aerosol particles introduced into the top of the chamber with a butanol condensation particle counter (CPC; TSI model 3010). The ice activated fraction (AF) is calculated as the ratio of detected ice crystals to the number concentration of kaolinite aerosol:

$$\text{AF} = \frac{\text{Number of ice crystals}}{\text{Number of aerosol particles}}. \quad (1)$$

The combined uncertainty in the activated fraction due to measurement uncertainties of the OPC (10%) and CPC (10%) is 14%. The discrimination of ice crystals from unactivated dust particles by the OPC depends on their size. Salam et al. (2006) showed that hygroscopic growth of kaolinite particles at supercooled conditions close to water saturation is only minor. Miscounting swelling kaolinite particles as ice crystals can therefore be excluded as a source of error. The activated fraction was measured either at constant temperature and increasing RH$_i$ or by scanning through temperature while holding RH$_i$ constant. Temperature and relative humidity conditions across the sample layer in ZINC vary by less than ±0.5 K and ±1% RH$_i$, respectively.

For a series of measurements close to water saturation, the droplet to ice crystal ratio was measured with the ice optical depolarization detector (IODE) described in Nicolet et al. (2010). The IODE detector discriminates ice crystals from droplets by the difference of their depolarization property on linearly polarized incident laser light. IODE was mounted at the transition from the main chamber of ZINC to the evaporation section (cf. Fig. 2) to detect the condensed water droplets before they are evaporated in the evaporation section. Only droplets larger than 2 μm can be detected. The combined use of the IODE detector measuring the ratio of ice crystals to water droplets and the OPC/CPC data measuring the ratio of formed ice crystals to the total amount of dust particles allows us to determine the IN and CCN activated particle fraction at a given experimental condition (cf. section 4).

b. Dust sample

Size-selected kaolinite (Fluka) particles were used as IN in this study. Kaolinite is a common component of desert dust and tropical soils (Atkinson and Waugh 1979; Young 1980). Kaolinite is known to be a relatively pure clay that varies little in composition (e.g., Pinti et al. 2012). This makes it ideal to study the mechanisms of ice nucleation where uniformity of the test material is crucial. The same type of kaolinite dust has been utilized...
in previous investigations of deposition nucleation (Welti et al. 2009; Wheeler and Bertram 2012), immersion freezing (Lüönd et al. 2010; Pinti et al. 2012; Welti et al. 2012), and contact freezing measurements (Svensson et al. 2009; Ladino et al. 2011). Particles of 200-, 400-, and 800-nm mobility diameter were selected with a DMA to investigate the effect of the particle surface area. Scanning electron microscope (SEM) pictures of four individual particles from the same kaolinite sample can be found in Ladino et al. (2011).

3. Experimental results

The dataset is presented as 5-s-averaged values. The increase in the activated fraction as a function of RH$_i$ for 200-, 400-, and 800-nm kaolinite particles is shown in Fig. 3 and the measured ice nucleation activity as a function of temperature and RH$_i$ is shown in Fig. 4.

a. Effects of temperature and relative humidity

As temperature decreases, the activated fraction for a constant RH$_i$ increases. At temperatures above approximately 235 K and in the region below water saturation, the activated fraction is observed to increase with increasing RH$_i$. A sharp increase in the activated fraction at water-saturated conditions most pronounced in the 800-nm dataset (shown in the third row of Fig. 3) suggests that, in addition to deposition nucleation, a condensation freezing mechanism contributes to the activated fraction under these conditions. Another distinct increase in ice nucleation is observed at temperatures typical for the onset of homogeneous freezing (<235 K), even below water saturation. At temperatures below 235 K and above 110% RH$_i$, ice nucleation by kaolinite appears to be almost independent of ice supersaturation or reaching water-saturated conditions. Opposite to deposition nucleation, this independence from vapor pressure is what would be expected for ice nucleation in a liquid—namely, homogeneous nucleation, immersion freezing, or condensation freezing, for example, according to the mechanism illustrated in Fig. 1. Because of the experimental setup where particles are exposed to a certain saturation at a constant temperature during the 12-s residence time, immersion freezing can be excluded (cf. definitions in section 1). At temperatures below 223 K, higher RH$_i$ values have to be reached before efficient ice formation is observed. This might indicate a temperature and RH$_i$ optimum for the onset of ice nucleation, which probably reflects a dependence not only on the relative humidity, but also on the absolute vapor pressure. In summary, a saturation- and temperature-dependent onset of ice nucleation (1% activated fraction) is observed. Efficient ice formation (above 10% activated fraction) below water saturation has been measured below 235 K and above water saturation between 235 and 241 K depending on the IN size. In these regions, the ice active fraction is almost independent of increasing saturation.

b. Effect of particle size

Larger particles are observed to be active ice nuclei at higher temperatures and require lower RH$_i$ to be activated (cf. Fig. 3). This trend is in agreement with previous studies on deposition nucleation (e.g., Berezinski et al. 1988; Archuleta et al. 2005; Welti et al. 2009) and CNT (e.g., Pruppacher and Klett 1997). Looking at Fig. 4, a discontinuous increase in the activated fraction between 235 and 241 K can be found for 800-nm particles as soon as water saturation is reached, whereas for smaller 200- and 400-nm particles this increase in the activated fraction can only be observed below 237 K. The onset of condensation freezing (IV) in addition to deposition nucleation could be the cause for the jump in the activated fraction at water-saturated conditions at temperatures higher than 235 K. For temperatures below 235 K, 800-nm particles reach the same maximum activated fraction as in the cases where a discontinuity at water saturation is observed above 235 K (cf. Fig. 3). Assuming a condensation mechanism is important for ice nucleation in those regimes, the only partial ice activation (up to 30% AF) of the monodisperse particle ensemble indicates that condensation of liquid water only occurs on a fraction of kaolinite particles with the same size. For the 200- and 400-nm data below 235 K, the increase of the activated fraction with increasing RH$_i$ becomes steeper.
with lower temperatures. The increase of the activated fraction for data below 235 K is generally gentler for smaller particles (cf. Fig. 3); that is, increasingly higher supersaturation with respect to ice is necessary to initiate ice nucleation on the same fraction of particles with decreasing particle size.

