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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The Leipzig Cloud Interaction Simulator (LACIS): operating principle and theoretical studies concerning homogeneous and heterogeneous ice nucleation" *by* S. Hartmann et al.

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MAJOR COMMENTS referee # 2:

(1) From the data shown in Fig. 6 and Fig. 7 the conclusion is drawn that classical nucleation theory (CNT) together with the assumption of a constant contact angle fails to predict immersion freezing, whereas the simulated freezing behavior according to the parameterization given in Niedermeier et al. (2010) is in good agreement with

the measured data. My concern about this comparison is that I do not see the fundamental difference of these two approaches. Throughout the paper, the reader gets the impression that two different theoretical concepts of describing immersion freezing were applied, which in my opinion is not the case. Equation (11) has been derived from equation (10) by Niedermeier et al. (2010), so the basic concept in eq. (11) is the same as for CNT with a constant contact angle (or constant parameter f_{het}). To me, the major difference between the two formulations is that nucleation kinetics and some IN size information has been incorporated in the fitting parameter "a". I presume that the curves in Fig. 7 were obtained with one value for f_{het}, so I don't see why these curves are not equally based on CNT with constant IN surface properties. Therefore, comparison of Fig. 7 and Fig. 6 raises the question if the better agreement of the simulations based on the parameterization by Niedermeier et al (2010) isn't simply due to the fact that two free parameters had been used to fit eq. (11) to the measured data, whereas for the curves in Fig. 6 nucleation kinetics had to be calculated explicitly, and the IN surface area is fixed. At any rate, the authors should make the substantial difference in the description of immersion freezing by CNT with constant contact angle and by the approach in Niedermeier et al. (2010) clearer, if there is any. (2) I suppose that a conclusion from the paper (even if not stated explicitly) would be that immersion freezing should be parameterized according to the formulation in eq. (11)? In my opinion, the authors should discuss potential implications of their results to the description of immersion freezing more extensively, when they state that the model simulations were performed for the evaluation of different theoretical approaches to describe homogeneous and heterogeneous ice nucleation (page 25601, line 3). Does equation (11) well represent the physics of immersion freezing, or is the good agreement with the measured data rather due to a sufficient amount of free parameters (one of which incorporating the IN active surface area and the ice nucleation kinetics) in the fitting function? To answer this question, experiments with different particle sizes would be useful (whereas this possibly exceeds the scope of the present manuscript). I guess if the physics of immersion freezing is well represented by the model, the fit pa-

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rameter "a" in eq. (11) should just change by the increase or decrease of the IN surface.

Two different formulations are used for simulating the immersion freezing process in the model: (a) CNT assuming constant contact angle and (b) CNT-based parameterization derived in (Niedermeier et al., 2010). The referee is right about the fact that these two approaches are not fundamentally different.
In case of model approach (a), the contact angle is realized by holding the energy reduction factor f_{het} constant over the whole temperature range investigated.
Considering the second approach (b), the ice nucleation rate coefficient contains two fitting parameters: a prefactor a and the reduction factor f_{het} as also applied in version (a). In principle, the CNT-based parameterization is a simplified description following CNT. It captures the essential temperature dependence in a simple way, and it is expressed as a function of the supercooling temperature $T_s = T_0 - T$. Besides the T-dependence of the water-to-ice saturation ratio, the temperature dependence of the interfacial free energy between water and ice is also accounted for. The parameterization also includes particle surface area and the relatively uncertain kinetic aspects of the CNT in an adjustable parameter (for example, the activated complex approach used for the traditional prefactor has never been well validated, to our knowledge). This fitting parameter a contains only quantities with no or relatively weak T-dependence such as flux of water molecules to the ice embryos. Therefore, the parameterization contains the basic T-dependence inherent in CNT and the fitting parameters are constant over the T-range investigated. The fundamental difference between CNT and the developed CNT-based parameterization results from the fact that both free parameters a and f_{het} are fitted to the experimental data assuming constant temperature (equal to the wall temperature of the last section) during ice nucleation and an ice nucleation time of 1.56 s.
To delimit both model approaches, the following text is added in the manuscript: "In principle, this parameterization is a simplified description following CNT, because it captures the essential temperature dependence in a simple way. It is distinguished

