Responses to reviewers, ACP-2015-896 "An approximation for homogeneous freezing temperature of water droplets " by K. -T. O and R. Wood

Review comments in black. Responses provided in red

Responses to anonymous Referee #2

In this work classical nucleation theory is used to derive an approximation to the homogeneous freezing temperature, Tf , of water droplets. Tf 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 Tf on the mean droplet volume and the water activity. Homogeneous ice nucleation is a important pathway of cirrus formation in the upper troposphere. Although strides has been made in its understanding and parameterization, many questions remain open and the topic is still of importance for the atmospheric 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 is current form, this work is not suitable for publication in ACP.

We thank the referee #2 for the review.

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.

The term "stochastic nature" has been used in Koop et al. (1998) and Knopf and Lopez (2009) to describe the deviation of the observed homogeneous freezing temperatures. In principle, this "stochastic nature" originates from the fact that the embryo interaction in the water droplet is a random process, **so there is always a spread of homogeneous freezing temperatures even in an idealized case that all the observed droplets have exactly same size and water activity**. The paragraph in P.31871, line 1 -15 illustrates these principles. The Boltzmann distribution used in our study only gives the "average" distribution of particles over various energy states and does not provide any information regarding the stochastic nature illustrated above. **In other words, the Boltzmann distribution provides the *average* state of a stochastic (random) interaction system of embryos.** Thus, we think it is reasonable to state that *by using the Boltzmann distribution, stochastic behavior of homogeneous freezing temperature can not be studied here*.

We agree that the term "stochastic nature" could be misunderstood as referee 1 suggests, and have changed the term "stochastic nature" to "stochastic feature" in our manuscript since the word "feature" may be more appropriate to describe the distribution of freezing temperatures observed in the experiment. The more complete discussion and definition of the stochastic feature have been added to Page 31871, line 10: " Hereafter we refer the distribution of homogeneous freezing temperatures owing to $N_{total\_droplets}$ when all the droplets have exactly same V and a_w as a stochastic feature."

Instead the authors wrongly associate the stochastic behavior with the variability resulted from variation in experimental conditions.

We disagree. The paragraph in P.31871, line 1 -15 clearly states that the stochastic behavior results from the spread of the τ_{meta_remove} among droplets even if all the droplets have **"same size and water activity".** *According to CNT, the stochastic feature of the ice nucleation process can basically explain* *the distribution of freezing temperatures observed in the fraction experiment (Pruppacher and Klett, 1997, Eq. (7-71); Koop et al., 1998; Niedermeier et al., 2011). However, current technology to produce water droplets for such experiments introduces a spread of sizes, and the freezing temperatures show a clear dependence on droplet volume (Fig. 1), so the spread in sizes of water droplets used in the experiments may be important for explaining the distribution of freezing temperatures observed in the experiment* (from P.31877, line 15-20). As shown in the Fig. 5 and Table 2 (new added), the spread in droplet size may be an important factor governing the spread of the homogeneous freezing temperatures.

We think there are couple semantic problems in our manuscript causing this misunderstanding, and the details will be provided in the specific comments.

There is also confusion about the meaning of the expressions in CNT, mistaking a thermodynamic limit with an average over a given time interval.

Here, referee #2 regards the Boltzmann distribution of the critical embryo (i.e. Eq. 1 in our manuscript) as the simplified "thermodynamics limit" of CNT by choosing a given time scale and pre-exponential factor, and argues that we mistake this thermodynamics limit as an average over a given time interval. The Boltzmann distribution is certainly not a thermodynamics limit but is a "average" distribution of particles at a given thermodynamics state (i.e. temperature, pressure).

