We thank the referee for the careful review that revealed several sections in our manuscript that were insufficiently explained. The main changes in the revised manuscript concern

(i) the description of condensation and immersion freezing which is better clarified by addition of the corresponding model equations, and

(ii) the treatment of the 'deterministic' scheme that we now only apply to conditions where immersion freezing can occur, i.e. when conditions are supersaturated with respect to water. Since condensation freezing and immersion freezing can be both described by the CNT framework and depend on the surface properties of the IN (effective contact angle θ), we apply the contact angle distributions for the full temperature/supersaturation range that is covered in the parcel model simulations. All simulations using the deterministic scheme have been repeated and figures have been replaced.

All specific reviewer comments are addressed below in detail. We note that the equation numbers in the response refer to the new numbering in the revised manuscript.

Review by referee #2

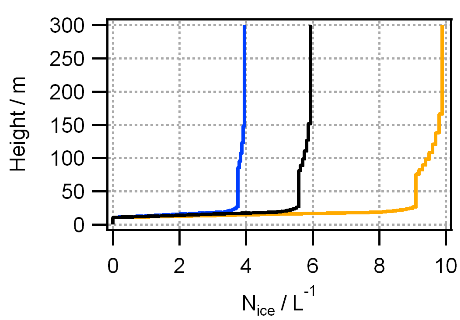
In this work the authors use parcel model simulations to study the sensitivity of the cloud ice crystal concentration and the ice water content to the ice nucleation scheme in immersion and condensation freezing. The authors conclude that the different ice nucleation schemes are likely to disagree when extrapolated outside the conditions used to retrieve their parameters. This may lead to significant variation in ice crystal number and ice water content during the cloud development. This is an interesting study, relevant for the scientific community, however some clarifications are needed before it can be published.

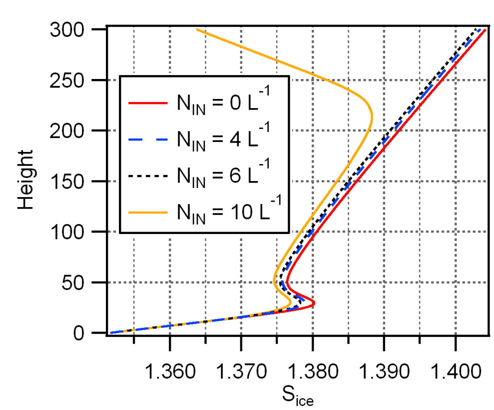
General Comments

Reviewer comment: In the study the authors set the maximum IN concentration and use the parameterizations to calculate a relative freezing fraction. Most of the simulations are run with NIN = 4 L-1. Although a sensible choice, using a different value will lead to a different feedback on the supersaturation, and to different conclusions in the the parcel model simulations.

Response: In mixed-phase clouds, the supersaturation is mostly determined by the updraft (cooling) and the condensation of water vapor on the much more numerous droplets as compared to the few ice particles in situations where both phases coexist, i.e. the deposition term in Eq.-13 is much smaller than the condensation term.

For demonstration, the adjacent figure shows the super-saturation and N_{ice} in simulations





where $N_{IN} = 0\ L^{-1}$, $4\ L^{-1}$, $6\ L^{-1}$ and $10\ L^{-1}$ are assumed.

In our previous model study ((Ervens et al., 2011)), we explored the sensitivity of different N_{IN} to the phase distribution (ice/liquid water) in mixed-phase clouds and found that this parameter, together with updraft velocity, has a significant impact on the onset of the Bergeron-Findeisen-Process. In the present study, we mostly focus on situations where both phases grow independently of one other ('stable mixed-phase clouds').

While the absolute number of frozen particles and thus IWC will change with different assumed N_{IN}, the overall conclusions in the present study – "different ice nucleation schemes cannot be extrapolated to a wide range of conditions" – will not change.

Reviewer comment: In their description of the different schemes the authors focus on the representation of the distribution of contact angles on the immersed IN. It is known that droplet volume also has an impact on nucleation rates and it would be appropriate to discuss how this may fit into each of the parameterizations. If the impact of the droplet volume on nucleation rates is neglected then this must be explicitly stated.

Response: Classical nucleation theory implemented in our model follows the approach by (Khvorostyanov and Curry, 2004) that represents a combination of deliquescence (condensation) and immersion freezing. In the revised manuscript we include the complete set of equations for both immersion and condensation freezing (Section 2.1) in order to clarify that droplet radius (volume) is explicitly considered in all schemes that are based on CNT (1θ, soccer (int) and (ext), and θPDF).