4. Condensation versus immersion freezing

Generally, similar ice nucleation efficiencies can be expected in the condensation as in the immersion freezing mode since in both processes the ice active sites of the particles are covered by a water layer (Diehl et al. 2001). In the studies of Pitter and Pruppacher (1973) and Schaller and Fukuta (1979), similar freezing temperatures for both processes have been reported. To distinguish the two processes, DeMott (1994) suggested that condensation freezing should be the formation of ice, dependent on water supersaturation, which exceeds the number of ice crystals that could result from immersion freezing. Following this definition, the frozen fraction [Eq. (2)] obtained from IODE measurements after a particle residence time of 12 s and at water-saturated conditions in ZINC is compared to a theoretical fit curve to immersion freezing data from a previous study using the IMCA/ZINC experimental setup (Lüönd et al. 2010):

\[
\text{Frozen Fraction} = \frac{\text{Number of ice crystals}}{\text{Number of ice crystals} + \text{Number of droplets}}
\]  

The size-resolved frozen fraction as a function of temperature and the theoretical immersion freezing curves calculated from CNT and using the immersion freezing contact angle distribution reported in Lüönd et al. (2010) are shown in Fig. 5. Similar frozen fractions for condensation freezing are obtained at up to 4-K higher temperatures compared to immersion freezing. However, because of the uncertainties associated with the measurements and the theoretical curves shown in Fig. 5, the observed differences are only qualitative and could be insignificant. The measurement of systematically higher frozen fractions for condensation freezing can have three causes: First, a higher nucleation rate in the condensation mode, indicating condensation freezing occurring by one of the first three processes (I, II, III) proposed in section 1. Second, only a fraction of the mostly hydrophobic kaolinite particles activate heterogeneously as CCN at supercooled temperatures within the 12-s residence time of the experiment. On the immersed particle ice can nucleate on the droplet–particle interface similar to the immersion mode, whereas on the fraction of particles inactive as CCN, ice formation from deposition nucleation can take place. The apparent frozen fraction of the combination of ice formed by deposition nucleation and condensation freezing (IV) is
higher than from immersion freezing experiments where all particles are immersed in droplets. The observed frozen fraction in excess of that of immersion freezing could also be due to condensation freezing (I, II, or III) plus deposition nucleation, in which the latter has a measurable contribution owing to a low fraction of particles active in the condensation mode. Third, all particles activate as CCN (like in an immersion freezing experiment) but owing to a delayed activation and slow droplet growth at low temperatures, some of the formed droplets are too small (<2 μm) to be detected by IODE. This leads to too few detected droplets and, hence, to a too-high frozen fraction. The amount of condensed water on a particle is dependent on the temperature, whereupon at lower temperatures less water is expected to condense on a CCN within the residence time of the experiment; that is, at lower temperatures, heterogeneous CCN activation of the insoluble kaolinite particles and droplet growth by condensation could be too slow to grow droplets of detectable size in 12 s. Assuming a partial CCN activation, the unfrozen fraction of CCN active aerosol particles can be estimated by multiplying the measured droplet to ice ratio with the total activated ice fraction:

\[
\text{CCN Fraction} = \frac{\text{Number of droplets}}{\text{Number of ice crystals}} \times \text{AF}. \quad (3)
\]

An example of the fraction of unfrozen droplets, obtained from an experiment with conditions of constant water saturation while temperature was increased is shown in Fig. 6 together with the ice active fraction, detected after a residence time of 12 s. If condensation freezing (IV) is the prevailing nucleation mode above water saturation, the observed ice crystals plus droplets represent the sum of CCN active kaolinite particles in this experiment. For 200-nm particles the maximum CCN active fraction can be estimated to be below 4% in the temperature range between 240 and 260 K. Treating CCN activation of insoluble dust particles as a vapor pressure–dependent stochastic process (Pruppacher and Klett 1997), little CCN activation is expected at low temperatures for a 12-s exposure time; that is, particles that activated as CCN with some delay probably do not grow to a detectable size of 2 μm.

5. Deposition nucleation versus condensation freezing

The main criterion for the distinction between condensation freezing and deposition nucleation is the requirement of liquid water before condensation freezing operates (Ovtchinnikov and Kogan 2000). To assess the contribution of deposition nucleation to ice formation above water saturation, we apply fit routines (described in section 5b) to the part of the dataset for measurements below water saturation with the assumption that water-saturated conditions are needed for condensation freezing or homogeneous nucleation to occur. Further, we exclude the formation of droplets with reduced water activity below water saturation that could freeze homogeneously below 235 K. This assumption is justified by the fact that the soluble material on the kaolinite particles used is small (cf. section 6). Given the two assumptions above, deposition nucleation is the dominant active mechanism. Qualitative evidence for a condensation freezing mechanism being active exclusively at water-saturated conditions between 235 and 241 K can be seen in the 800-nm dataset in the third row of Fig. 4.

The resulting best-fit contact angles are then used to calculate the activated fraction in the whole temperature–saturation space also above water saturation. If the above assumptions are true, this allows us to estimate the contribution of deposition nucleation and to separate it from homogeneous nucleation and condensation freezing in the experimentally measured ice fraction. A surface area–dependent comparison of deposition nucleation based on this analysis, condensation freezing (IV), and the experimental data at water-saturated conditions is given in appendix A.

We are going to demonstrate in this section that this analysis leads to conflicts that suggest that the assumption of deposition nucleation as described in CNT, being the only active ice nucleation mechanism below water saturation, is not adequate to describe the empirical data. This leads to two possible interpretations: deposition nucleation is not well described by CNT at these conditions, or another ice nucleation mechanism is active. We present arguments for a condensation or homogeneous freezing mechanism to become active at a certain degree of supercooling and far below water saturation. As a consequence, the calculated parameterization for the contact angles and activation energy barrier for deposition nucleation can be biased. The intended quantitative separation of deposition nucleation from condensation freezing and homogeneous nucleation above water saturation using CNT does, therefore, not work. In the following, we describe the relevant theory and relationships that were used for these calculations and will be relevant for future discussion of the results.

a. CNT calculations for deposition nucleation

Under the assumption that deposition nucleation is a stochastic process that can be described by CNT, the heterogeneous nucleation rate coefficient \( J \) can be calculated as
Table 1. Fit parameters for a single contact angle (single $\alpha$) and a contact angle distribution ($\alpha$-pdf) obtained by minimizing the sum of squared errors between data below water saturation in the whole temperature range studied and either Eq. (15) or (18).

