

Reviews for Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-969, 2016.

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We thank both anonymous reviewers and P. A. Alpert for their positive review and the detailed comments on the manuscript. We have revised the manuscript accordingly (see track-changes in the manuscript). Our replies to your comments are given below in blue after the specific comment.

1 Review 1

5 1.1 General comment:

In order to find an appropriate (CNT-based) parameterization for immersion freezing (induced by mineral dusts) in GCMs, the authors tested various combinations of different descriptions for interfacial free energy σ_w , activation energy $\Delta g^\#$ as well as different possibilities to include contact angle (single contact angle, contact angle distribution and temperature dependent contact angle). To do so, the different schemes are fitted against laboratory heterogeneous freezing data for different dusts
10 (spanning several temperature, particle surface and time ranges).

I have to admit that after first reading I have been in two minds about recommending this paper for publication in ACP. On the one hand the authors e.g. vividly demonstrate that contact angle values gained for one substance largely depend on the values/parameterizations used for σ_w and $\Delta g^\#$ so that contact angle values obtained in different studies for a given substance do not necessarily agree. This is important if these contact angle values are used in GCMs but connected with other σ_w and $\Delta g^\#$
15 values/parameterizations. On the other hand e.g. I doubt the physics behind some of the presented parameterization schemes (see specific comments). However, due to the importance for the heterogeneous ice nucleation community I would recommend this paper for publication after the following comments have been addressed.

We attempt to clarify the physics behind some of the presented parameterization schemes below. However, the microphysical details how freezing of supercooled water is triggered heterogeneously are not very well understood so that some approaches
20 are based on speculative assumptions. It is not the aim of this article to judge how reasonable the assumptions are, but to show different strategies to handle heterogeneous freezing with CNT based parametrizations and to investigate how well these parameterizations describe a selection of laboratory data.

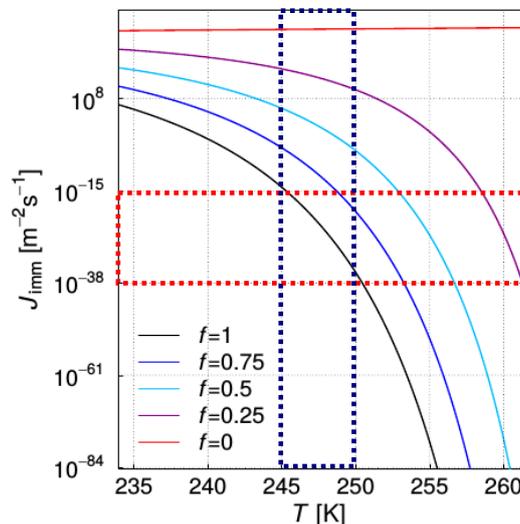
1.2 Specific comments:

Page 1, line 10-11: I do not understand the meaning of the sentence starting with “We show that additional...”. Please clarify. What is “ J_{imm} ”?

We changed that in the manuscript. We also added an explanation for J_{imm} .

- 5 Page 4, line 12-13: I agree that in case of heterogeneous ice nucleation the freezing curve is shifted to higher T compared to the homogeneous case. But does the curve necessarily has to be less steep? Looking on Fig. A3 in the paper of Hoose and Möhler (2012) it can be seen that the heterogeneous nucleation rate is steeper for higher temperatures (depending on the parameterizations used in CNT). So what causes the heterogeneous freezing curve to be less steep compared to the homogeneous case?
- 10 The temperature dependence of the nucleation rate J_{imm} (or J_{hom}) is controlled by the temperature dependence of the Gibbs free energy barrier ΔG and the activation energy barrier Δg^\ddagger , which have opposite temperature dependences. In the case of immersion freezing ΔG is reduced and therefore the contribution of Δg^\ddagger is more important, which leads to a flattening of the heterogeneous nucleation curve compared to homogeneous nucleation. Looking at measurements of the frozen fraction as a function of T (homogeneous freezing compared to immersion freezing) one can see that indeed the curves for immersion
- 15 freezing are less steep compared to homogeneous freezing.