The derivation of our Eq. (1) is in the scope of statistical mechanics and the detailed treatments can be found in many good references on the subject (e.g, Landau and Lifshitz, 1958) as suggested by Pruppacher and Klett (1997) in the appendix A-7.1. For example, as illustrated in P.107 in Landau and Lifshitz (1958), *"Applying the Gibbs distribution formula to the gas molecules, we can say that the probability that a molecule is in the kth state is proportional to exp(-ε_k/T), and therefore so is the* ***mean number*** $\overline{n_k}$ *of molecules in that state, i.e.* $\overline{n_k}$*=aexp(-ε_k/T) (37.2),…. The distribution of molecules of an ideal gas among the various states that is given by formula (37.2) is called the Boltzmann distribution…"*. The detailed derivation of the Boltzmann distribution used in Pruppacher and Klett (1997) can also be found in the *Statistical physics and cosmology Part IIA Mathematical Tripos* written by Prof. P.K. Townsend at University of Cambridge, where P.32 clearly note that *" The* ***average value*** *of n_k is therefore …, so that* $\overline{n_k} = kT\partial logZ_k/\partial\mu$ ", which is the Eq. (7-6) used in Pruppacher and Klett, (1997).

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.

Referee #2 regards the Boltzmann distribution of the critical embryo (i.e. Eq. 1 in our manuscript) as the "thermodynamics limit", "simplification", and "application" of the ice nucleation rate formula of CNT.

The Boltzmann statistics gives a probability distribution of particles (i.e. embryos) in a system with various possible states. The probability that a particle in the i_{th} state is proportional to $e^{-\varepsilon i/kT}$, where ε_i is the state energy (i.e. formation energy of the embryo), and the "mean number" of critical embryos in thermal equilibrium can be given by the Boltzmann distribution as described by our Eq. (1) (see P.107 in Landau and Lifshitz (1958) for details). The Boltzmann distribution only gives a "mean number", which does not provide any information regarding time, so it's definitely appropriate to suggest that the application of it can not consider the time dependence of homogeneous ice nucleation process. In our study, we derive the temperature when the mean number of the critical embryos inside a droplet is unity given by the Boltzmann distribution.

The Boltzmann distribution was discovered by Ludwig Boltzmann in 1877 (Landau and Lifshitz, 1958), and is certainly "not" a "simpler application" of CNT (i.e. mainly developed after 1900s) choosing a given time scale and pre-exponential factor as referee #2 suggests. Instead, the formula of ice nucleation rate is indeed the application of the Boltzmann distribution. The CNT formula of ice nucleation rate is derived from the Boltzmann distribution and the kinetic adsorption/desorption flux system based on the assumption that the embryos' population can be appropriately described by the

Boltzmann distribution (please see Defour and Defay, 1963, P.173 and P.189 for detailed derivation).

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.

A reply is provided in the specific comments below.

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 important limitations, particularly when the nucleation rate or the droplet volume are low.

Agree. We have added several paragraphs regarding the limitation of our approximation and more complete details regarding the experimental uncertainties. See more details provided in the specific comments.

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.

Agree. For Fig. 1, we have added Table 1 to provide the details of the experimental data used in the comparison. For Fig. 4, we have added the experimental data from Knopf and Lopez (2009) and Knopf and Rigg (2011). For Fig. 5, we have added Table 2 to provide the detailed values of experimental data and our approximation. In addition, we have added the discussion regarding experimental uncertainties in the homogeneous freezing experiments as referee 1 suggests.

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

In Fig. 1, the dotted line include the ranges of droplet size and observed freezing temperatures (i.e. spread of the droplet size, spread of the observed freezing temperature) and the uncertainties of the experiments. We have added Table 1 in our manucript, which shows that the spread of the observed temperature and droplet size is much larger than the experimental uncertainty. Thus, the dotted lines through each data point should not be considered as the experimental errors, and we suggest here that the spread of the observed freezing temperature can be partly explained by the spread of the droplet size used in the experiment as illustrated in Sect. 3.2.

The limitation of our proposed approximation have been added and provided in the specific comments.

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)

Agree. We have added following sentence in P.31869. line 19: "The unified explanation of the observed dependnecies of the homogeneous freezing temperature on droplet size and water activity have been proposed by several studies based on different theoretical frameworks such as ice nucleation rate J and density fluctuation (e.g. Pruppacher 1995; Baker and Baker 2004; Khvorostyanov and Curry 2009; Barahona 2014)."