<table>
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<th>Model</th>
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<th>Value</th>
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<tr>
<td></td>
<td>$\sigma$</td>
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\[
J(T, S_i, \alpha) = k(T, S_i, \alpha) \exp \left[ -\frac{\Delta G(T) f_{het}(\alpha)}{kT} \right], \quad (4)
\]

where $k$ is the Boltzmann constant and $T$ is temperature.

In the numerator $\Delta G$ is the change in Gibbs free energy due to the formation of an ice cluster given by

\[
\Delta G(T, S_i) = \frac{16\pi v_{ic}^2(T)\sigma_{iv}^2}{3 (kT \cosh^{-1} S_i)^2}, \quad (5)
\]

where $v_{ic}(T)$ denotes the volume of a water molecule in the ice embryo, $S_i$ the saturation ratio with respect to ice, and $\sigma_{iv}$ is the ice-vapor specific interfacial free energy between the ice embryo and the vapor phase.

The geometric factor $f_{het}$ in Eq. (4), which describes the reduction in the free-energy barrier as a function of the contact angle $\alpha$ between an ice germ and the particle substrate (Chakraverty and Pound 1964; Pruppacher and Klett 1997), is defined as

\[
f_{het}(\alpha) = \frac{[2 + \cos(\alpha)][1 - \cos(\alpha)]^2}{4}. \quad (6)
\]

The preexponential factor or kinetic coefficient $K$ in Eq. (4) describes the rate at which molecules from the vapor phase are incorporated into an ice germ (i.e., the kinetic part of the nucleation process). Based on the kinetic coefficient of homogeneous nucleation, $K$ has been estimated to be on the order of $10^{23}$ m$^{-2}$ s$^{-1}$ by Fletcher (1969) assuming a type 2 mechanism (cf. section 1) of deposition nucleation (Pruppacher and Klett 1997). Results obtained using this preexponential factor are presented in appendix B. Here, we use the approach reported in Chen et al. (2008) to derive $K$ from the experimental results. Taking into account the dependencies of $K$ on ambient conditions and particle type, the kinetic factor can be described as

\[
K(T, S_i, \alpha) = A Z n \exp \left[ -\frac{\Delta F(T, S_i)}{kT} \right]. \quad (7)
\]

Here, $A$ (s$^{-1}$) describes the molecule flux to the ice germ, $Z$ is the Zeldovich factor (Vehkamäki et al. 2007), $n$ (m$^{-2}$) is the number density of water molecules in contact with the IN surface, and $\Delta F(J)$ is the activation free-energy barrier [cf. discussion in section 5a(1)].

According to Chen et al. (2008) and references therein, the water molecule flux to an ice germ is given by

\[
A(T, S_i) = 4\pi r_g^2 S_i p_{H_2O_i}^*(T) 3 \pi m_w kT \sinh^{-1} S_i, \quad (8)
\]

where $r_g$ is the radius of a critical ice germ, $p_{H_2O_i}^*$ is the saturation vapor pressure over ice, and $m_w$ is the mass of a water molecule. The water molecule flux depends mainly on the temperature and ice germ size. We derived values in the range of $A \approx 10^8$–$10^{10}$s$^{-1}$ between 218 and 258 K.

The Zeldovich factor is calculated as

\[
Z(T, S_i) = \frac{v_{ic}(T) \Delta G(T, S_i) f_{het}}{4 \pi r_g^3 kT \sinh^{-1} S_i}, \quad (9)
\]

Equations (8) and (9) assume that the ice germ has a spherical shape. The radius of an ice germ can be expressed as

\[
r_g(T, S_i) = \frac{2v_{ic}(T)\sigma_{iv}}{kT \sinh S_i}, \quad (10)
\]

where $v_{ic}$ is the temperature-dependent volume of a water molecule in ice. The packing density of adsorbed water molecules can be calculated by
\[ n(T, S) = \frac{S_{P_{H_{2}O,I}}(T)}{\nu(2\pi m_{w}kT)^{1/2}}, \]  
(11)

where \( \nu \) is the frequency of vibration of adsorbed water molecules. For a temperature range of 218–258 K, \( n \) increases from approximately \( 3 \times 10^9 \) to \( 3 \times 10^{11} \text{ m}^{-2} \).

\( \Delta F \) can be derived from the experimental data. We use Eq. (16a) from Chen et al. (2008), which takes into account the size of the IN and the dependence of the ice embryo size on ambient parameters.

1) ACTIVATION ENERGY BARRIER \( \Delta F \) FOR DEPOSITION NUCLEATION

Assuming a deposition nucleation mechanism type 1 (cf. section 1), \( \Delta F \) consists of the diffusion energy barrier for adsorbed water molecules to diffuse on the surface of the substrate to the ice embryo (\( \Delta F_{\text{diff}} \)) and the energy of desorption of molecules from the IN surface (\( \Delta F_{\text{des}} \)). Following Pruppacher and Klett (1997), \( \Delta F \) can be written as

\[ \Delta F = \Delta F_{\text{diff}} - 2\Delta F_{\text{des}}. \]  
(12)

The activation energy barrier calculated from the experimental data, assuming \( \alpha = 5^\circ \) (cf. Table 1), gives a positive value for \( \Delta F \) on the order of \( 10^{-21} - 10^{-19} \text{ J} \) in the temperature range from 218 to 264 K (Fig. 7). As a comparison, the energy of diffusion for immersion freezing (according to Zobrist et al. 2007) yields a value of \( 4 \times 10^{-20} - 6 \times 10^{-20} \text{ J} \) in this temperature regime. (An alternative method to derive \( \Delta F \) together with corresponding contact angles is described in appendix C and results are shown in Fig. Cl.)

