Atmos. Chem. Phys. Discuss., 14, C456–C462, 2014
www.atmos-chem-phys-discuss.net/14/C456/2014/

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 #2

Received and published: 13 March 2014

General comments:

An alternative description of the dividing surface between an ice embryo and the surrounding liquid phase, which does not make use of the surface tension, is developed. As the surface tension is associated with a large uncertainty especially in the case of nucleation in a solution droplet this is a valuable discovery. However, calling this a new theoretical approach and new model of homogeneous nucleation oversells the finding. The title needs to be changed.

Several parts of the manuscript could benefit more precise information instead of reduced and sometimes over simplified statements followed by references to the literature.

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Interactive Discussion

Discussion Paper

In addition to addressing the specific comments below, the author especially needs to address the questions concerning the formula used to derive the number of molecules at the surface (pages 1533/1534) before this paper can be considered for publication in ACP.

Specific comments:

1526 line 21: Cziczo et al. 2013 reported that even cirrus clouds preferably form via heterogeneous nucleation. This could be mentioned to highlight the actuality of the topic.

1527 line 2: What are the "significant gaps in the understanding" mentioned here? Isn't this statement ad odd to the following statement (line 4ff.) that MD simulations lead to a fundamental understanding of homogeneous nucleation?

1527 line 28: An explanation why the measurement of σiw is difficult and uncertain could be added here.

1528 line 1-2: Explain what "role" the mentioned parameters play?

1528 line 5-7: How does σ_iw obtained by fitting experimental data with CNT differ from theoretical estimates? What are the estimates based on? How can be judged if theoretical estimates or the experiment and CNT based values are better? Using σ_iw as a free fitting parameter to represent experimental data, inherently unties the variable from being comparable to theory? It is not obvious to me why this practice is casting doubt into CNT.

1528 line 8: state what "shortcomings of CNT" you refer to.

1528 line 14: please explain in more detail what is meant by "this picture is complicated by. . ."

1528 line 22: Marcolli et al. 2007 investigated immersion freezing of ATD in pure water. Check if reference is appropriate.

ACPD
14, C456–C462, 2014

1528 line 26-27: It is mentioned that there is no information on the nucleation mechanism in Koop et al., (2000). But as you state in the following, Koop et al., (2000) report that by using σ(a_w) and ΔG(a_w) they are able to reconcile their result with CNT. This could be read as information on the mechanism.

1528 line 29: It is not true that there is no thermodynamic formulation available in the literature. E.g. Dufour and Defay (1963) comprehensively discuss the case of ice nucleation in a solution droplet.

1529 line1-6: The approximation of a constant sigma (the so called "capillary approximation") only ignores the dependence of surface tension on the curvature of the ice germ i.e. the increased pressure due to curvature. Making sigma a variable of temperature and water activity takes care of this shortcoming. A better justification of your concerns about obtaining σ_iw from experimental data is desirable.

1529 line19-22: This manuscript provides a novel description of the dividing surface within or at least strongly related to CNT. Calling it a new theoretical approach and new model of homogeneous nucleation oversells the finding.

1531/32: It is difficult to understand that the ice germ should provide a solid matrix which is not the interface. This should be explained better.

1533 line9: Should the number of molecules at the surface not be sn_sˆ2/3? If as suspected, the number of molecules at the surface depends on the total number of atoms in the bulk of the germ instead of the total number (which includes the number of molecules at the surface), all formulas starting with Eq. (16) have to be corrected. Please check that your formula n_ls=snˆ2/3 is correct and explain why it should not read n_ls =sn_sˆ2/3.

1534 Eq. (18) Can n* be derived if n_ls =sn_sˆ2/3?

1534 What is the combined uncertainty from all parameters in Eq. (19) compared to Eq. (23)?

ACPD
14, C456–C462, 2014

1535 Eq. (21) ΔGact according to Zobrist et al., 2007 is used. What is the error made by not using a ΔGact(a_w) as proposed by Koop et al., 2000?

1536 line6: Digilov 2004 is discussing metals; Spaepen 1994 refers to results by Wood and Walton 1970. Please check if the references are appropriate.

1536 line8: Marcolli 2007 used parameters of Zobrist 2007 and did not provide a new fit. Please check if the reference is appropriate.