For immersion freezing

$$r_{germ} = \frac{2\sigma_{is}}{\rho_{ice} L_m^{ef} ln\left(\frac{T_0}{T}\right) + \frac{RT\rho_{ice}}{M_w} H_c - \frac{2\sigma_{sa}}{r_d}} \tag{4}$$

with

$$H_c = \frac{2\sigma_{sa} M_w}{\rho_w RT\ r_d} - \frac{\nu\Phi(1-\varepsilon_{insol}) M_w \rho_s r_s^3}{M_s \rho_w (r_s^3 - r_d^3)} \tag{5}$$

Since particles at $S_w < 1$ are near equilibrium

$$\ln S_w = H_c \tag{6}$$

for deliquesced particles, it can be assumed

$$r_{germ} = \frac{2\sigma_{is}}{\rho_{ice} L_m^{ef} ln\left(\frac{T_0}{T}\right) S_w^{\left(\frac{RT}{M_w L_m^{ef}}\right)} - \frac{2\sigma_{sa}}{r_d}} \tag{7}$$

The definitions of all parameters are added in the manuscript (Section 2.1.1).

Reviewer comment: The expression used for the "deterministic" approach neglects the effect of supersaturation on ice crystal production and should not be used for water-subsaturated conditions. Even if a deterministic approach is used, it is known that supersaturation is an important factor in condensation freezing. In fact, the authors mention several empirical parameterizations that include supersaturation but end up using a temperature-only dependent parameterization, which is an error.

Response: We thank the reviewer for pointing out this inconsistency with known sensitivities of ice nucleation in different saturation regimes.

The deterministic approach, (Eq-12) has been derived based on laboratory studies by (Lüönd et al., 2010) and thus it describes the freezing behavior under the experimental conditions consistently to the stochastic approaches. Since the motivation of our study is to compare the five schemes that have been derived based on one set of experimental data, we do not apply an additional deterministic scheme here that explicitly includes S.

However, we agree with the reviewer that the application of Eq-12 to water-subsaturated conditions is not justified since this expression was derived at water-supersaturated conditions and thus should not be extrapolated to all temperature regimes that cover $S_w < 1$.

Instead of using Eq-12 over the complete temperature range, we have changed our model and assume now $F_{fr} = 0$ if $S_w < 1$, i.e. shortly after beginning of the simulations and in cases where the Bergeron-Findeisen-Process occurs (Figure 4e, f). We have redone all simulations and changed all Figures accordingly.

Reviewer comment: It seems that the only distinction between the internal vs. externally mixed "soccer ball" cases is the sampling of contact angles from the overall distribution, which is assumed to be the same in both cases. The authors sample 20 subdistributions from the overall contact angle distribution for the externally mixed case. It seems that if they would use a larger sample the internally and externally cases would converge. A more consistent approach would assume several independent contact angle distributions for the externally mixed case.

Response: If we were to assume an 'infinite' number of nucleation sites on each particle, it is true that the two soccer ball schemes should yield the same results. However, under those conditions of 'complete sampling' of the contact angle distribution, all particle surfaces would comprise the same contact angle distribution – and, thus, the particles would be internally mixed with respect to their surface properties, which contradicts findings in experimental studies where only a random distribution of surface properties throughout an IN distribution could explain the observed freezing behavior (e.g., ((Marcolli et al., 2007; Vali, 2008)). Such behavior might instead be explained by a model in which not all possible contact angles are present on each particle, and thus some particles are 'worse IN' than those that include the very rare small contact angles.

We agree with the reviewer that a different number of nucleation sites and externally-mixed particle types would change the relative differences between the two soccer ball schemes. However, since we focus on seeking trends in nucleation behavior due to different schemes, we think that our choices are reasonable. We added some text in Section 4.1.1. in the discussion of Figure 4.

Reviewer comment: It is not clear what assumptions about the water activity around the IN (i.e., inside the droplet) are used to calculate immersion and condensation freezing rates.

Response: We have expanded Section 2.1 by including the equations added above in our responses. Since the water activity is defined as

$$a_w = \exp\left(\frac{\nu \Phi m_s M_w}{M_s m_w}\right)$$

these equations show the link between the water activity and the germ radius that affects the nucleation rate.

Specific Comments

Reviewer comment: Page 7169. Line 24. Please reference at least some of the studies showing temporal dependency at constant T.

Response: We cite now several studies in the introduction that discuss the stochastic nature of freezing and show time-dependent evolution of the frozen fractions.