Evaluating the steepness of different curves relative to each other is also a matter of perspective. Looking at the figure below it can be seen that when comparing the curves within the red box, the steepness increases with decreasing f (hom. freezing vs. het. freezing). Looking at the curves within the same temperature range (blue box), however, the steepness of the curve decreases in case of heterogeneous freezing. The second case is the situation we were referring to. We added a better explanation in the manuscript.



Chapter 2.1.3: I have a problem with the interpretation of the temperature dependent contact angle scheme. In a physical sense the contact angle is "determined by the condition of mechanical equilibrium, i.e., there must be no net force component along the solid surface" (Pruppacher and Klett, 1997, P. 136). Due to the decrease of the interfacial free energies with temperature does the contact angle then should decrease with decreasing temperature for a given particle (let's assume homogeneous surface conditions)? Here, the contact angle increases with decreasing T. I would interpret this behavior in that way that particles with larger contact angles (higher energy barrier) can be activated with decreasing temperature. Is this in agreement to your description?

Yes, this is in agreement. The $\alpha(T)$ scheme accounts for the change of the contact angles being activated at different T resulting in a shift of the contact angle distribution towards larger average contact angle with supercooling. The lower the temperature, the higher the chance that particles with larger contact angles can be activated. We clarified that in the text.

Chapter 3.1: I have some trouble with those schemes fitting $\Delta g^\#$. In lines 27 to 30 you mention that an aerosol type specific $\Delta g^\#$ value is physically questionable. On the other hand this statement is reversed on the next page saying that the particle itself might influence the diffusion of water molecules to the ice cluster. I agree that the attachment of water molecules to the ice cluster is influenced due to the presence of the ice nucleating particle i.e., the INP "blocks" water molecules since the ice cluster is just a cap and not spherical (in terms of CNT) as for the homogeneous case. But I think that n_s in CNT takes care of this. Are there any mechanisms which could confirm your hypothesis of aerosol-type specific $\Delta g^\#$? Is there a specific term in CNT which would take care of this? Or does $\Delta g^\#$ represent here just a fitting parameter without physical meaning?

n_s is the number of water molecules in contact with the unit area of an ice germ and is mostly estimated based on the molecular density of water. The activation energy $\Delta g^\#$ describes the diffusion of a water molecule across the water-ice boundary. Most authors assume that this diffusion process for immersion freezing is equivalent to the one for homogeneous freezing. In case of heterogeneous freezing the diffusion could be disturbed by the presence of IN in the water (surface charges, polarizability of the particle surface, etc.). Our hypothesis is that the activation energy $\Delta g^\#$ is different within a pure supercooled water droplet compared to a supercooled water droplet containing an insoluble aerosol particle (IN), because the IN (eventually containing surface charges) effects the hydrogen bond network and due to that could influence the diffusion process. One example study looking at the influence of surface charge on ice nucleation is the study of Edwards and Evans (1962). We added this reference.

On page 8, line 19-20 you mention that a single contact angle is not able to represent the experimental results for mineral dust. This has also been shown in e.g. Lüönd et al. (2010), Welti et al. (2012), etc. But is this a general finding? What about other substances like biological particles?

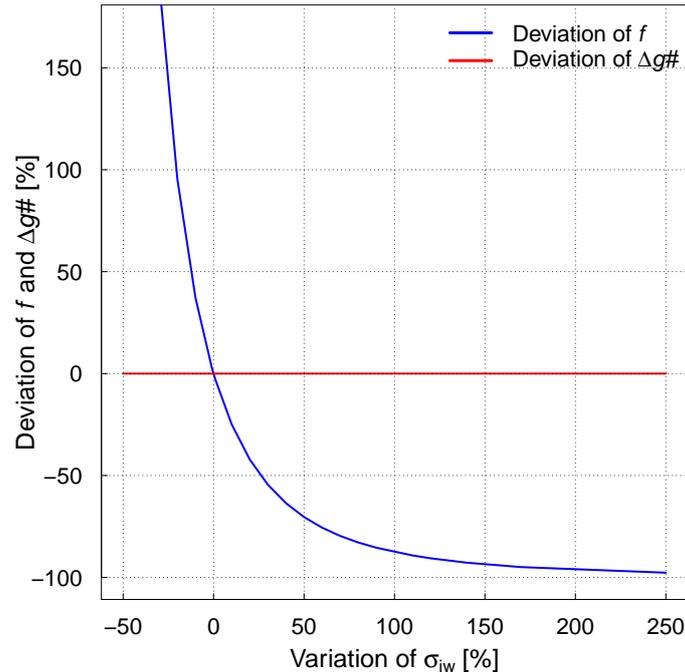
We only investigated the behavior of a single contact angle to describe heterogeneous freezing of mineral dust. We did not look at biological particles, therefore we can not make a general statement about the ability of a single contact angle to parameterize their freezing. Also ice nucleation by AgI seems to be captured by a single alpha. Possibly a single alpha scheme can be used for highly efficient IN triggering ice formation at low supercooling.