Equation (12) implies that if \( \Delta F \) is positive, surface diffusion of adsorbed water molecules toward the ice embryo cannot take place; that is, \( \Delta F_{\text{diff}} > 2\Delta F_{\text{des}} \). For the water molecules to diffuse on the substrate instead of desorbing, the energy barrier for molecules to desorb away from the substrate \( \Delta F_{\text{des}} \) has to be larger than \( \Delta F_{\text{diff}} \) (Federer 1968). This implies that if the observed ice formation was due to deposition nucleation it can be attributed to the type 2 mechanism. \( \Delta F \) can then be interpreted as the energy barrier to adsorb water molecules directly from the gas phase on a growing ice cluster; that is, the activation energy barrier is equal to the free energy of adsorption (\( \Delta F_{\text{ads}} \)):

\[ \Delta F = \Delta F_{\text{ads}}. \]  
(13)

\( \Delta F \) decreases with temperature and increasing ice saturation. To illustrate the strong decrease at low relative humidities, \( \Delta F \) for \( RH_i = 105\% - 110\% \) is highlighted in light green in Fig. 7. Between \( RH_i = 110\% \) and 165\%, \( \Delta F \) decreases by a factor of 1–3. The reduced Gibbs energy barrier of germ formation (\( \Delta G_{\text{het}} \)) is plotted alongside the \( \Delta F \) data in Fig. 7. Contrary to, for example, Fletcher (1969) we find \( \Delta F \) instead of \( \Delta G_{\text{het}} \) to be the higher and therefore limiting energy barrier. Figure 7 suggests that the adsorption of water molecules on the interface of the ice germ might be a limiting component for the deposition nucleation rate, causing only partial activation in an ensemble of monodisperse dust particles as is usually observed in laboratory studies.

The decrease in \( \Delta F \) toward lower temperatures can be attributed to a decrease in the adsorption energy barrier, for example, due to reduced molecular motion. We use the following temperature-dependent fit to the data (shown as dashed curve in Fig. 7) for the contact angle parameterization discussed in section 5b:

\[ \Delta F = 10^{-19} J \times \exp[0.03678 \times (T - 273.15 \text{ K})]. \]  
(14)

2) PREEXPONENTIAL FACTOR

Using the empirical fit to \( \Delta F \) [Eq. (14), shown in Fig. 7], we calculate the resulting preexponential factor [see Eq. (7)] to be on the order of \( 10^{9} - 10^{11} \text{ m}^{-2} \text{s}^{-1} \). This is substantially different from the value of \( 10^{24} \text{ m}^{-2} \text{s}^{-1} \) suggested by Fletcher (1969), which is commonly used to calculate contact angles from deposition nucleation experiments. Trainer et al. (2009) found a preexponential of approximately \( 10^{20} \text{ m}^{-2} \text{s}^{-1} \) most appropriate for their low-temperature deposition nucleation experiments on a silicon wafer. Independent of \( \Delta F \), the preexponential factor calculated according to Eq. (7) is smaller than previously reported values. We find \( K < 10^{19} \text{ m}^{-2} \text{s}^{-1} \) for any combination of temperature, contact angle, and relative humidity with respect to water (\( RH_i \)) below 120\%.

The preexponential factor can also be interpreted as the surface density of active sites (Cantor 2003). By multiplying the preexponential factor by the particle surface area and experimental time the probability to find an active site on a particle can be calculated to be below 0.3, which implies that there is on average less than one active site per particle. The fact that only a minor fraction of up to 30\% from the 200- to 800-nm particles activate in the 12-s residence time in ZINC is consistent with the result that the preexponential factor is in the range of \( 10^{9} - 10^{11} \text{ m}^{-2} \text{s}^{-1} \). Multiplying \( K \) by the 12-s residence time yields values in a range comparable to the ice nucleation active surface site density (INAS) for deposition nucleation on mineral dust particles (\( 10^{9} - 10^{12} \text{ m}^{-2} \)), which has been found from the analysis of several previous experiments, collected in the work of Hoose and Möhler (2012).
b. Contact angle parameterization

Assuming that a single $\alpha$ (i.e., an epitaxial property among the particle population and on the whole surface of each individual particle) is controlling the efficiency of deposition nucleation, the activated fraction can be calculated as

$$AF_{d,\text{single}} = 1 - \exp[-J(T, S, \alpha)4\pi r_N^2 t_{\text{ZINC}}],$$

(15)

where $r_N$ is the radius of the IN and $t_{\text{ZINC}}$ is the particle residence time in the main part of the ZINC experiment where ice nucleation can occur.

To test the validity of a constant contact angle, Eq. (15) can be used to derive an apparent $\alpha$ for each individual data point instead of calculating the best-fit contact angle for the whole dataset. This results in a temperature- and saturation-dependent change of the average active contact angle as shown in Fig. 8.

Fitting the average contact angle empirically as a function of saturation and temperature, we derive

$$\alpha(S, T) = 0.09 \times (S - 1)^{0.44} \ln(T - 196 \text{ K}).$$

(16)

The activated fraction obtained from using Eq. (16) with Eq. (15) is shown in appendix D together with the resulting deviation from the experimental results. The change in contact angle with RH and temperature can be interpreted either as a dependence of $\sigma_{\text{iv}}$ on ice embryo size (Tolman 1949) and temperature or as an actual change in the properties of ice active surface sites. The latter could be caused by a transition from a liquid to a solid (icelike) state of adsorbed water on the surface of the particles. Such has been reported in the study of Barnes and Sänger (1961) to take place on AgI in the temperature range, where AgI particles become active ice nuclei. They proposed that the physical state of surface adsorbed water could be responsible for the initiation of ice formation (i.e., it could act as active sites). It was also noted that the adsorbed water is nonuniformly distributed on a particle surface, thereby causing the transition to take place on different parts of the particle under different conditions.

Using a temperature- and ice embryo size-dependent surface tension leads to only small changes in the calculated activated fraction and no better agreement between the CNT-model results and the experimental data. The difference in the model results by including the revised surface tension is presented in appendix E.

A third interpretation is that the calculated contact angles represent an apparent average contact angle of an ensemble with a diversity of contact angles from particle to particle. Here we follow the third interpretation and assume the contact angle to be an intrinsic property of each particle—that is, $\alpha$ is independent of the ambient conditions under which ice nucleation takes place. The morphological differences from particle to particle [e.g., visible in the SEM pictures shown in Ladino et al. (2011)] support the assumption of varying surface properties rather than one ubiquitous, environment-dependent parameter.

