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 #1

This manuscript presents a new parameterization to predict homogeneous freezing temperatures of water and aqueous solution droplets in the atmosphere. Using the number of critical embryos formed in a droplet as a result of critical fluctuations, based on classical nucleation theory, the authors show that the derived temperature at which the number of critical embryo equals one, can reproduce experimental studies including freezing from water droplets and aqueous solution droplets. As a result, it is found that the spread of homogeneous freezing temperatures is largely governed by differences in droplet size (volume) distribution applied in the ice nucleation experiments. As such, this new parameterization is suggested for predicting homogeneous ice nucleation in the atmosphere.

We thank the reviewer for the clear summary and constructive review.

General comments:

Equation 1 is the foundation of this work. However, as far as I recall, not the mean number of critical embryos is derived but it gives the number of i-mers of certain size formed for a given fluctuation (as given e.g. in Pruppacher and Klett). This reflects the partitioning function of the grand canonical ensemble. More information has to be given why this equation should reflect a mean number of critical embryos and which size of the critical embryo was assumed. The size of the critical embryo may depend on other thermodynamic parameters. Please elaborate.

The derivation of 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. The Boltzmann distribution of critical embryo (i.e. Eq. (1) in our manuscript and Eq. (7-10) in Pruppacher and Klett, 1997) is derived from the partitioning function of the grand canonical ensemble, and it should be noted that the derived particle number of the Boltzmann distribution function is not a "constant" but is a "mean" number. 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 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). In addition, it should be noted that the Boltzmann distribution assumes the particles are in thermal equilibrium.

To clarify, the sentence in Page 31870, line 9 has been modified to: "and thus the *mean number* of the critical embryos inside a water droplet in thermal equilibrium can be predicted by a Boltzmann distribution (Landau and Liftshitz, 1958, P.107; Vali, 1999),". The sentence in Page 31868, line 4 has been modified to: "… droplet is unity is derived from the Boltzmann distribution function and explored as a…..". Following sentences have been added to Page 31870, line 15 : "The Boltzmann distribution form of the critical embryo is derived from the partitioning function of the grand canonical ensemble, and it should be noted that the derived particle number of the Boltzmann distribution function is not a "constant" but is a "mean" number (detailed derivation and explanations can be found in Landau and Liftshitz, 1958, P.107 and Sadovskii, 2012, Chapter 3.1)."

Regarding the size of the critical embryo, as illustrated in Vali (1999), "*The sum of the volume energy and the surface energy (i.e. formation energy) has a maximum at the critical germ size, indicating that below that size growth is energetically not favored, but beyond that size growth is spontaneous as increasing size leads to decreasing total potential for the cluster",* so the critical embryo size assumed in our study is the size has maximum formation energy, which is consistent with the classical definition of the critical embryo (Pruppacher and Klett, 1997; Defour and Defay, 1963). The size of the critical embryo is given in Eq. (5), which is derived by differentiating the formation energy of the embryo to obtain the maximum (detailed derivation in (7-27) of Pruppacher and Klett, 1997).

To clarify, the sentence in Page 31870, line 4 has been modified to: "The critical embryo defined as the i-mers having the highest formation energy is formed by the critical fluctuation ….".

As stated above, I like this work, but it is not clear to me what is gained with regard to atmospheric application compared to previous parameterization, e.g. by Koop et al. (2000)? Computationally, the formulation by Koop et al., it seems, is still more efficient. Usually in a model, one knows time, either as a model time step or by given updraft velocities, and if not, one could just assume a time constant for the Koop et al. formulation. 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. If the authors could make a case why this parameterization is of advantage in implementing into cloud models, this would strengthen this paper
Thank you for suggesting this. The most pronounced advantage of our approximation in the cloud modeling is "the temperature history" of droplets is not required to calculate the homogeneous freezing temperature as it is using the ice nucleation rate. When using the ice nucleation rate J(T(t)), the complete temperature history of droplets (i.e. temperature versus time) is required to calculate the complete integration of J(T(t)) with respect to time, which gains considerable complexity in cloud modeling. One can certain make some assumptions to simplify this complexity, but however, as pointed out by the 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",* the consideration of time dependence and the following complexity may be a secondary factor for the homogeneous ice formation in the atmosphere. From this standpoint, our approximation may be more efficient and simpler in implementing into cloud models.