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.

We agree it is the concentration of critical nuclei within the droplet. However, this is also the fluctation probability. As illustrated in P.472 in Landau and Lifshitz (1958) – *"the probability w of a fluctuation producing a nucleus is proportional to exp(-R_{min}/T), where R_{min} is the minimum work needed to form the nucleus"*.

As illustrated above in the general comments, the number of particle derived from the Boltzmann distribution is a "mean" value as illustrated in many classical statistical mechanics textbooks (e.g, P.107 in Landau and Lifshitz (1958)).

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

The nucleation work is indeed independent of droplet volume. We agree and we think there is a semantic problem in our original sentences causing the misunderstanding.

The original sentence: "*Because τ_{meta_remove} is the time needed for the occurrence of the critical fluctuation, τ_{meta_remove} is shorter at cooler temperature when the fluctuation probability is higher "or" in a droplet with more molecules.*" We want to point out that the time needed for metastability removing is shorter in a larger droplet "or" at cooler temperature.

To avoid confusion, this sentence has been modified to: "Because τ_{meta_remove} is the time needed for the occurrence of the critical fluctuation among water molecules, τ_{meta_remove} is shorter in a droplet with more molecules Vρ or at cooler temperature when the fluctuation probability exp(-$\Delta F_C(T,a_w)/k_bT$) is higher"

We agree τ_{meta_remove} is positively proportional to $(JV)^{-1}$, and because $JV \sim N_{c\_mean}\exp(-\Delta G_{activation\_energy})$, τ_{meta_remove} is also positively proportional to $(N_{c\_mean})^{-1}$ as we express in the manuscript.

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.

We agree the stochastic nature of ice nucleation does not originate from spreading in the droplet volume, which is exactly what we want to illustrate here. Thus, we think there is a semantic problem in this paragraph and have modified it.

Original P. 31871. Line 5-10

N_{c_mean} (V,a_w ,T) is the mean state, so there is always a spread of τ_{meta_remove} among droplets even though all the droplets have same V and a_w and are at exactly same temperature T. The spread of τ_{meta_remove} can be wider when there are more observed droplets $N_{total\_droplets}$, causing the stochastic nature of ice nucleation process that some droplets with shorter τ_{meta_remove} can always be frozen at higher temperature, or in shorter time for droplets at the same temperature.

To clarify, P. 31871. Line 6-10 have been modified as-

"Embryo interaction is a stochastic process and N_{c_mean} (V,a_w,T) simply expresses mean state, so there is always a spread of τ_{meta_remove} among droplets even in a idealized case that all the droplets used in the experiment have exactly the same V and a_w and are at exactly the same temperature T. The spread of τ_{meta_remove} can be wider when there are more observed droplets $N_{total\_droplets}$ which in principle can explain the fraction experiments that some droplets with shorter τ_{meta_remove} can always be frozen at higher temperature, or in shorter time for droplets at the same temperature even when the droplets have a monodisperse size distribution and exactly same a_w. Hereafter we refer the distribution of homogeneous freezing temperatures owing to $N_{total\_droplets}$ when all the droplets have exactly same V and a_w as a stochastic feature."

Page 31871, Lines 15-17. Again this is a misrepresentation. The goal of CNT is not to derive τ_{meta_remove} from N_{c_mean} (V,a_w ,T), but to derive the nucleation rate, J.

Because J~1/τ_{meta_remove}, we don't think there is any difference between deriving J and deriving τ_{meta_remove}. We have decided to remove the part discussing ice nucleation rate in our manuscript to shorten the length of the manuscript and focus on the approximation proposed here.

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).