Reviewer comment: Page 7172. Line 5. Please specify what model is used to calculate rgerm in condensation and immersion.

Response: We use the approach by (Khvorostyanov and Curry, 2004). We clarified this and included the equations for r_{germ} for condensation and immersion freezing (Eqs. 4-7).

Reviewer comment: Page 7172. Equation (3). This expression is valid only if J is constant (box model calculations). Please describe what approximation is taken to calculate ∫ J dt for the parcel model calculations.

Response: The calculation of J is updated every 1 second using the actual values of all parameters that J depends on. These parameters (ice and droplet diameters, supersaturation, temperature, pressure) are calculated iteratively within each 1-second-time step by solving simultaneously a set of differential equations that describe their temporal evolution until convergence within a given accuracy (relative tolerance 1e-6; absolute tolerance for deviation of drop and ice diameters: 1e-13 cm) is reached. I.e. Eq. 8 is used to update J at 1 s intervals and P is the probability of freezing related to the number of unfrozen IN,

$$N_{IN,unfrozen}(t) = N_{IN}(t=0) - N_{IN,frozen}(t)$$

whereas $N_{IN}(t=0) = 4\ L^{-1}$ (or $1\ L^{-1}$ for simulations in Figure 7 and 8d-f).

CNT predicts the nucleation of a (small) number of IN at any temperature at every model time step (1 second). In theory, this would lead to a new ice class from each IN size class (*i*) every second in the model simulations, which would result in e.g., to up to 3000 ice classes in the w = 10 cm/s simulations (300 m / 10 cm/s / 1 s) if we assume a monodisperse, internally-mixed IN distribution. This number multiplies with the number of 'externally mixed' particles (20) in the soccer(ext) scheme and the θPDF scheme and with the number of IN size classes (1 for most simulations, 10 for simulations in Figure 8), i.e. $i \leq 600{,}000$.

In order to keep *i* computationally manageable throughout the simulations, we use 'probability steps', i.e. we only fill a new ice class if 2.5% of an IN size class and particle type of this size (in the externally mixed schemes) is predicted to freeze. While for the 1θ or the soccer(int) scheme, it might be feasible to use a finer resolution, we have chosen the same steps for all simulations for the sake of consistency.

The advantage of this method as compared to other methods that combine ice particles of similar sizes into bins is that we can always track every individual ice particles back to its original aerosol particle and its properties (size, contact angles …) whereas this information is lost in the usual binning methods.

`Reviewer comment:` `Page 7172. Eq. (4). Please explain how this equation is derived. I also find confusing what the authors mean by the "overall freezing probability". Is this the fraction of frozen droplets? Or is it the expectancy of finding a droplet frozen in the population?`

Response: The θPDF scheme assumes externally mixed particles that have one contact angle each. Eq-9 describes the probability that particles within the IN population freeze. E.g. if a single particle out of a population of 100 particles had a probability of 1 (and all others P = 0), 1% of this population is predicted to freeze, i.e.

$$P_{PDF} = 1/100 \cdot (1 \cdot 1 + 99 \cdot 0) = 0.01$$

Thus, statistically 1 out of 100 particles will activate which is equivalent to a probability of all particles of P = 0.01.

We reworded the sentence

"The freezing probability of a particle within such a population of N particles is calculated as a weighted average of the freezing probabilities of all individual particles."

`Reviewer comment:` `Page 7175. Eq. (6). This expression is suitable only for activated droplets. For subsaturated regimes any credible expression must include the effect of supersaturation.`

Response: Since this expression has been derived from immersion freezing experiments, we agree that it is not valid at conditions where $S_w < 1$. We extended the text in Section 2.1. and 4

and clarify that (i) condensation freezing is strongly dependent on supersaturation and (ii) that is why we use Eq-12 only for supersaturated conditions with respect to water.
As opposed to the simulations in the original version of the paper, we changed this approach in our model and present new model results in all respective figures.

