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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Analysis of the effect of water activity on ice formation using a new thermodynamic framework" *by* D. Barahona

Anonymous Referee #1

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This manuscript introduces a new framework within classical nucleation theory (CNT) to describe homogeneous ice nucleation from a supercooled liquid and its dependence on water activity. The novel approach is to eliminate the interfacial tension between ice and liquid phase and replacing it with a new concept of an interface that is assumed to be made of liquid molecules "trapped" by the solid matrix. The resulting equations describing germ size and nucleation work are dependent on temperature and water activity. Finally, this approach allows a phenomenological derivation of the established water activity based homogeneous ice nucleation model.

General comments:

This manuscript presents a novel concept of introducing the water activity dependency

within the general expressions of CNT. This is a neat idea and definitely worth publishing. However, I find places where more care is needed to discriminate between the definitions of theory, framework, approaches, and concepts. Furthermore, I feel some statements, not affecting the main conclusions, are incorrect/misleading and have to be revised. Though, my general and specific comments should be addressed by the author, overall I am in favor of publishing this study.

It should be made much clearer that this new approach/framework/concept is a novel extension of CNT. In principle, the derivation follows exactly CNT ending with similar equations and terms (nucleation rate, Gibbs free energy etc.) except that the energy for making an interface between the ice and surrounding liquid has been modified by a potentially better model. However, this new model of the interface has similar weaknesses as the capillary approximation of CNT. For example, can the Gibbs interfacial model be indeed applied to a cluster of a few molecules in size that makes the critical ice germ? I am not disagreeing with this new concept, in fact I like it, but also in this case one has to wonder if the physics of a "bulk interface" are the same as for a tiny molecular cluster. This is the same issue with assuming that bulk parameters describing the ice-water interface can be applied to the critical ice germ. I think this caveat should be mentioned and I feel this does not render the conclusions of this study.

Specific comments:

p. 1526, l. 9: Change "theory" with "approach".

p. 1528, l. 22: References: Wang and Knopf did not study homogeneous ice nucleation. The better choices would be: Knopf and Lopez, PCCP, 2009 and Alpert et al., ACP, 2011.

p. 1529, l. 4: Define "K00".

p. 1529, l. 2-6: "However in these studies σ_{iw} is typically modified to adjust CNT to K00, and the results obtained in this way are not independent of Koop et al. (2000)

data. In fact, Koop et al. (2000) suggested that CNT and K00 can be reconciled if σ_{iw} is allowed to vary with aw (also shown by Alpert et al., 2011) although no theoretical support was provided for it."

These statements are misleading do not accurately reflect the work of K00 nor does it support the author's work. K00 is based on several independent measurements and since then, many other studies have reproduced and supported the K00 approach. Homogeneous freezing data can be expressed by either the K00 approach or by CNT when interfacial tension is dependent on water activity. Clearly, both approaches are independent of each other even so they are based off of the same theory. The observed temperature or aw trend of freezing data suggest to modify CNT, not K00. It is very obvious that when allowing interfacial tension to be dependent on aw that CNT can reproduce the data as shown in Alpert et al., PCCP, 2011. No one would expect that the interfacial tension between ice and water is the same as for ice and an aqueous organic or inorganic solution. This is similar to the difference of interfacial tension between water and air and an aqueous solution and air.

While K00 did not give a framework for σ_{iw}, it is clear that theory exists to describe the change in surface tension, for example the Gibbs-Thomson equation recently reviewed by Kaptay, J. Nanosci. Nanotech. (2011). In fact, this manuscript does not give any new theoretical framework for σ_{iw} either, as the authors' approach makes only an assumption that there exists an "interfacial phase" and follows CNT closely. While this assumption may be supported by other work as nicely detailed and reviewed in the manuscript, no "theoretical support" is given by the author. At best, both this study and K00 suggest that σ_{iw} should vary with aw. For these reasons, these sentences should be altered as follows.

"However in these studies σ_{iw} is typically modified to adjust CNT to K00. In fact, Koop et al. (2000) suggested that CNT and K00 can be reconciled if σ_{iw} is allowed to vary with aw (also shown by Alpert et al., 2011)."

p. 1529, l. 19-21: "In this work a new theoretical approach is proposed to describe ice formation by homogeneous nucleation. The new model relies on a novel picture of the solid-liquid transition placing emphasis on the entropy changes across the interface." With regard to the general comments, this should be reworded to, e.g. "In this work a new approach to CNT is proposed to describe ice formation by homogeneous nucleation, which relies on a novel picture...".

p. 1533, l. 15: The factor 1.46 is reported from an older study. The results will crucially depend on this factor which is in the exponent and raised to the 3rd power. So, small variation will have a significant effect on the Gibbs free energy. It would be very beneficial to show how J_{hom}, n^* etc. depend on variation of this factor. A sensitivity analysis could be conducted.

p. 1535, l. 6: The G_{act} term should be better explained at this point in the manuscript. This term is discussed at several later places in the manuscript and only there one gets an idea what is meant by this term and why it is different from derived G_{nuc}. I recommend to elaborate here and save space at the places of discussion below. Also, the studies e.g. by Zobrist et al., 2007, Alpert et al., 2011, Knopf and Forrester, 2011 explicitly treat G_{act}.