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from the pure CNT approach because a prefactor, which depends on IN surface area and the theoretically uncertain activated complex lifetime and activation energy, is also left as a fitting parameter." (p.25592, l.10)
Assuming CNT with constant contact angle (model approach (a)) over the temperature range investigated, the measured temperature dependence of the ice fraction could not be reproduced, because f_{het} flattens the slope the ice fraction as function of temperature only slightly. In case of model (b), by the means of the additional fitting parameter a, which basically determines the position of the curve concerning the ordinate, the experimental results could be reproduced. In contrast to real experiments, the FLUENT/FPM simulations, even though being based on the same nucleation rate coefficient, account for the detailed temperature variation along the flow tube center line (Fig. 7). The small difference between the two data sets is indicative that the assumptions made in (Niedermeier et al., 2010) concerning both nucleation temperature and ice nucleation time are justified. For verifying the parameterization concept itself, further investigations analyzing the immersion freezing behavior as function of temperature (wider temperature range than investigated in the present paper), IN surface (varying ice nucleus sizes), IN structure and chemical composition and ice nucleation time are fundamentally necessary.
As already stated in the answer to referee 1, the following text passages are added in the manuscript: 1) "Finally, reviewing the assumptions made during the derivation of the CNT-based parameterization for immersion freezing, it was found that the assumption of constant temperature during ice nucleation and the chosen nucleation time were justified, underlining the applicability of the method to determine the fitting coefficients in the parameterization equation." (p.25578, l.25)
2) "Consequently, the method assuming constant temperature during ice nucleation and the chosen nucleation time for determining the fitting coefficients in the CNT-based parameterization equation are justified and valid. For verifying the parameterization concept itself, further investigations analyzing the immersion freezing behavior as function of temperature (wider temperature range than investigated in the present

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paper), IN surface (varying ice nucleus sizes), IN structure and chemical composition and ice nucleation time are fundamentally necessary." (p.25600, l. 10 et seq.)
3) "Finally, reviewing the assumptions concerning constant temperature and ice nucleation time made in Niedermeier et al. (2010) when deriving a CNT-based parameterization for the nucleation rate coefficient in the immersion freezing mode, the good agreement between parameterization and simulation results shows that both assumptions were justified. This underlines the applicability of the method to determine the fitting coefficients in the CNT-based parameterization equation." (p.25601, l.26 et seq.)

MINOR POINTS:

p.25587, l.23: I appreciate the detailed description of the numerical model. However, equations (4) and (5) are difficult to understand without further explanation.

The following changes are made in the text: "The energy equation for an air-vapor mixture includes heat transport due to conduction (first term and first part of the second term Eq. 5) and vapor transport accounting for the Dufour effect (second part of second term Eq. 5). This is expressed as (p.25587, l.22-23) "
and "Hence Eq. 2 and Eq. 4 are coupled via mass transfer due to phase transition processes and resulting release/consumption of energy ($S_\mathrm{h} = L_i S_\mathrm{v}$ with L_i being either the latent heat of vaporization or fusion) on the one hand and on the other hand due to mass flux of water vapor."(p. 2588, l. 4-5)

p.25589, l.15: I would mention that this calculation of S_{hom} relies on the assumption that each nucleation event leads to one additional frozen droplet, which is justified as long as the droplet volume is small enough.

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The following text is added in the manuscript: “Thereby it is assumed that each ice nucleation event leads to an additional frozen droplet of the population. In case the number of ice nucleation events is equal to or exceeds the droplet population number within a time interval the droplet population will freeze instantaneously.” (p.25589, l.17)

p.25592, l.16: The term "thermodynamic effects" should be explained more precisely. Actually f_{het} describes the reduction of the nucleation energy barrier by the IN surface, i.e. the influence of the IN surface on thermodynamics.

