

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

Ickes Luisa^{1*}, Welti André¹⁺, and Lohmann Ulrike¹

¹IAC, ETH Zurich

*now at: IMK-AAF, KIT Karlsruhe

+now at: TROPOS Leipzig

Correspondence to: Luisa Ickes (luisa.ickes@env.ethz.ch)

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 2

5 The authors do a thorough examination of different possible ways of fitting the classical nucleation theory to immersion freezing experiments using various formulations for parameters of the theory. They compare the outcomes using three criteria: 1) How well each CNT formulation reproduces the experimental freezing curves; 2) How good are the size and time dependences of each formulation compared with experimental data (if available)? and 3) Are the values of the fit parameters microphysically reasonable? I believe that this is a useful paper that should eventually be published: at the moment CNT is the only theoretically
10 based approach that can be used as a basis for parametrizing immersion freezing for global models, and this paper provides valuable information for constructing such parametrizations. At the same time it should be kept in mind that CNT is by no means perfect.

I have really just one major comment. The authors make the following statement in the Conclusions: "Criterion 3 is difficult to evaluate coming from a macroscopic level as microphysical knowledge is missing at this point". I don't think the situation
15 is quite that bad. There is information available in the literature that can help at least discuss whether the contact angle distributions are physically reasonable, or consistent with information gained from other studies.

First, there are molecular dynamics papers that have investigated water (both liquid and ice) especially at kaolinite surfaces (e.g. Hu and Michaelidis, Surface Science 601, 5378, 2007; *ibid*, 602, 960, 2008; Croteau et al., J.Phys. Chem A, 114, 8396, 2010; Solc et al., Geoderma 169, 47, 2011). Please check these and discuss how realistic the contact angle distributions derived
20 in your study are.

We read the mentioned studies with great interest. However, only in Solč et al. 2011 a microscopic contact angle was calculated, which we could compare to our results. The derived contact angle is about 105° (that is equivalent to a geometric term f of 0.69). However, there are many assumptions needed to calculate the microscopic contact angle. Probably more

simulations and a more detailed comparison is needed in future. We added some more information about molecular dynamics paper and recent investigations in the text.

Secondly, there are observations of freezing microdroplets at different hydrophobic surfaces indicating that the contact angle does not change when freezing occurs (Jung et al., Langmuir 27, 3059, 2011; Heydari et al., J. Phys. Chem. C, 117, 21752, 2013). This information can be used in the context of Young equations. If you write down Young equations for contact angles of 1) a water cluster on a surface S, 2) an ice cluster on S (against air) and 3) an ice cluster on S, immersed in water, you can figure out what the contact angle of ice immersed in water should be if the contact angle of liquid water on the same surface is known (literature values of water contact angles can be found many minerals).

We are not sure if we understood the suggestion correctly. We used the Young equation for immersion freezing ($\cos(\alpha) = \frac{\sigma_{sw} - \sigma_{si}}{\sigma_{iw}}$; index s stands for surface (aerosol), i for ice and w for water) to calculate the interfacial tension between a surface (aerosol) and ice for kaolinite (Young, 1805). We got values of approx. 58 mJ/m² at 243 K increasing by approx. 0.2 mJ/m²/K with decreasing temperature. Similar results were already discussed by Welti et al. (2012). Because of that and since the different contact angles coming from different contact angle schemes yield approximately the same results, we do not see much value in adding this information or discussion to the paper.

Thirdly, one can make the following question (this time disregarding the assumption of equal contact angles for water and ice): Are the results in this work (i.e. contact angles of ice immersed in water) consistent (again, in the context of Young equations) with ice contact angles derived from deposition nucleation studies? This question should be answerable with the help of the different interfacial tensions used (water, ice, ice in water) and water contact angles. I suggest that you do these two exercises with the Young equations and discuss.

We calculated the contact angle for deposition nucleation from the different contact angles for immersion freezing using the following formula:

$$\cos(\alpha_{\text{dep}}) = \frac{\cos(\alpha_{\text{imm}})\sigma_{iw} + \sigma_{sv} - \sigma_{sw}}{\sigma_{vi}}.$$

For kaolinite the calculated contact angle for deposition freezing at 243 K is approx. 20°.

1.1 Minor:

– Contact angle values in Tables 3 and 5 don't seem consistent with the contact angle distributions in Fig. 9. Should the radian values be multiplied by π ? However, even in that case, the μ -values in Fig. 10 appear a bit strange: they are mostly below 90 degrees, although the modes of the distributions in Fig. 9 are all above 90 degrees, and the distributions appear to be skewed right. How come?

Thank you for spotting this. We phrased it wrongly what μ is and the illustration in Fig. 1 was also not correct. We wrote μ is the mean contact angle, but since it is a log-normal distribution μ is the ln of the mean contact angle instead. If you exponentiate μ and then multiply it with 180° and divide it by π you end up with the values plotted in Fig. 10. We changed the explanation for μ and adapted the illustration in Fig. 1.

The curves in Fig. 10 are fully symmetric and not skewed- maybe you got this impression because the x-axis is chosen such that the purple distribution (920 nm) is cut?

- What happened to Appendix A?

We are not sure if we understand that question. Appendix A can be found on page 26 and 27 (27 and 28 in the revised version; Fig. 7 and 8). We changed the references in the text directly referring to the figures.

- The order of Figs. 9 and 10 should be changed

Done, thanks.

- The English of the ms should be checked.

We thoroughly checked the language again and hope that the manuscript reads better now.

References

- Welti, A., Lüönd, F., Kanji, Z. A., Stetzer, O., and Lohmann, U.: Time dependence of immersion freezing, *Atmos. Chem. Phys.*, 12, 9893–9907, 2012.
- Young, T.: An essay on the cohesion of fluids, *Philos. Trans. R. Soc.*, 95, 65–87, 1805.