1536 Eq. (26): The fit provided by Murray et al., 2010a has a particularly weak temperature dependence. The more frequently used parameterisations of σ_iw(T) provided by Zobrist et al., 2007 or by Pruppacher and Klett, 1997 might change the comparison.

1536 Eq. (27): Plenty of new data on homogeneous nucleation has become available since the Koop et al., 2000 paper. To get the best possible parameterisation and avoid comparing the fit to the same data it is based on, the newer data should be used.

1536 line 21: Digilov, 2004 cites one value for σ_iw at 0°C measured by Hobbs and Ketcham, 1969 and also Pruppacher and Klett, 1997 did not do their own measurements on σiw. Please check if the references are appropriate.

1537/1538: Please highlight what the reader can learn from section 3.1. The fact that fit curves generally agree to the data they are fitted to is trivial. A physical explanation of the observed discrepancies of the J curves from the different parameterisations is needed instead.

1537 line 10-11: The experiments by Murray et al., 20010a and Riechers et al., 2013 were conducted in a much smaller temperature range than the data points shown in Fig.2. Generally, reporting nucleation rate coefficients higher than ∼10ˆ20 mˆ-3/s is not meaningful as very little experimental data is available to compare to and it has no relevance for atmospheric ice formation.

1537 line 26: Declare what “models” you refer to.

ACPD
14, C456–C462, 2014

1538 line5-6: Explain the connection between experimental scattering of data and differences of the NNF and K00 model results.

1538 line12-13: Explain in more detail why this is “one of the main drawbacks of CNT”. What other main drawbacks does the theory have? What is their relative importance? An analysis of the sensitivity of NNF on the individual parameters would be of interest to underline the advantages of using this description of the interface.

1538 line 19: Is there a temperature range in which the K00 parameterization is applicable?

1538 line21-23: It is generally true that experiments are “limited” to a fraction frozen of 1. Thus taking about frozen fraction > 1 does not make sense. Experimental data showing the decrease in J at the predicted temperatures should be cited here to underline the validity of the calculations.

1539 line 13: Mention to what kind of deficiencies in CNT Ford (2001) is referring.

1540 line 11-13: Explain why, despite the argumentation given here, you use Eq. (30) and show the result in Fig. 3?

1540 line 24: Explain why the compressibility limit of water is a sufficient criterion to show the physical possibility of the interface description given in this work.

1541 line 5: An introduction and explanation of Δaw could help at this point to follow the discussion.

1541 line 16: Replace “observed T_f” with “the fraction frozen at a certain temperature”

1541 line 22-24: Please explain and highlight more clearly how your new approach and the assumptions made show that hom. nucleation of ice in supercooled solutions is independent on the nature of the solute.

1542 line 3-4: Why does the root determine T_f? More explanation is needed.

ACPD
14, C456–C462, 2014

1542 line 5: Replace T with T_f, explain why T_f is the best value to look at.

1542 line5ff: This section is hard to follow. What is the physical reason of the oscillation of the freezing function? More detailed explanation and structuring of arguments might help.

1544 line 1: Replace " a new nucleation framework" with "a new framework to represent the solid-liquid interface".

1544 line 18: An extended discussion of the conclusion made here would be beneficial.

1544 line 24: I disagree that the missing dependency of σiw on aw is a shortcoming of CNT itself, and rather a missing element in some widely used parameterisations of σiw.

1545 line1: Specify what considerations are neglected and in which part of CNT.

1545 line 12: Clarify how non-equilibrium effects and glass formation can explain the difference in the K00 and NNF approach where neither one considers these effects.

Fig. 3 please add gridlines. Why does n* increase towards lower temperatures in the framework of NNT? Does the discussion in section 3.2 indicate that Fig.3 is an invalid comparison? If this is the case it should be made clear in the figure caption.

Technical correction:

Order lists of multiple citations either according to the date of publication or chronologically.

1529 line 9 "to used to" delete first "to"

1538 line 2: replace "inaccuracy" with "uncertainty"

1538 line 5: "within within"

1543 line 20: . . . play a critical role . . .

ACPD
14, C456–C462, 2014

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

ACPD

14, C456–C462, 2014