As recommended “thermodynamic effects” is replaced with “i.e. the influence of the IN surface on thermodynamics” (p.25592, l.16).

p.25594, l.15: It has been stated on p. 25585, l. 18 that supersaturation in LACIS establishes due to the coupled water and heat diffusion which occur at a slightly different rate. To my knowledge the diffusivity of water is higher than the one of temperature, therefore one might raise the question why subsaturation does not establish rather than supersaturation upon cooling of the air in LACIS (in a water-based CPC, supersaturation is established with a transition from cold to warm temperatures). I suppose that the influence of the absolute temperature and water vapor gradients prevailing in the chamber on saturation profile in LACIS is at least as important as the diffusion constants of water vapor and temperature. As the saturation profile in LACIS is of high importance for the droplet activation process, it would be beneficial to discuss the influence of diffusivities and the temperature and water vapor gradients on the resulting saturation profile a bit more. E.g. are the flow velocity and the tube diameter crucial to the formation of supersaturation?

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A detailed discussion of the coupled heat and mass transfer processes can be found in (Stratmann et al., 2004). The reason why the system supersaturates with respect to water, despite the Lewis number (ratio of thermal diffusivity to mass diffusivity) being smaller than 1, can be found in the non-linearity of the vapor pressure curve. In this context, flow velocities are of secondary importance, it's the temperature difference that matters. Following sentence is modified in the paper: "With higher inlet dew point temperature compared to the wall temperature, supersaturation can be achieved as a result of the simultaneous heat and vapor diffusion, which occur at slightly different rates, because of the non-linearity of the water vapor pressure curve." (p.25585, l.17-19)

p.25595, l.6: I suppose the critical supersaturation refers to Koehler activation of the seed particles? How is CCN activation treated for pure mineral dust particles?

The hygroscopic growth and the droplet activation of the seed particles is described by the Koehler theory in the model. During FROST measurement campaign it was found, that the mineral dust particles are not completely insoluble but have a small amount of soluble material on their surface. Consequently the ATD particles activate at lower supersaturations than predicted by Koehler theory assuming an insoluble mineral dust core (only Kelvin term $a_w = 1$). In order to account for this effect an equivalent ammonium sulfate coating (mass fraction of 0.019 internally mixed with the mineral dust) is assumed. This is already described in the present paper: "When studying homogeneous and heterogeneous ice nucleation, IN were assumed to be spherical with diameters of 187 or 300 nm, internally mixed consisting of an insoluble ATD core and a small amount (mass fraction of 0.019) of ammonium sulfate. The latter was done to reproduce the activation behavior observed in CCN measurements during the FROST campaign." (p.25593, l.17-21).
The single particle growth law according to (Barrett and Clement, 1988) (Eq. 6)

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contains the Koehler equation accounting for Kelvin and Raoult effect. This information is already given in the manuscript: “For the description of the dynamic growth of water droplets and ice particles, the single particle growth law according to Barrett and Clement (1988) is used for the droplets and ice particles ... S_i and $S_{i,j}$ describe the saturation ratios in the gas phase and over the particle surface, whereby Kelvin and Raoult effects are accounted for.” (p. 25589, l.3) To elucidate that the Koehler equation is meant, the parenthetical remark “(Koehler equation)” is inserted. (p. 25589, l.3)

p.25595, l.18: I find it difficult to conclude from the model simulation that immersion freezing is the only ice nucleation process happening at the given conditions, since the heterogeneous ice nucleation rate coefficient implemented in the model only contains the formulation for immersion freezing.

The referee is correct that from the modeling results alone it cannot be concluded that immersion freezing is the only ice nucleation process happening. However in (Niedermeier et al., 2010) a discussion concerning the importance of the different freezing processes can be found: “The question arises, which freezing modes occur when running LACIS as described above. ... To test if deposition nucleation occurred inside the tube, specific two-section measurements were performed wherein LACIS was operated in the water subsaturated and ice supersaturated mode. These additional experiments were carried out for two different inlet dew-points (265.95 K and 260.15 K) to detect possible deposition nucleation in two different temperature intervals (from $T_S = 28$ K to 30 K for dewpoint of 265.95 K and from $T_S = 36$ K to 38 K for dew-point of 260.15 K, see Fig. 7). For the lower T_S interval no deposition nucleation was observable. For the higher T_S interval deposition nucleation was detectable but the counted number of ice crystals was so low that deposition nucleation can be neglected for the FROST measurements. Evaporation freezing could occur as the droplets generated in LACIS evaporate due to the Wegener-Bergeron- Findeisen