To address, we have revised our conclusion to: "The limitation of our method proposed here is that the time dependence and the stochastic feature of homogeneous freezing temperature can not be considered because the Boltzmann distribution applied here is a average distribution and does not provide any information regarding time. Combining the well-known Boltzmann distribution for the mean number of critical embryos $N_{c\_mean}(V,a_w,T)$ and their formation energy $\Delta F_c(T,a_w)$ from CNT formulae, $T_{Nc=1}(V,a_w)$ is derived as a function of volume and water activity of water droplets. With the comparison made in Sect. 3.1 to 3.2, it can be summarized that under most atmospheric conditions, homogeneous freezing temperatures can be well described by the new approximation $T_{Nc=1}(V,a_w)$ proposed here without considering information of the applied cooling rate (i.e. time dependence) and the number of droplets used in the experiment (i.e. stochastic feature) for d>10μm and $a_w > 0.85$. Future experimental study is suggested to focus on the homogeneous freezing process of droplets with high solute concentration ($a_w < 0.85$) and small volume (d < 10μm). The experimental spread in homogeneous freezing temperatures of water droplets may be partly explained by the size distribution of droplets used in the experiments. The advantage of our approximation in the cloud modeling is "the temperature history" of droplets is not required to calculate the homogeneous freezing temperature as it is when using ice nucleation rate (i.e. Eq. (7-71) in Pruppacher and Klett, 1997). When using the ice nucleation rate J(T(t)), the complete temperature history of droplets is needed to calculate the integration of J(T(t)) with respect to time in order to consider the time dependence and stochastic feature, which can introduce considerable complexity in cloud modeling. However, based on the experimental studies of homogeneous freezing temperature collected and discussed in our study, we suggest in most of the practical experiments and realistic atmospheric conditions (i.e. $\gamma_{cooling} < 20$ K min^{-1}), the time dependence and the stochastic feature of homogeneous freezing temperature may be a secondary factor compared to the effect of volume and water activity. The approximation proposed here is relatively simpler to be implemented into cloud models and may improve the representation of homogeneous ice nucleation in the atmosphere."

It would be interesting to know at which spread in size distribution, time considerations (or vice versa i.e. time versus volume effect) are important. This could help guiding experiments.

The results shown in Fig. 1 and Fig. 4 suggest that the time considerations may be important when the droplet volume and water activity are low (i.e. where the deviations are considerable), but since there is no information of $\gamma_{cooling}$ provided in these experimental studies, we can not evaluate the importance here.

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."

Specific comments:

p. 31868, l.5-6: "Without consideration of time dependence and stochastic nature. . .". I understand why you write this here but it could be misunderstood that homogeneous ice nucleation is not time dependent or not stochastic, which it obvious is. In fact, your basic equation is derived from CNT that assumes fluctuations. Here, you can neglect time dependence since the nucleation rate is so steep with respect to changes in T. I suggest to clarify this statement.

Agree. This sentence has been modified to: " Without including the information of the applied cooling rate $\gamma_{cooling}$ and the number of observed droplets $N_{total\_droplets}$ in the calculation, the approximation $T_{Nc=1}$ is able to reproduce the dependence of homogeneous freezing temperature on drop size V and water activity a_w of aqueous drops observed in a wide range of experimental studies for droplet diameter > 10µm and $a_w > 0.85$, suggesting the effect of $\gamma_{cooling}$ and $N_{total\_droplets}$ may be secondary compared to the effect of V and a_w on homogeneous freezing temperatures in these size and water activity ranges under realistic atmospheric conditions."

We have changed the term "stochastic nature" to "stochastic feature" in our manuscript based on the comments of referee 2. 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."

p. 31868, l. 16: Would it not be better to call it ice melting temperature instead of equilibrium temperature?
Agree. Done.

p. 31868, l. 21: ...of temperature and time...? Previous experiments when deriving nucleation rate coefficients interpreted their data using droplet volume and time including Koop et al. (2000).
Agree. Done.

p. 31868, l. 23 following: Regarding the Riechers et al. study. Do you mean they are the only one who reported droplet size distribution for one given droplet size (i.e. the deviation from a monodisperse droplet distribution)? Maybe clarify
Yes, to our knowledge, among the homogeneous ice nucleation studies, Riechers et al. (2013) provides the most detailed information regarding the size distribution of droplets used in the experiments (i.e, mean and standard deviation) with the data of $f_{frozen\_droplets}$ v.s. temperature. We agree these sentences could be misunderstood and are not necessary in the introduction section, so have removed them.

p. 31871, l. 5: Why should the fluctuation probability be higher in larger volumes? The fluctuation probability is in principle an energy term and thus is independent of volume. It depends on temperature, supersaturation, surface tension but not volume? Since in this parameterization molecular fluxes are not considered, there is no volume dependence. Please elaborate since this statement is not clear from given information.