To consider the individual differences in shape or surface structure that might exist from particle to particle even when they have the same surface area, the occurrence of a certain contact angle among the particles can be represented by a lognormal probability density function (pdf; Marcolli et al. 2007):

$$p(\alpha) = \frac{1}{\alpha(2\pi\sigma^2)^{1/2}} \exp \left( -\frac{(\ln\alpha - \mu)^2}{2\sigma^2} \right),$$

(17)

where $\mu$ is the mean contact angle and $\sigma^2$ is the variance. The activated fraction of a particle ensemble with a contact angle distribution can be calculated as
AF_{d, \alpha-pdf} = 1 - \int_0^\pi p(\alpha) \exp[-J(T, S_1, \alpha)4\pi\gamma_N^2t_{ZINC}] d\alpha.

(18)

Fit parameters \( \mu \) and \( \sigma \) for the so-called \( \alpha \)-pdf approach (e.g., Lüönd et al. 2010) and \( \alpha \) in the previously described single contact angle parameterization are found by minimizing the sum of square error of either Eq. (15) or (18) from the experimental data. The resulting contact angle and the contact angle distribution are shown in Fig. 9 and values are given in Table 1.

Using the calculated single contact angle and contact angle distribution respectively, the activated fraction as a function of temperature and relative humidity can be calculated by the formulas given in section 5a. Resulting contour diagrams are shown in Fig. 10.

The difference in the calculated and measured activated fraction shown in Figs. 10 and 4 is presented in Fig. 11. Above 235 K, agreement between measurements and CNT calculations is found for 200- and 400-nm particles but not for 800-nm particles. Both the single contact angle and the \( \alpha \)-pdf model capture the onset and amount of ice formation, but the observed discontinuous change in the ice active fraction at water saturation for 800-nm particles and at 235 K for all three particle sizes is not predicted by theory.

According to this analysis, the observed ice nucleation on 200- and 400-nm particles above water saturation

Fig. 10. Calculated contour diagrams of activated fraction of deposition nucleation: (a) assuming one constant contact angle and (b) \( \alpha \)-pdf for (top)–(bottom) 200-, 400-, and 800-nm particles. Conditions of water saturation (RH_w = 100%) are indicated as the dashed line. The homogeneous freezing temperature of 235 K is shown as the dotted vertical line. White lines highlight conditions of 0.1%, 1%, and 10% activated fraction.

Fig. 11. \( \Delta AF \) obtained from the CNT-based models and the experimental data: (a) single-contact-angle model minus data and (b) \( \alpha \)-pdf model minus data. Results for (top)–(bottom) 200, 400, and 800 nm are shown. Water saturation is indicated as the dashed line, and vertical dotted lines highlight a temperature of 235 K. A possible reason for the mismatch between model and experiment could be that another nucleation mechanism is active below 235 K.
could be attributed to deposition nucleation alone. But there are two reasons why deposition nucleation is probably not the responsible nucleation mode for the observed ice formation below 235 K and subsaturated conditions with respect to water.

First, the best-fit contact angle of deposition nucleation is incompatible with the contact angles for immersion freezing. By using an average immersion freezing contact angle of $\alpha_{\text{imm}} = 91^\circ$, which Welti et al. (2012) obtained for the same kaolinite sample, and applying the Young relations (Young 1805) to estimate the deposition nucleation contact angle (following Isaka 1966), $\alpha_{\text{dep}}$ can be derived from

$$\cos(\alpha_{\text{dep}}) = \frac{\cos(\alpha_{\text{imm}}) \times \sigma_{\text{sw}} + (\sigma_{\text{sl}} - \sigma_{\text{sw}})}{\sigma_{\text{sw}}}.$$  \hspace{1cm} (19)

Here, $\sigma_{\text{sw}}$ and $\sigma_{\text{sl}}$ are the surface tension between ice and water or vapor that can be found in Pruppacher and Klett (1997) or Hale and Plummer (1974) and $\sigma_{\text{sw}}$ and $\sigma_{\text{sl}}$ are the surface tension between substrate and water or vapor, which are taken from Helmy et al. (2004).

The contact angle of deposition nucleation obtained from Eq. (19) is approximately $\alpha_{\text{dep}} = 40^\circ$. We note that surface tensions depend upon the curvature of a surface (Tolman 1949; cf. appendix E) and that values obtained on a macroscopic interface as in Helmy et al. (2004) can only be used as a rough approximation [as pointed out by Reiss (1952)]. The best-fitting contact angle assuming deposition nucleation as the nucleation mode for the presented measurements of about 5$^\circ$ differs significantly from the 40$^\circ$ value obtained from Eq. (19).

A higher and a lower contact angle of 105$^\circ$ and 72$^\circ$, respectively, for the same kaolinite sample in the immersion freezing mode has been reported from a differential caliometry study by Pinti et al. (2012). Using these values as upper and lower limits in Eq. (19) results in a predicted deposition contact angle of approximately 36$^\circ$ and 45$^\circ$, respectively. Also, these contact angles are incompatible with the best-fit contact angles to the experimental results presented in section 3.

The second reason is that the assumption of a spherical cap geometry of the ice germ, which is implicit in the performed CNT calculation, is in contradiction to the calculated contact angle of less than 5$^\circ$. The maximal height $h$ of a spherical ice embryo cap can be calculated by basic geometry as

$$h = r_g \times [1 - \cos(\alpha)].$$ \hspace{1cm} (20)

A contact angle of 5$^\circ$ leads to a maximal cap height of less than the height of a water monolayer. The assumption of a spherical cap embryo is therefore not fulfilled in this case and the concept of $f_{\text{imm}}$ is no longer valid (Cantor 2003). Such a small contact angle might indicate that ice nucleation takes place in capillary structures, steps, or in cracks where the required amount of water molecules to form a critical ice embryo is considerably reduced (Chakravarty and Pound 1964; Fukuta 1966). Or, it can be concluded that the observed nucleation mechanism is not pure deposition nucleation but biased by another ice nucleation mode. The underlying assumptions of the analysis conducted in section 5 would therefore be falsified. The derived contact angle and preexponential factor based on our experimental data would not represent pure deposition nucleation but incorrectly parameterize the ice activated fraction by several nucleation mechanisms—namely, deposition nucleation and condensation freezing or homogeneous nucleation below water saturation—but appearing as one.