`Reviewer comment:` `Page 7175. Line 19. Do the droplets grow during the simulation? What are their sizes? Are they assumed to be in equilibrium?`

Response: The system is not in equilibrium and thus, Eq-13 is applied to calculate the change in supersaturation that in turn affects droplet and ice growth. A variable-coefficient ordinary differential equation solver (VODE, (Brown et al., 1989)) is used to simultaneously solve the equations for growth of droplets/deliquesced particles r_d and ice particles r_i (together with the equation for supersaturation, T, and P):

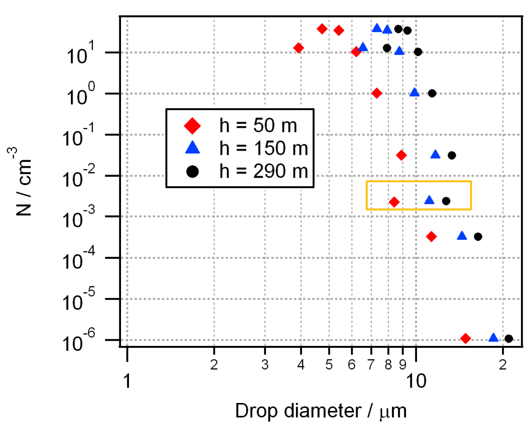
$$\frac{dr_d}{dt} = \frac{1}{r_d}\,\frac{S_w - exp\left[\frac{2M_w\sigma}{RT\varrho_w r_d} - \frac{\nu\phi\, m_s M_w}{M_s m_w}\right]}{\frac{\varrho_w RT}{D_v\, M_w e_w} + \frac{L_e \varrho_w}{k_a T}\cdot\left(\frac{L_e M_w}{RT} - 1\right)}$$

$$\frac{dr_i}{dt} = \frac{1}{r_i}\,\frac{\frac{e_w}{e_i} S_w - 1}{\frac{RT}{D_v\, M_w e_i} + \frac{L_{vi}}{T k_a}\cdot\left(\frac{L_{vi} M_w}{RT} - 1\right)}\,\frac{C}{r_i \varrho_{dep}}$$

D_v	modified diffusivity	e_i	saturation vapor pressure over ice
k_a	modified thermal conductivity	L_{vi}	latent heat of sublimation
L_e	latent heat of evaporation	C	capacitance of ice particle
e_w	saturation vapor pressure over water	ρ_{dep}	deposition density of ice particle

Since these are standard equations as used in many applications (cf (Pruppacher and Klett, 2003)), we do not include them in the manuscript as we feel that a reference to the original parcel model is sufficient.

Typical drop size distributions from our simulations (for simulations shown in Figure 4c, d) are shown in the adjacent figure for three different heights in the cloud. The smallest CCN sizes have not activated into cloud droplets and they remain as interstitial particles with sizes < 1 µm (not shown).



Note that for most simulations, ice is only formed on a fraction of the single CCN/drop class that is marked with the orange box (except in Section 4.2). While this assumption might not be realistic in terms of atmospheric conditions, it allows us to neglect the IN size effect and to focus on feedbacks of the onset of freezing to ice growth and supersaturation due to the different ice nucleation schemes.

Reviewer comment: Page 7177. Line 15. The expression used to calculate the nucleation rate assumes equilibrium which would not be the case once the droplets grow beyond their critical diameter. Please explain how the water activity inside each droplet is calculated.

Response: During the model simulations, equilibrium is only assumed at t = 0 when equilibrium diameters for $S_w = 0.99$ for all particles are calculated. The subsequent growth of particles and droplets is solved in every time step by the equations for dr_d/dt and dr_i/dt. For the situation where cloud droplets grow beyond their activation diameters, we use Eq. (4) and (7) to calculate the germ radius that explicitly includes the droplet diameter. Even though deliquesced particles at $S_w < 1$ might be near their equilibrium diameters, we always use the explicit differential equations that predict their diameters as a function of the surrounding saturation.

Reviewer comment: Page 7178. Eq. (9). Is this an approximation or an equality?

Response: Eq-15 follows immediately from Eq-14 that gives in a numerical form the condition under which similar F_{fr} (or N_{ice}) are expected from the 1θ and the soccer(int) scheme. Similar frozen fractions (Eq-14) are predicted if the nucleation rates are similar (Eq-15); thus, the 'approximately equal sign' is correct in this case.

Reviewer comment: Page 7179. Line 5. This may not be so obvious. One can always find a value such that J1θ = Σ SjJj .

Response: We realized that our text was misleading. Of course, a single θ can be always found that can reproduce the behavior of a θ selection. In the revised text we state more specifically (end of Section 3.1):

"It is obvious that for different θ distributions and/or selections, the single θ that represents best the freezing behavior of these distributions will be different."

Reviewer comment: Page 7179. Line 18. This sentence is confusing. How is increasing J with increasing DIN a test for time-independency?