In Pruppacher (1995), in order to get the agreements between the observed homogeneous freezing temperatures and the theoretical estimates derived by ice nucleation rate, the value of activation energy is fitted. We agree there are several theoretical and experimental studies working on the derivation of the activation energy. However, the disagreements among the studies are still large as shown in Ickes et al. 2015, Fig. 1. The part discussing ice nucleation rate has been removed.

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.

Koop et al. (1998) reported that observed homogeneous freezing temperatures do not significantly depend on the cooling rate of the droplets for cooling rate smaller than 20 K min^{-1}. It actually suggests that τ_{meta_remove}(~1/J) is a very steep function of temperature at the observed homogeneous freezing temperatures. As referee 1 mentioned, "*The neglect of time in this study works because close to the homogeneous freezing limit the nucleation rate coefficient is a very steep function of temperature. As such, in explanation of the spread in ice nucleation experiments, there will always be an effect of time but possibly negligible compared to the volume effect*".

The term "mean" used to describe the Boltzmann distribution can be found in many classical statistical mechanics textbooks. The Boltzmann distribution is not the thermodynamic limit and is not derived from the ice nucleation rate formula as we illustrate above in the general comments.

Page 31872, Line 19. Here and in other places. Use lower (higher) instead of cooler (warmer).
Agree. Done.
Page 31872, Line 23. Remove "then"
Agree. Done.

Page 31873, Lines 1-4. How are these values obtained? It is not clear how they "explain" the observed dependencies.
These values are derived from Eq. (2) numerically. This sentence has been modified to: "…of water activity and drop size, which are derived numerically from Eq. (2). "

Agree. The sentence "may explain the….."has been removed.
Page 31873, Lines 4-5. This sentence must go somewhere else, where the comparison against experimental results is shown.

Agree. Done. This sentence has been moved to the result section.

Page 31873, Line 25. Remove the words "of the".
Agree. Done.

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

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.
Agree. Done.

Page 31874, Line 12. Maybe use "instead" as opposed to "therefore".
Agree. Done.

Page 31874, Lines 15-16. So which one is used?
All of them are used. Following sentence has been added to Page 31874, Lines 16 : "and these three values will all be used in our calculation."

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

Page 31874, Line 5. It must be "properties".
We assume the referee 2 refer to Page 31875, Line 1.
We have added the detailed formula of C and removed this sentence.

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

The Fig. 2 of Ickes et al. (2015) has the most detailed review regarding the theoretical and experimental estimation of the interfacial tension. The values of the interfacial tension used in our study are about the median of all the values derived from the previous studies. Because the interfacial tension is not the focus of our study here, it may not be necessary to plot the estimate of the interfacial tension against other expression.

To address, following sentence has been added in Page 31874, Line 16: "According to Ickes et al. (2015), the values of the interfacial energy used here are about the median of all the values derived from the previous studies"

Page 31875, Line 15-17. This is only true for T > 235 K and droplets above 10 µm. Not clear why the slope is mentioned at all since it is Tf which is compared not dTf /dD and why it is somehow a prove of the validity of the model. To make any assessment on dTf /dD it should be calculated directly, not mentioned implicitly.

Agree. The sentence have been revised to: "For droplet diameter > 10µm, the theoretical values of $T_{Nc=1}(V,a_{w=1})$ derived by the value of $\sigma_{i/w,e}$ from TIP4P water model agree very well with most of the experimental data $T_f(V,a_{w=1})$. Using the values of $\sigma_{i/w,e}$ from TIP4P/2005 and TIP4P-Ew leads to a shift downward of 1~2 K of $T_{Nc=1}(V,a_{w=1})$."

Agree. The discussion on the slope has been removed

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.
$T_{nc=1}(V,a_w)$ is the temperature when the mean number of critical embryo is unity inside a droplet with size V and a_w defined by our Eq. (2). Thus, it cannot be weighted by the droplet size distribution.

We agree the effect of droplet size distribution used in the experiment is important, which is discussed in the Sect. 3.2 of our manuscript.

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.

The detailed information regarding cooling rate has been added in Table 1.