6. Discussion

Enhanced ice nucleation at 110% RH$_i$ below a temperature of 235 K was observed. The attempt to explain this feature with a classical nucleation theory–based parameterization of deposition nucleation led to unphysical results. Therefore, the observation challenges the classical picture of deposition nucleation being the most active ice nucleation pathway below water-saturated conditions. In the following, we discuss capillary condensation and hydriptic sites as possibilities that could explain enhanced ice nucleation at low temperatures and below water saturation.

Below 235 K, homogeneous nucleation in adsorbed or capillary condensed water could be active in the whole saturation range where ice formation was detected (Marcolli 2013; Christenson 2013). However, energetically preferable heterogeneous ice nucleation on the capillary wall could be expected to take place already at higher temperatures. A possible reason that enhanced ice formation is only observed below homogeneous freezing temperatures could be the presence of a disordered quasi–liquid water layer on the capillary wall preventing heterogeneous ice germ formation (Marcolli 2013 and references therein).

The onset of droplet formation below 235 K is expected to cause a distinct increase in the ice crystal number concentration owing to homogeneous nucleation. The observed absence of a jump in ice nucleation close to water-saturated conditions below 235 K indicates little CCN active kaolinite particles. The measurements presented in Fig. 6 corroborate low CCN activity of the used kaolinite particles also at temperatures up to 260 K. The
finding that the only distinctive jump in the ice active fraction below 235 K occurs already between 110% and 120% RH, might indicate that no CCN activation is necessary and already small amounts of sorbed liquid water is sufficient to allow ice formation via condensation freezing mechanisms. Small amounts of soluble impurities (hydrophilic sites) as possible source for enhanced clustered water adsorption even below water saturation have been proposed by (Archuleta et al. 2005). The existence of trace amounts of soluble material on otherwise insoluble mineral dust particles deployed from natural sources and their importance to enhance water condensation have been addressed in the work of Fan et al. (2004) and Twery et al. (2009).

Measurements of the conductivity in the excess water with which dust samples have been washed confirm the presence of such, especially in natural samples. In the kaolinite sample used for the measurements reported here we found soluble material equivalent to 0.28 milligrams of NaCl per gram of dust, whereas a sample of Arizona test dust contained an equivalent of 3.78 mg g⁻¹. The effect of hydrophilic islands could be especially large for particles with small surface areas. If the adsorbed or condensed water volume is large enough, then ice formation due to either condensation freezing or homogeneous nucleation might be possible even below water saturation.

In the laboratory study by Seisel et al. (2005), multilayer water adsorption on mineral dust particles (Saharan dust) was observed below 1% RHw at supercooled temperatures. It has been reported by Croteau et al. (2010) that adsorption of liquidlike water on kaolinite particle surfaces takes place at 235 K and far below water saturation (~60% RHw) even without the presence of soluble components. Adsorbed water is thought to be in a more bonded or oriented state compared to water just condensed on a surface (Birstein 1955). Hu and Michaelides (2007, 2008) have shown that this is especially true for water adsorbed on the surface of kaolinite.

Water adsorption could cause soluble substances on the surface of kaolinite particles to deliquesce below water saturation. We suggest that the dissolving soluble substances could enhance ice nucleation below about 235 K and suppress deposition nucleation above this temperature in two ways: (i) a salt solution covering parts of the IN surface inhibits ice formation by occupying possible ice active surface features [as previously proposed by Koehler et al. (2010)] and (ii) covering subcritical ice embryos that formed from the vapor phase, which possibly would stabilize the ice embryos, but inhibits heterogeneous freezing owing to the effect of the solute compared to pure water (Seinfeld and Pandis 1998; Alpert et al. 2011). At temperatures below the heterogeneous freezing point of the solution, the same process could enhance ice formation by covering subcritical embryos that are too small to be stable in the vapor phase but have the critical size to be stable immersed in a liquid [equivalent to the condensation freezing (II) mechanism shown in Fig. 1]. Birstein (1955) observed increasing water adsorption with decreasing temperatures on silver iodide and Seisel et al. (2005) experimentally confirmed this observation to be also true for mineral dust and soot. Enhanced water adsorption decreases the effect of the solute owing to dilution. Field et al. (2006) and Phillips et al. (2008) suggested that a jump in ice formation activity that was observed below 235 K and below water saturation could be explained by reaching a point of sufficient solute dilution. Also, reaching higher saturation conditions would cause the solution to be more diluted, which would allow condensation freezing to become possible at higher temperatures (Möhler et al. 2008).

In summary, a cover of the substrate with a solution droplet might partially inhibit deposition nucleation and condensation freezing by shielding active sites from the vapor phase, preventing the formation of ice embryos by deposition nucleation and by depression of the heterogeneous freezing temperature in the covering liquid phase. At sufficiently low temperatures or sufficient dilution of the solute, a growing liquid layer might enhance ice formation by stabilizing subcritical ice germs (cf. Fig. 1) and allowing condensation freezing to become important below water saturation.

Depending on the size and shape of pores on the particle surface, capillary condensation due to the inverse Kelvin effect can take place at saturations even below ice saturation (Marcollini 2013; Christenson 2013). Heterogeneous nucleation in capillary confinements can be facilitated (Fukuta 1966) and homogeneous nucleation can occur at sufficient supercooling.

7. Conclusions

We measured the ice active fraction of 200-, 400-, and 800-nm kaolinite particles in a temperature range of 218–258 K from ice saturation up to 180% RH. A jump in the ice active fraction can be observed at temperatures below about 235 K, setting in above 110% RHw, and an increase at water-saturated conditions for temperatures higher than 235 K. The water saturation–dependent increase in the activated fraction is most pronounced for 800-nm particles. The ice activated fraction above water saturation cannot be attributed to an immersion freezing–like mechanism (condensation
IV) alone but indicates that an additional nucleation mechanism is active. The additional mechanism could either be deposition nucleation or an ice nucleation mechanism involving the adsorption of water—namely, condensation freezing (I, II, III). An equivalent increase in the activated fraction below water saturation (starting at 110% RH) was observed at temperatures below 235 K. In section 5, arguments have been presented against deposition nucleation as described by CNT being the only process observed below water saturation and temperatures below 235 K. The fact that the activated fraction seems to lose the dependence on relative humidity strongly suggests that under these conditions sufficient adsorption or capillary condensation of water occurs that favors ice nucleation by a condensation freezing mechanism or, as indicated by the temperature threshold (T, 235 K), of homogeneous nucleation within capillary-held water. Adsorption/condensation of a sufficient amount of water can take place below water saturation on surface features like concave zones, capillaries, cracks, or steps owing to an inverse Kelvin effect (Christenson 2013) or on hydrophilic salt islands, which allow water to adsorb more readily. These surface structures are also thought of subsequently facilitating ice nucleation (Fukuta 1966; Fletcher 1969; Rogers and Yau 1989; Pruppacher and Klett 1997).