p. 1536, l. 23: "...although no parameterization was reported." If I understand the paper by Alpert et al. (2011) correctly, J_{hom} is taken from K00 and using parameterizations of Zobrist et al. (2007), σ_{iw} can be determined analytically. Therefore, no parameterization is needed to be reported as it could be found from previous studies. The author should remove this statement.

p. 1536, l. 24: "...shows reasonable agreement." J_{hom} depends very strongly on σ_{iw} and so agreement between Eq. 27 and results by Alpert et al. should be quantified and not vaguely described as reasonable. Even if σ_{iw} differs by a few percent, this may cause changes in J_{hom} by orders of magnitude. Also here and later on, it seems K00 is applied to values outside suggested water activity criterion range. So, some of the comparison may not be appropriate/fair.

p. 1537, 1st paragraph: If the author could perform a sensitivity analysis on applied parameters, this would elevate the quality of this manuscript.

p. 1537-1538: Discussion of Murray et al. and Riechers et al. data: Riechers et al. have a unique dynamic temperature calibration. It very likely represents a very accurate J_{hom} measurement in terms of temperature. The study by Knopf and Rigg group achieves similar values and thus corroborate Riechers et al. If one would have to bet on the best value, it will most likely be Riechers et al. Also Riechers et al. do not predict any J_{hom}, they determine it experimentally. Thus, please omit "although no independent works have corroborated their conclusions." A lower J_{hom} for pure water would also shift the K00 freezing line accordingly.

p. 1537-1538: Be consistent in using R13 or Riechers et al. (2013) here and in the whole manuscript. I suggest to write it out in the text. Figure legend can be different.

p. 1538, l. 4 and following until end of page: First, K00 can only be applied to maximum J_{hom} rates of about $10^{18} cm^{-3} s^{-1}$ as stated in their publication. Any extrapolation beyond this is a false representation as K00 only applies to a defined range of Δaw values. If this is appropriately represented then there is much less deviation between formulations. Also, the temperature and water activity range of the results using this new approach has to be discussed as well (see comments above on uncertainties). K00 is based on independent experiments whereas this framework is not based on experiments. So, comparison and discussion of Fig. 2 as done, I feel, may not be appropriate.

p. 1538, l. 14-29: The discussion of experiments and frozen fractions is not correct. The experiments end when all droplets have frozen, i.e. f=1. Of course, f>1 is impossible. Therefore, I assume, for regions of f>1, it is meant a lower temperature and corresponding higher J_{hom}? To observe J_{hom} at lower temperatures, much smaller droplets have to be applied, which then freeze at lower temperatures and higher J_{hom}

values. Homogeneous ice nucleation studies performed as a function of water activity are performed at atmospherically relevant temperature ranges and thus ranges in J_{hom}. Therefore, it is not necessary to extrapolate to higher J_{hom} from the experimentally derived data. There seems to be a misconception of how the experiments are conducted and analyzed. Furthermore, K00 is falsely represented, yet again, as the parameterization is extended up to $10^{36} cm^{-3} s^{-1}$ when limits are directly stated in K00. Frankly speaking, this entire section should be discarded. In particular, if K00 is applied to suggested range, there is no need for this discussion.

p. 1539, l. 9: As mentioned above, no one would expect σ_{iw} to be independent of the type of aqueous solution and thus aw. CNT does not state anywhere that σ_{iw} should not depend on aw. However, most ice nucleation studies are performed in pure water and this is the likely reason why the dependence of σ_{iw} on aw is not found much discussed.

p. 1540, l. 5: Does the EDS work fine for these tiny molecular clusters? See comments above. And how much does it depend on the parameters defining EDS?

p. 1541, l. 20 and following: There are uncertainties in K00 and this approach. I assume within both their uncertainties included, no statements can be made about any differences besides that the scatter in the data is too large to judge which approach is more accurate.

p. 1543, l. 20 and following: It is incorrect to state that CNT (classical picture) applies a pre-exponential factor independent of temperature. This is not the case. Some experimental data are analyzed assuming it to be constant because of incomplete parameters to provide a complete description (e.g. neglecting diffusion). In contrast, e.g. Zobrist et al. (2007) and studies by the Knopf group, include this pre-exponential factor and its dependency on temperature and type of aqueous solution.

p. 1545, l. 11-16: The association with the formation of glasses comes somehow out of the blue. As mentioned above, I think the uncertainty of the models is too large to make any claim that there is a significant discrepancy between these two approaches. Nothing is gained with these statements and thus should be omitted.

p. 1545, l. 19-21: I do not understand how the new approach will reduce the uncertainty in J_{hom} associated with the parameterization of σ_{iw} in theoretical models. Since this is in the conclusions, it should be discussed in detail earlier in the manuscript, but it is not. There is no uncertainty estimate discussed in this model. Also, how could the author be certain that the assumptions of the interfacial phase are correct? This statement is not necessary and unsupported and should be removed.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 1525, 2014.