Response: We agree that this sentence was somewhat confusing. We reworded it and express it more generally in Section 3.2:

"Such rapid, i.e. (nearly) time-independent freezing of all particles within a very short time scale has been interpreted as apparent singular freezing behavior ((Niedermeier et al., 2011))."

Reviewer comment: Page 7182. Line 24. Using a model that does not depend on supersaturation, even if empirical, for water-subsaturated regimes is not correct. The authors are looking at the impact of neglecting the effect of supersaturation rather than the impact of using a deterministic approach.

Response: We agree and restrict the application of Eq-12 only to conditions when $S_w > 1$ in the revised set of simulations.

Reviewer comment: Page 7182. Line 27. The described behavior results from the specific conditions and assumptions used in a single simulation and must not be generalized.

Response: We agree with the reviewer that the sentence implied a general agreement of stochastic and deterministic approaches. In the revised version, we state more carefully (end of Section 4.1.1)
"…the deterministic scheme (Eq-12), predicts similar N_{ice} to the stochastic schemes (at cloud top) under the conditions used in the current simulations."

Reviewer comment: Page 7184. Line 8. It must be mentioned that the feedback on supersaturation only affects condensation freezing. Once activated the droplets are no longer in equilibrium and the water activity is not determined by Si.

Response: In the new calculations where no ice nucleation is included for the deterministic approach when $S_w < 1$, these findings do not hold true anymore. Above the height when $S_w < 1$, only IWC further increases by the growth of existing ice particles but no additional nucleation events occur.
We never assume equilibrium in our calculations since at all saturation regimes ($S_w < 1$; $S_w \geq 1$), time-dependent equations are solved and thus the competition for water vapor between growing particles and droplets is taken into account. These competition effects are minor if $S_w < 1$ and thus sizes for deliquesced particles near their equilibrium diameters are predicted by solving the differential equation for dr_d/dt.

Reviewer comment: Page 7185. Line 8-10. These are a very narrow temperature ranges. How do they compare to observations? Would this indicate that the contact angle distributions are too narrow?

Response: It has been discussed previously that the 1θ model predicts too rapid freezing and a too narrow range of temperatures of the onset of freezing ((Eidhammer et al., 2010)). Observations indeed show a nearly continuous range of freezing temperatures (e.g., (DeMott et al., 2010).
However, while we restrict our simulations here to using the data sets derived for a single component (kaolinite), in the atmosphere it is likely that particles comprise mixtures of many

compounds and surface properties that continuously change due to processing. This variability leads to a much wider ranges of IN surface properties (contact angle distributions).

Page 7188. Line 25. It is not clear what is meant by stability in this context.

Response: In general, mixtures of supercooled droplets and ice particles are microphysically unstable due to the higher vapor pressure of ice as compared to liquid water. But yet, mixed-phase clouds are commonly observed (e.g., (Morrison et al., 2012)). Such persistent clouds are called 'stable' since both phases coexist.

Since our model is limited in terms of the myriad feedbacks that control this stability, we only simulate a single ascent of an air parcel throughout a cloud with a depth of 300 m. In simulations over longer time scales and/or multiple cloud cycles, different onset temperatures of freezing by the various nucleation schemes might translate into different ice removal processes which will affect the phase distribution in subsequent cloud cycles.

Since we refer in the same section to our previous model study ((Ervens et al., 2011)) where we discuss in detail the limitations of the parcel model in terms of the predictability of cloud lifetime, we do not add any further text here.

Reviewer comment: Page 7190. Lines 1-4 and Lines 20-25. These conclusions refer only to the specific assumptions of the simulations. For example, setting a larger maximum IN concentration would lead to stronger feedbacks and likely to larger differences in IWC between nucleation schemes.

Response: l. 1-4: The statement that the supersaturation in mixed-phase clouds is mostly determined by the condensation term (i.e. water vapor condensation on droplets) can be indeed generalized since the number concentration of droplets is always much higher than that of ice particles. As soon as ice growth becomes so efficient that the water vapor supply can only be replenished by evaporation of droplets (Bergeron-Findeisen process), the cloud will glaciate. The ice particles will precipitate leading to the demise of the cloud.

l. 20-25: While the specific ice particle sizes depend on several conditions such as temperature range (inherent growth ratio), time scale etc, the finding of similar particle sizes upon similar growth time scales is a solid conclusion. Such behavior is expected if ice growth occurs without any competition effects, i.e. under conditions when both phases coexist. We specify these conditions in the revised text. Our numerous simulations for a much wider range of conditions and parameter spaces support this conclusion ((Ervens et al., 2011)).

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