

Interactive comment on “An approximation for homogeneous freezing temperature of water droplets” by K.-T. O and R. Wood

Anonymous Referee #2

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1 General Assessment

In this work classical nucleation theory is used to derive an approximation to the homogeneous freezing temperature, T_f , of water droplets. T_f is defined as the temperature at which the “mean” number of critical embryos in a droplet is equal to one, and without consideration of time dependency. The authors show that this approximation is able to roughly reproduce the dependencies of T_f on the mean droplet volume and the water activity.

Homogeneous ice nucleation is an important pathway of cirrus formation in the upper troposphere. Although strides have been made in its understanding and parameterization, many questions remain open and the topic is still of importance for the atmospheric

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community. This work is thus within the scope of ACP. However the manuscript suffers in many aspects from a lack of proper conceptual background and understanding. The analysis of the implications and limitations of the approximation is shallow and requires major improvement. The central contribution of the paper seems to be simply the application of CNT implicitly choosing a given time scale and pre-exponential factor, not neglecting them as the authors suggest. On the other hand, within all of its flaws this work managed to show something of value: Properly parameterized, CNT converges to the water activity criterion at the thermodynamic limit. The authors may want to point this out in a rewrite of this work. However in its current form, this work is not suitable for publication in ACP.

2 General Comments

In general there is confusion about the stochastic nature of ice nucleation. Even though equations with an embedded stochastic component are used, it is assumed that the stochastic behavior is in fact neglected. Instead the authors wrongly associate the stochastic behavior with the variability resulted from variation in experimental conditions. There is also confusion about the meaning of the expressions in CNT, mistaking a thermodynamic limit with an average over a given time interval.

The approximation to the freezing temperature proposed can be understood as simply using CNT with fixed preexponential factors and observation time scale and therefore has been done in many previous works. In the validation of the model the authors also miss the fact that the measured freezing temperature depends on predetermined nucleation thresholds set by the experimental conditions.

The limitations of the proposed model need to be explored and analyzed. In several cases discrepancy between reported data and the model was explained as artifacts of the data even though the proposed model is just an approximation and may have im-

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portant limitations, particularly when the nucleation rate or the droplet volume are low. Moreover, the analysis of Figures 1, 4 and 5, disregards several of the discrepancies between the data and the model and requires much more detail.

Finally, the dispersion between the data sets, and the associated experimental errors, is too large to formulate any conclusions on the effect of the dispersion on droplet volume, the cooling rate, and the total number of droplets on freezing temperatures. Rough agreement with the proposed model, which itself is a rough approximation, should not be used to arrive to such conclusions. Instead the authors should focus on analyzing under which conditions their limited model is good enough to explain the data and what accuracy may be expected.

3 Specific Comments

Page 31869, Line 22. Such unified explanation already exist, which is essentially CNT when droplet size variation is accounted for. See for example Khvorostyanov and Curry (2009).

Page 31870, Line 9 and Eq. (1). This is not a fluctuation probability. It is the concentration of critical nuclei within the droplet when the cluster population in in equilibrium. Do not use the word “mean”, since it implies a temporal average.

Page 31871, Lines 5-6. This is conceptually wrong. The nucleation work is independent of droplet volume. Within the proposed scheme $\tau_{meta-remove} \propto (JV)^{-1}$ being J the nucleation rate.

Page 31871, Lines 3-11. Essentially this whole explanation is wrong. The stochastic nature of ice nucleation does no originate from spreading in the droplet volume.

Page 31871, Lines 15-17. Again this is a misrepresentation. The goal of CNT is not to derive $\tau_{meta-remove}$ from N_{c-mean} , but to derive the nucleation rate, J .

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Page 31871, Lines 24-25. This is not true. The activation energy is usually derived from the self-diffusivity of water of from thermodynamic arguments (See for example Ickes et al., 2015 and Barahona, 2015).

Page 31872, Line 7. It should be evident that this expression indicates that the proposed approximation (Eq. 1) is a thermodynamic limit not a mean value.

Page 31872, Line 16. This equation is similar to Eq. (30) of Barahona (2014). Essentially the proposed approximation can be understood as implicitly selecting values for the preexponential factor and the time scale in the nucleation rate expression, as done in many works. This should be discussed.

Page 31872, Line 19. Here and in other places. Use lower (higher) instead of cooler (warmer).

Page 31872, Line 23. Remove “then”.

Page 31873, Lines 1-4. How are these values obtained? It is not clear how they “explain” the observed dependencies.

Page 31873, Lines 4-5. This sentence must go somewhere else, where the comparison against experimental results is shown.

Page 31873, Line 25. Remove the words “of the”.

Page 31874, Line 5. Equilibrium is right but melting is not. The melting temperature depends on concentration and experimental conditions.

Page 31874, Lines 6-7. Calling the derivatives “dependencies” is wrong. In fact there is no need to call this terms anything since what they are is evident.

Page 31874, Line 12. Maybe use “instead” as opposed to “therefore”.

Page 31874, Lines 15-16. So which one is used?

Page 31874, Lines 25. Please give the value of C.