An open question that remains is to what degree and at what saturation mainly insoluble dust particles will act as CCN at low temperatures. The role of potentially present soluble substances on the surface especially for natural samples should be investigated experimentally. Whether the topographical features on the particle surface that trigger ice formation are the same as those responsible for CCN activation of insoluble particles needs further clarification.

Based on field measurements of ice crystal residuals (Chen et al. 1998; Prenni et al. 2007) and laboratory studies (Fletcher 1959; Welti et al. 2009; Pruppacher and Klett 1997; and references therein) it has been reported that deposition nucleation on particles smaller than approximately 100 nm is inefficient. From the experiments presented here, it can be seen that the influence of particle size becomes smaller below 235 K. This could be evidence that particles that are too small to be efficient deposition nuclei might however be able to act as ice nuclei (e.g., by sufficient adsorption/condensation of water and ice nucleation within this water volume). The importance of particle size for different nucleation mechanisms could be investigated experimentally by conducting continuous-flow diffusion chamber or cloud chamber measurements using polydisperse particles and looking at the size distribution of the residuals in ice crystals activated below water saturation, above and below 235 K.

Ice nucleation experiments using designed IN with defined porosity could be conducted to test the importance of capillary condensation and ice nucleation in confinements. To deconvolve the importance of soluble material for water adsorption and on heterogeneous nucleation mechanisms, experiments on unwashed and washed dust samples together with a quantitative chemical analysis of the soluble fraction could be made. Data from the above proposed experiments would help to further investigate the mechanism and importance of liquid water condensation and of condensation freezing or homogeneous ice nucleation below water saturation.

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APPENDIX A

Surface Area–Dependent Freezing Temperatures for Deposition Nucleation and Condensation Freezing (IV) at Water Saturation

As the analysis described in sections 4 and 5 shows, condensation freezing or deposition nucleation could be

![Comparison of particle size effect on the temperature of (left) 1% and (right) 10% activated fraction above water saturation to deposition nucleation and immersion freezing (condensation freezing IV) curves at water saturation calculated from CNT. Measurements of 1% and 10% activated fraction of 200-, 400-, and 800-nm particles are shown.](image-url)
the responsible mechanism for ice formation above 235 K at water-saturated conditions. A comparison of the effect of particle surface area on freezing temperature as predicted by CNT for deposition nucleation and immersion freezing (condensation freezing IV) to measurements at 1% and 10% activated fraction and water-saturated conditions is shown in Fig. A1. For the 1%-activated-fraction data, immersion freezing (condensation freezing IV) is not efficient enough to be the responsible nucleation mode, but the data fit to the deposition curve obtained from the analysis discussed in section 5b. This would imply that under mixed-phase-cloud conditions interstitial particles that did not activate as CCN can act as deposition nuclei and initiate cloud glaciation by the Bergeron–Findeisen process. For an activated fraction of 10%, however, only 1% and 6% of the ice formation on 200 and 400 nm can be attributed to deposition nucleation. Another mechanism has to be active. This could be condensation freezing or homogeneous nucleation in capillary-held water present on a fraction of the particles.

**APPENDIX B**

**Effect of a Constant Preexponential Factor on the Modeled Activated Fraction**

The preexponential factor proposed by Fletcher (1969) was used to derive the best-fitting single contact angle for the stochastic model and a contact angle distribution to be used with the $\alpha$-pdf model. The resulting fit parameters are given in Table B1.

The activated fraction as a function of temperature and relative humidity derived using these parameters are shown in Figs. B1 and B2.

**TABLE B1.** Fit parameters using a constant preexponential according to Fletcher (1969) for a single contact angle ($\alpha$) and contact angle distribution ($\alpha$-pdf) obtained by minimizing the sum of squared errors between data below water saturation in the whole temperature range studied and either Eq. (15) or (18).

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Value</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single $\alpha$</td>
<td>$\alpha$</td>
<td>28.31°</td>
<td>0.096</td>
</tr>
<tr>
<td>$\alpha$-pdf</td>
<td>$\mu$</td>
<td>49.41°</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td>$\sigma$</td>
<td>0.6202</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. B1.** (top) Model calculations of the activated fraction using the constant preexponential factor of Fletcher (1969) and assuming one constant contact angle within the particle population. (middle) The experimental data. (bottom) The mismatch in the activated fraction between model and experiment. Each column represents one particle size as indicated in the figure. Water saturation is indicated as the dashed line.
A constant preexponential (kinetic) factor results in a more linear temperature dependence than observed in the experimental data presented in section 3. In agreement with Wheeler and Bertram (2012), we find a substantial mismatch between the experimental data and a single contact angle stochastic scheme using a constant preexponential factor. However, the $\alpha$-pdf model together with the preexponential factor of Fletcher (1969) yields to the lowest sum of squared error between the fit and the experimental data. The derived contact angles of $28.3^\circ$ for the single $\alpha$ and the median contact angle of $49.4^\circ$ for the $\alpha$-pdf model are closer to a contact angle of $\alpha_{\text{dep}} = 50^\circ$, which has been found in section 5b using the Young relation in the form given in Eq. (19).