We agree the Fig. 1 in our manuscript does not have enough evidence to make this statement and have decided to remove it. Since Koop et al. (1998) and Murray et al. (2010) showed difference dependencies of homogeneous freezing temperatures on cooling rates, we agree it is still an open question. However, based on the comparison made in Fig. 1, Fig. 4 and Fig. 5, we think it is fair to suggest that the effect of cooling rate and the total number of observed droplets may be secondary compared to the effect of drop size and water activity on homogeneous freezing temperatures for droplet diameter >10μm and $a_w > 0.85$. As suggested by referee 1, "*The neglect of time in this study works because close to the homogeneous freezing limit the nucleation rate coefficient is a very steep function of temperature. As such, in explanation of the spread in ice nucleation experiments, there will always be an effect of time but possibly negligible compared to the volume effect*".

Most part of the dotted lines should be regarded as the spread of droplet size and observed freezing temperatures but not the error bars as shown in our new Table. 1.

We agree the width of the droplet size is important and is exactly the conclusion we made in Section 3.2.

We agree the agreement is only true for diameter > 10μm, and have revised the sentence.

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.
We agree the agreement is only true for diameter > 10μm, and have revised the sentence.

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.
Agree. The experimental data of Knopf and Lopez (2009) and Knopf and Rigg (2011) have been added and discussed.

Page 31876, lines 15. This is true only for $a_w > 0.85$.
Agree. The sentence has been revised to: "the result shows that the approximation $T_{Nc=1}(V,a_{w=1})$ is in good agreement with the experimental data for $a_w > 0.85$."

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

Agree. The sentences have been revised to: "Without considering the time dependence ($\gamma_{cooling}$ varying from 1 K min^{-1} to 10 K min^{-1} among all the experiments) and the stochastic feature"

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 Tf .

We agree we have no evidence to show that the scatter in the data "certainly" comes from dispersion in the droplet size. To clarify, the sentences have been revised to: "The scattering of the experimental data between the theoretical estimates for $a_w > 0.85$ (i.e. $T_{Nc=1}$ for d =1 to 80 μm) suggests that the spread of droplet size applied in the experiments may play an important role in the spread of homogeneous freezing temperatures."

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.

We agree the measured freezing temperature depends on predetermined nucleation thresholds set by the experimetnal conditions (i.e. $T_{50\%}$, $T_{10\%}$), and have added Table. 1 to provide the detailed information of the experimental data used in the Fig. 1. The reason why experiments need to set a nucleation threshold is that there is always a distribution of freezing temperatures observed in the experiments, which in principle can be attributed to the stochastic feature of homogeneous freezing temperature as we illustrated above. In fact, we do not miss the fact there is predetermined nucleation thresholds. We actually suggest that the spread of homogeneous freezing temperatures is partly governed by the spread of droplet size used in the experiment and is an important factor why predetermined nucleation thresholds is needed in the experiments.

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 Tf (Figure 1 also suggest that it is not accurate at low T). A simple explanation would be that as aw decreases and the flux of molecules to the ice germ decreases (activation energy increases). The thermodynamic limit TNc=1 becomes less accurate since kinetics is playing a larger role.
According to Koop et al. (1998), Knopf and Lopez (2009) and the review of the referee 1, the deviations at low water activity may be most likely due to our incomplete understanding of a_w and the corresponding uncertainties.

On the other hand, we agree our method may becomes less accurate for low a_w and small droplet size. To address this – we have added following sentences in P.31880, line 20: "The results shown in Fig. 1 and Fig. 4 suggest that the time consideration may be more important when droplet volume and water activity are low where the experimental data show considerable inconsistency (i.e. $a_w < 0.85$ and $d < 10\mu m$), and future experiments are suggested to emphasize these droplet size and water activity ranges."