Page 9, line 18-20: I do not understand why this procedure has been performed. Some further explanations here would be great.

This exercise was done to exemplary show the consequence of using fit parameters together with a CNT formulation, which was not the one used to derive the fit parameters. We included an additional explanation to make this clearer.

5 Page 10, line 26-27: The curve in Fig. 4a does not approach -100%...

We only show the part of the curve where changes are large. The plot with an increased range is added below.



Page 10, line 30: It looks like that the compensation in Fig. 4b is not completely linear.

Thanks for recognizing this, we did not see that at the first glance. While the deviation of μ with variation of $\Delta g^\#$ is linear, the deviation of σ is linear for a small variation of $\Delta g^\#$ (until 30% approximately), but is nonlinear for larger variations of $\Delta g^\#$. We adapted the text accordingly.

Chapter 6 and Appendix C (especially Fig. 9), concerning particle size dependence: Do you know the reason for the change of the contact angle distribution with particle size for the kaolinite sample? In general, does the ice nucleation ability of a given substance has to scale with particle size? How pure is the used kaolinite sample as well as the other samples and is it possible that the chemical composition of the samples change with size and therefore the ice nucleating ability? Is there any bias in the measured frozen fractions due to multiple charged and therefore larger particles? A recent paper by Hartmann et al. (2016)

shows that due to commonly used particle generation methods multiple charged particles (they also used a FLUKA kaolinite sample in their study) can be present which bias the determined frozen fraction.

No, we do not know for sure the reason for the change of the contact angle distribution. In general we think that it is not unlikely that the ice nucleation ability of a given substance changes with size- that can also be seen in the active sites scheme, where an increase in size of the IN increases the chance that this IN contains an active site to trigger freezing at a specific temperature. From Fig. 9 one can thus conclude that an increase in size of the IN leads to a wider spread of possible contact angles (wider alpha-pdf distribution) and to a shift to smaller contact angles with size (because the chance to have a small contact angle increases).

For solid IN, the larger the surface area the higher the freezing temperature. This is generally the case but the change in freezing temperature with size depends logarithmic on the surface area and therefore approaches a constant temperature.

The used kaolinite sample was relatively pure, the contamination was less than 10%. Such a low contamination does not show any effect on the measurement and is negligible. We can not answer the question if the contamination level significantly changed with size.

The size selection was done with caution to prevent multiple charges. An elaborate size selection setup was used: a cascade of impactors and cyclones to reduce the amount of large particles after aerosol generation and neutralize the particles by impactions of ions followed by size selection with a Differential Mass Analyzer (DMA). However, multiple charges exist in the smaller size range (mainly 100 and 200 nm). The larger the particle the less they are effected by multiple charges. At a later state a CPMA was additionally included in the setup to make sure that no multiple charges exist. The mentioned updated setup was used for the microcline measurements presented in this paper.

The multiple charges were estimated for the kaolinite sample (Lüönd et al. 2012?). Correcting the size accordingly and refitting the dataset shows that the uncertainty due to multiple charges is not significant. The new curves lie within the error-range of the data points. Only for the 100 and 200 nm dataset there is some deviation from the original curve.