APPENDIX C

Determining Contact Angles and Heights of the Activation Energy Barrier from Pairs of Size-Selected Data

The activated fraction of an IN of surface area $A$ at certain ambient conditions ($T, S_i$) and residence time $t_{\text{ZINC}}$ can be determined experimentally (cf. section 2a). Within the framework of CNT the activated fraction is given by

$$AF = 1 - \exp(-JAt_{\text{ZINC}}). \quad (C1)$$

Generally, the determination of contact angle is coupled to the choice of the preexponential factor $K$ [cf. Eq. (7) and discussion in section 5a(2)]. Using a data pair from two different measurements—one from particles exhibiting a surface area $A_1$ and one obtained from particles with a different surface area $A_2$, where $T_1 = T_2$, $t_{\text{ZINC},1} = t_{\text{ZINC},2}$, $S_{1,1} \neq S_{1,2}$, and $AF_1 = AF_2$—one contact angle reproducing the two measurement results can be calculated.

If $AF_1 = AF_2$ and $t_{\text{ZINC},1} = t_{\text{ZINC},2}$, then

$$J_1A_1 = J_2A_2. \quad (C2)$$

Using Eqs. (C1), (C2), (4), and (5) and the assumption that $K = \text{constant}$ for the $S_i$ range that separates the two measurements yields
Equation (C3) can be rearranged to determine \( f_{\text{het}} \) at a given temperature under the assumption that \( f_{\text{het}} \) is independent of \( S_i \) and can be expressed as a function of temperature only. Corresponding contact angles shown in Fig. C1a are determined using Eq. (6).

We can then calculate \( \kappa \) using Eq. (4) in the form

\[
\kappa(T) = \frac{J(T, S)}{\exp\{-[\Delta G(T)]_{\text{het}}(\alpha)/kT\}}
\]  

FIG. C1. (a) Contact angles as a function of temperature calculated according to the method described in appendix B and (b) \( \Delta F \) for deposition nucleation, obtained using the method described in appendix C (see text for details). For comparison, the empirical fit curve from the analysis in section 5a(1) is shown as the dashed line.

\[
\ln \frac{A_1}{A_2} = \frac{16 \pi v_{\text{ps}}^2(T) \sigma_{\text{ss}}^\text{L} f_{\text{het}}}{3 k^3 T^3} \ln \frac{S_{2,i}^2}{S_{1,i}^2} - \ln S_{2,i}^2, \quad \text{(C3)}
\]

Equation (C3) can be rearranged to determine \( f_{\text{het}} \) at a given temperature under the assumption that \( f_{\text{het}} \) is independent of \( S_i \) and can be expressed as a function of temperature only. Corresponding contact angles shown in Fig. C1a are determined using Eq. (6).

We can then calculate \( \kappa \) using Eq. (4) in the form

\[
\kappa(T) = \frac{J(T, S)}{\exp\{-[\Delta G(T)]_{\text{het}}(\alpha)/kT\}}
\]  

FIG. D1. (top) Model calculations of the activated fraction assuming a temperature- and saturation-dependent contact angle \( \alpha(S, T) \). (middle) The experimental data. (bottom) \( \Delta AF \) between model and experiment. Each column represents one particle size as indicated in the figure. Water saturation is indicated as the dashed line.
and Eq. (C1) in the form
\[ J(T, S_i) = -\ln[1 - AF(T, S_i)] / A_{\text{ZINC}}. \]  
\( \text{(C5)} \)

Combining (C4) and (C5) yields
\[ K(T) = -\ln(1 - AF) / A_{\text{ZINC}} \exp\left\{-[\Delta G(T, S_i)\theta_{\text{het}}(\alpha)/kT]\right\}. \]  
\( \text{(C6)} \)

where \( K \) is composed of four factors as shown in Eq. (7). The first three terms (\( A, Z \), and \( n \)) are given in Eqs. (8), (9), and (11).

By rearranging Eq. (C6) the activation energy barrier \( \Delta F(T) \) can be derived:
\[ \Delta F(T) = \frac{-\ln(K/AZ^n)}{kT}. \]  
\( \text{(C7)} \)

Results of \( \Delta F(T) \) obtained with this method are shown in Fig. C1b together with the fit curve given in Eq. (14) as proposed in section 5a(1).

APPENDIX D

Model Results Using an Empirical Function for a Temperature- and Saturation-Dependent Contact Angle

Using Eq. (16) in a stochastic model to represent the experimental data results in an overprediction of the influence of particle size on the ice active fraction (Fig. D1). Also, the temperature and saturation dependence of ice nucleation is not captured more accurately in comparison to model calculations where a single contact angle was used (cf. Fig. 10a).

APPENDIX E

Influence of the Curvature Effect on Surface Tension on the Calculated Activated Fraction

Taking into account the dependence of the surface tension upon the curvature of the critical ice germ surface, the surface tension \( \sigma'_{iv} \) can be derived according to Bogdan (1997):
\[ \sigma'_{iv} = \frac{\sigma'_{iv}}{1 + (2\delta/r_g^2)}. \]  
\( \text{(E1)} \)

where \( \delta \) designates the Tolman length for ice, \( r_g \) is the radius of an ice germ given in Eq. (E2), and \( \sigma'_{iv} \) denotes the surface tension of a flat ice surface. A temperature-dependent expression for \( \sigma'_{iv} \) can be found in Hale and Plummer (1974):
\[ r_g(T, S_i) = \frac{2

Neglecting the curvature effect of the critical ice embryo on surface tension leads to only a minor deviation in the model parameters and therefore the model results

Fig. E1. (a) Difference in the calculated activated fraction by including a temperature- and ice embryo size-dependent surface tension in the single contact angle model and (b) difference in the calculated activated fraction by including a temperature- and ice embryo size-dependent surface tension in the \( \alpha \)-pdf model. The difference in the activated fraction is shown for (top)–(bottom) 200-, 400-, and 800-nm particles.
obtained in section 5. The largest effect can be found for ice nucleation on 800-nm particles, where the calculated activated fraction can differ by up to +6% and −20%. The differences between the model results are shown in Fig. E1 for the calculations using Eq. (7) to derive the preexponential factor and in Fig. E2 for the models using $K = 10^{24} \text{m}^{-2}\text{s}^{-1}$ according to Fletcher (1969). The main difference shown in Fig. E2 is caused by a shift in the activated fraction toward lower relative humidity.

It can be inferred from the effect of reduced surface tension with smaller ice germ size that the presence of an adsorbed or capillary condensed liquid phase, which would drastically reduce surface tension and the critical germ size (e.g., via the condensation freezing mechanism shown in Fig. 1), might generate the observed pattern in the activated fraction below water saturation.

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