Page 31877, lines 1-10. The limitations of the model must be discussed as well.
Agree. The discussion of the limitations of the model have been added in Page 31872, lines 10: "The number of critical embryos derived from the Boltzmann distribution is a mean value and does not provide any information regarding freezing time, so it can not be used to study the dependence of the homogeneous freezing temperature on cooling rate (i.e. time dependence) and number of droplets used in the experiments (i.e. stochastic feature)"

Page 31877, line 3. This is a confusing statement. I suggest simply "variation in TNc=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.
Agree. Done.

Page 31877, lines 15-18. It is not clear what this statement refers to. Also it needs a reference.
References have been added : "(Pruppacher and Klett, 1997, Eq. (7-71); Koop et al., 1998; Niedermeier et al., 2011)" The more complete discussion on stochastic feature has been added in Sect. 2.

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 Tf due to time, or, that they implicitly assume a infinite flux of water molecules to the germ?

We agree "without consideration of stochastic nature" could be misunderstood as referee 1 suggests so we have removed it. We have changed the term "stochastic nature" to "stochastic feature" in our manuscript as explained above in the general comments.

The exponential term in the Boltzmann distribution is the probability of occurrence of the critical fluctuation (Landau and Lifshitz, 1980, P.472-473), so Eq. (1) is derived based on the existence of fluctuation, which is a stochastic event. However, the number of critical embryos derived from the Boltzmann distribution is a mean state, which depends on V, a_w, and temperature, but does not provide any information regarding the variation of N_{c_mean} due to time and number of observed droplets. More detailed discussion on the Boltzmann distribution has been provided above.

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

We have added Table 2 to provide these values. The details of the calculation have been provided in Page 31878, lines 3-11.

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).

The term "stochastic nature" has been used in Koop et al. (1998) and Knoft and Lopez (2009) to describe the deviation of the observed homogeneous freezing temperatures when the droplets have identical volume and water activity. In principle, this "stochastic nature" originates from the fact that the embryo interaction in the water droplet is a random process, so there is always a spread of the observed freezing temperature even in a idealized case that all the droplets have exactly same size and water activity. Our method used here can only study the dependence of homogeneous freezing temperature on droplet volume and water activity, but a limitation is that it can not be used to study the dependence on cooling rate (i.e. time dependence) and number of droplets used in the experiment (i.e. stochastic feature).

Here, we suggest the stochastic feature and the time dependence (i.e. the factors we can not study here) are secondary factors compared to the effect of droplet volume and water activity on homogeneous freezing temperature.

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

Done. We have added Table 2.

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 Tf 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.

We agree "without consideration of stochastic nature" could be misunderstood as referee 1 suggests so we have removed it. We have changed the term "stochastic nature" to "stochastic feature" in our manuscript as explained above in the general comments. The more complete discussion and definition of the stochastic feature have been provided above.

Thanks for the correction. The sentence has been modified to: "From the comparison made in Fig. 5". The details of the comparison have been added in Table 2.

As we mentioned in the manuscript, Riechers et al. (2013) reported that during cooling, the majority of the droplets are frozen over a temperature interval of 0.84–0.98 K. The range between the theoretical estimates T_f^{onset} (i.e. $T_{nc=1}$ of the biggest droplet used in the experiment) and T_f^{end} (i.e. $T_{nc=1}$ of the smallest droplet used in the experiment) is 0.42-1.06K. This suggests that the spread of the droplet size may be the important factor governing the spread of the observed homogeneous freezing temperature in the experiment.

To clarify, following sentence has been added to Page 31878, line 26: ", suggesting the spread in droplet size (i.e. a disperse distribution) may be an important factor governing the spread of the homogeneous freezing temperatures observed in a given fraction experiment."

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.

The details regarding the experiments have been added in Table 1.
The limitation of our method has been provided in the Sect. 2 and Sect. 5 as illustrated above.

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

Yes.

Page 31880, lines 25. This is a theoretical limit, it is not shown by the experiments. Figure 5, Caption. Is the red line missing?

We agree and have removed this sentence.

The caption has been revised.

We have decided to change the title of the manuscript to: "Exploring an approximation for the homogeneous freezing temperature of water droplets"

References

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