Conclusions: I am wondering why the alpha-pdf scheme is worse compared to the other two schemes when trying to represent the measured frozen fractions as a function of temperature for the various dusts and dust sizes. But in contrast, the time dependence of freezing can only be reasonably represented by the alpha-pdf scheme. In the latter case this was shown for a given dust (kaolinite) and one size only. The questions arises again: Is there an influence of size dependent composition or multiple charged particles (see comment above) which bias the fitting as a function of T and size?

Since we only have size and time dependent measurements in case of kaolinite, it is difficult to say that the alpha-pdf scheme is in general worse than the two others. However, the reason that the formulas give better fit results in the other two cases could be only mathematical. The effect of multiple charges is negligible for the results (see answer above).

In general, the conclusion is too vague. From my point of view, this study is a good contribution in order to find appropriate parameterizations based on CNT for GCMs. But I would suggest to clearly state the limits of parameterizing the immersion freezing behavior of mineral dusts due to e.g., limited amount of data available, bias due to possible multiple charges/size-

dependent particle composition issues, etc. and that further experimental studies as a function of temperature and time are needed (only one sentence, the last one on page 15, is not sufficient).

Thanks for pointing this out. We emphasized the limits/lack of experimental studies more in the conclusion.

Appendix: In general, there is no warm or cold temperature. The temperature can only be high or low. In some cases, plots/tables are shown based on f , others are based on contact angle α . It is difficult to directly inter-compare the results. Could you please refer to only one parameter or both f and α ?

Indeed, thanks, this is corrected. The reason for showing sometimes f , sometimes α on the plots/tables is that the fit parameter itself is different in the different cases. It is possible to convert f to α using Eq. 3. We added the converted/approximated values of f to make a comparison easier.

10 1.3 Technical notes:

Page 9, line 4: the schemes are mixed up here: CNT #7 is the $\alpha(T)$ scheme and CNT #5 and #6 are the α -pdf schemes.

This is corrected.

Page 12, line 18: Should it read "..., which was found to not represent...?"

Yes, thanks.

15 Page 15, line 6: "have been compiled" instead of "are compiled"?

Done.

In the upper left plots of Fig. 7 and 8 the highest temperature value (i.e., 260 K) is truncated.

Thanks for pointing that out, that is fine now.

Figure 8, lower right panel: The mean freezing temperature is about 237 K. Does this "agree" with the high mean contact angle of 0.3?

There was a mistake in the plotting script for Fig. 7 and 8, thanks for noticing. We corrected it. Additionally we changed the values for the fixed variables (like μ) to values, which are closer to the resulting fit parameters from Table 3. The mean freezing temperature for the α -pdf scheme when using a mean contact angle of 0.5 (Fig. 8 lower panel) is approximately 239 K. That goes along with Fig. 5 (fits and measurement points for kaolinite).

25 Caption of Fig. 8: There is a "decreasing" missing in the sentence starting with: "contact angle gets larger with decreasing T because...".

Yes, thanks.

On page 33, line 5-6. There is the verb missing in the sentence "... FF is fitted or the active site density directly."

This is corrected, thanks.

Fig. 11: The color coding is less than ideal. It is difficult to see which of the lines correspond to which study.

The colors are changed now.

1.4 References:

- 5 Hartmann, S., Wex, H., Clauss, T., Augustin-Bauditz, S., Niedermeier, D., Rösch, M., and Stratmann, F. (2016), Immersion Freezing of Kaolinite: Scaling with Particle Surface Area, *J. Atmos. Sci.*, 73(1), 263-278.
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10 kaolinite particles in the immersion mode, *J. Geophys. Res. – Atmos.*, 115(D14).
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Welti, A., Lüönd, F., Kanji, Z. A., Stetzer, O., and Lohmann, U. (2012), Time dependence of immersion freezing: an experimental study on size selected kaolinite particles, *Atmos. Chem. Phys.*, 12(20), 9893-9907.

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Edwards, G. R. and Evans, L. F.: Effect of surface charge on ice nucleation by silver iodide, *Trans. Faraday Soc.*, 58, 1649–1655, 1962.