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effect. However, the one-section measurements clearly show that liquid droplets and ice crystals coexist. Because the droplet size distribution is narrow, the ice particles are most likely not formed by evaporation freezing (and also not through a condensation freezing process). In other words the ice formation observed must be due to the process of immersion freezing. In addition, the smooth ice fraction behavior determined from the two-section measurements for T_S between 34 K and 37.5 K is suggestive for the occurrence of a single heterogenous freezing mode, namely immersion freezing." (p.3609, last paragraph left column - second to last paragraph right column) We added the following sentence to the text: "This supports the observations presented and discussed in (Niedermeier et al., 2010), suggesting that immersion freezing is the dominant ice nucleation mechanism." (p.25595, l.19)

p.25597, l.28: What is the reason why the numerical model might slightly overpredict the droplet volume?

There are multiple reasons why the numerical model slightly overpredicts the droplet sizes. A thorough discussion of these reasons is far beyond the scope of this paper. One possible reason is uncertainty in the boundary condition description, mainly at the tube wall boundaries. This together with the fact, that the comparison between theoretical and experimental results can be considered very good, led us to the decision to remove the sentence from the manuscript. (p.25597, l.27-28 - p.25598, l.1)

p.25598, l.24: I am not very comfortable with the term "singular model" in connection with a model involving a nucleation rate. Although I am aware that Marcolli et al. (2007) also used the term "singular" for a model assuming a contact angle distribution, my understanding of the singular hypothesis is that freezing is deterministic. Any formulation involving a nucleation rate coefficient, however, remains stochastic in nature, irrespective of the assumptions made concerning the IN surface.

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The formulation “singular model” was basically chosen to apply a similar terminology as done in Marcolli et al. (2007). We consider both model types as stochastic-singular models, because the stochastic nature is described by the nucleation rate and the singular behavior is considered in accounting for contact angle or active site distribution where one contact angle or one active site is most effective and therefore it determines the freezing of the whole system (deterministic). We changed the sentence to “Simulations assuming a stochastic-singular model with contact angle distribution, where the contact angles vary between the particles considered, or accounting for a distribution of active sites led also to better agreement.” (p. 25598, l.24) Recently, a stochastic model with singular behavior based on the model of (Marcolli et al., 2007) is further developed and interpreted by our group and gives more insight into this topic (Niedermeier et al., 2011).

p.25599, l.24: Would not CNT already predict the temperature dependence of the nucleation rate to be different for homogeneous and heterogeneous freezing? The derivative of the nucleation rate coefficient with respect to temperature is proportional to the energy barrier, which is considerably lower in the heterogeneous case. Therefore one should expect the homogeneous nucleation rate to increase at a stronger rate with decreasing temperature than the heterogeneous nucleation rate.

Indeed, as to be seen from Fig. 6, homogeneous and heterogeneous ice nucleation rates according to CNT feature slightly different temperature dependencies (for homogeneous ice nucleation: blue line and for the heterogeneous case gray lines in Fig. 6). However these different dependencies are not sufficient to explain the experimental findings. Nothing changed in the text.

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p.25600, l.10: This is too general a statement. The agreement between the orange and the red curve in Fig. 7 justifies the assumption concerning the constant freezing temperature and the freezing time. However, I don't see how the method of determining the fitting coefficients can be justified with this.

The authors agree with the referee concerning this point. For changes in the text, please refer to major points.

Technical comments:

p.25580, l.23: At this point, the meaning of "nucleation time" is not really clear to the reader.

It isn't clear to the authors what is being referred to.

p.25582, l.13: "atmospherically" instead of "atmospherical"

This is modified in the text.

p.25582, l.17: "electrical" instead of "electric"

This is modified in the text.

p.25592, l.20: I guess the fitting parameter "a" should have the units per second per square meter.

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The fitting parameter "a" has the unit s_{-1}. This is changed in the text.(p.25592, l.20)

p.25599, l.5: The structure of the sentence does not make sense.

The sentence is modified to: "Similar to Fig. 6, Fig. 7 depicts ice fractions as a function of temperature with the experimental data (orange and black squares) being identical in both figures." (p.25599, l.5)

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