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Page 31874, Line 5. It must be “properties”.

Page 31875, Lines 2-3. Please plot the estimate of the interfacial tension against other expressions.

Page 31875, Line 15-17. This is only true for $T > 235$ K and droplets above $10\ \mu\text{m}$. Not clear why the slope is mentioned at all since it is T_f which is compared not $\frac{dT_f}{dD}$ and why it is somehow a prove of the validity of the model. To make any assessment on $\frac{dT_f}{dD}$ it should be calculated directly, not mentioned implicitly.

Page 31875, Line 15-17. In their calculations the authors assume a monodisperse size distribution, which is probably not true in most of the experiments. In a true comparison $T_{Nc=1}$ should be weighted by the droplet size distribution.

Page 31875, lines 17-23. I don't think there is any evidence to make this statement. There is no information on $\gamma_{cooling}$ in Fig. 1. The error bars in most of the data are wider than the expected variation in T_f from cooling rate. The dispersion in the size of the droplets is not accounted for; increasing the width of the droplet size distribution tend to smooth the variation in T_f from other factors. T_f from different data sets clearly do not fall on the same line.

Page 31875, lines 23-26. The data of Murray et al. (2010) is not the only exception. Clearly the data from Earle et al. (2010), Pound et al. (1953), Riechers et al. (2013), Kuhns and Mason (1967), and Cziczo and Abbat (1999) do not follow the predicted curve.

Page 31876, lines 9-12. Koop et al. (2000) use data from different sources and they should be labeled as such in the Figure. Furthermore, similar studies have been performed by other groups during the last decade (some cited in the work) and should be included.

Page 31876, lines 15. This is true only for $a_w > 0.85$.

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Page 31876, lines 16-17. This is confusing statement; $\frac{dT_{Nc=1}}{d\gamma_{cooling}}$ is not shown in Figure 4, just $T_{Nc=1}$.

Page 31876, lines 18-20. Another unsupported statement. The authors have no evidence to show that the scatter in the data comes from dispersion in the droplet size. The statement seems to be based only on a rough agreement with their model which itself is a rough approximation to T_f .

Page 31876, lines 10-20. The freezing temperature is not a thermodynamic property and depends on experimentally predetermined nucleation thresholds, so this is not an objective evaluation of the model. See general comments above.

Page 31876, lines 20-27. Here the work focuses on experimental artifacts to explain the discrepancy between the model and the measurements, forgetting that the model itself is but a rough approximation to T_f (Figure 1 also suggest that it is not accurate at low T). A simple explanation would be that as a_w decreases and the flux of molecules to the ice germ decreases (activation energy increases). The thermodynamic limit $T_{Nc=1}$ becomes less accurate since kinetics is playing a larger role.

Page 31877, lines 1-10. The limitations of the model must be discussed as well.

Page 31877, line 3. This is a confusing statement. I suggest simply “variation in $T_{Nc=1}$ ” without involving derivatives. Also in Line 7 and other parts of the work derivatives are referred to as “the dependencies” which is confusing and unnecessary.

Page 31877, lines 15-18. It is not clear what this statement refers to. Also it needs a reference.

Page 31878, lines 1-3. This statement seems wrong. The stochastic nature of ice nucleation is fundamentally embedded in the expressions used. The fact that Eq. (1) is based on Boltzmann type distribution of cluster sizes at equilibrium is a reflection of that. Do the authors mean that they do not consider variation in T_f due to time, or, that they implicitly assume a infinite flux of water molecules to the germ?

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Page 31878, lines 3-11. Why is it necessary to define all of these values? They are never shown. Also, is this calculation simply $T_f = \int_0^\infty P(V)T_{Nc=1}(V)dV$ at each temperature?

Page 31878, lines 15-20. Again it is not clear what is understood by the stochastic nature of ice nucleation, and why it is used here to justify the discrepancy with the data. The authors should be more self-critical and discuss the limitations of their approach. A steeper curve in Fig. 5 is consistent with the increasing effect of kinetics at lower temperature and, with the breaking of the thermodynamic assumption in smaller droplets (consistent with the discrepancy between the model and the data in Figure 1).

Page 31878, line 21. These values must be explicitly shown.

Page 31878, line 26-29. This is not the meaning of the stochastic nature of ice nucleation. It is not merely the distribution of freezing temperatures. Second, is it Fig. 4 or Fig. 5 what is being discussed? Finally, the error bars in the data span the whole range of variation in T_f from variation in droplet size and it is not clear that any conclusion on the effect of droplet size dispersion can be extracted from this. Mere comparison against a approximated model cannot be used as prove.

Page 31879, line 6. Neither the total number of droplets nor the cooling rate were studied as factors. The conclusion is based solely on the agreement of the rough approximation proposed with the data.

Page 31879, lines 7-15. Is this involved explanation just saying that in many cases $T_{Nc=1}$ is an acceptable approximation to the experimentally observed T_f ? Is not that the premise of the whole work?.

Page 31880, lines 25. This is a theoretical limit, it is not shown by the experiments.

Figure 5, Caption. Is the red line missing?