The fluctuation probability is indeed independent of volume. We agree. Actually, that is not what we meant to say in the original sentence. 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 larger droplet with more molecules *Vp* or at lower temperature when the fluctuation probability *exp()* is higher"

p. 31871, l. 17: Please add a reference at the end of this statement.

The detailed illustration of the kinetic absorption/desorption flux system applied in deriving CNT can be found in Defour and Defay, 1963, P.184-185. We have decided to remove the part discussing ice nucleation rate in this section.

p. 31872, Eq. 3: Why is the decadal log used for the sensitivity of droplet diameter.

The decadal log is used here because the dependence of T_{NC_1} on diameter is not linear, but the dependnece of T_{NC_1} on log10(diameter) is nearly linear as shown in the Fig. 1 of our manuscript. To clarify, following sentence has been added: "As shown in Figure 1, the dependence of T_{NC_1} on $\log_{10}$d is nearly linear, so the decadal log is used here to simply derive the linear dependence."

p. 31876, l. 6-10: Could you clarify this statement? What is the call for more "potentially important dependencies"? If not, maybe avoid this statement.

We have modified the sentence to: "the potential important dependencies such as applied cooling rate, size distribution of droplets and number of observed droplets used in experiments."

p. 31876, l. 19 and following (discussion Fig. 4): There are a couple of points regarding Fig. 4 which may be helpful for the authors: i) I am wondering why the authors did not also plot the data of Swanson, Knopf and Lopez (2009), and Knopf and Rigg (2011), the latter ones being a much more extensive data set? ii) Knopf and Rigg (2011) and Riechers et al., argue that J_hom by Koop et al. (2000) may be ~ 2 orders of magnitude too high. Does this effect interpretations/derivations of this study? iii) The reasoning for the deviation at lower aw is not complete. Abbatt and co-workers observed higher freezing temperatures due to heterogeneous ice nucleation. Swanson observed freezing below the homogeneous freezing line, this usually indicates other issues than a heterogeneous nucleation process. For example, the droplets may have possessed less water than indicated by experimental RH (not in equilibrium, mass transfer, etc.). In addition, at lower aw, the assumption that aw does not change with decreasing temperature may be less "true". See e.g. E-AIM model by Clegg and co- workers. Deviations at low aw could be due to our incomplete understanding of aw for certain aqueous solutions.

(i) and (ii). Thank you for suggesting this. The data from Knopf and Lopez (2009), and Knopf and Rigg (2011) have been added to Fig. 4, and the size ranges used in these studies have been considered into the theoretical derivation of $T_{nc=1}$. In the comparison of the homogeneous freezing temperatures as shown in Fig. 4, there is no pronounced difference among the data of Koop et al. (2000), Knopf and Lopez (2009) and Knopf and Rigg (2011).

(iii)We thank reviewer for the useful and more complete information. The paragraph in P.31876, line 21 has been modified to: "Abbatt et al. (2006) suggests that the disparity of the experimental data for low a_w can be partly attributed to a variety of heterogeneous process, which can result in the higher observed freezing temperatures. In addition, as suggested by knopf and Lopez (2009), the deviations at low water activity may be most likely due to our incomplete understanding of a_w for certain aqueous solutions and the corresponding uncertainties. Future experimental study is…….."

Technical corrections:
p. 31872, l. 11: missing space after first comma.
p. 31874, l. 22: Change “sold” to “solid”.
p. 31875, l. 10: Maybe instead “by” use “using”.
p. 31877, l. 14: Maybe “to” instead “with”.
p. 31878, l. 18: . . .shifted to. . ..
p. 31879, l. 21: ... higher than...
Done. Thanks for the corrections.

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

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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"

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Exploring an approximation for the homogeneous freezing temperature of water droplets

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Abstract

In this work, based on the well-known formulae of classical nucleation theory (CNT), the temperature $T_{N_c=1}$ at which the mean number of critical embryos inside a droplet is unity is derived from the Boltzmann distribution function and explored as an approximation for homogeneous freezing temperature of water droplets. Without including the information of the applied cooling rate $\gamma_{cooling}$ and the number of observed droplets $N_{total\_droplets}$ in the calculation, the approximation $T_{N_c=1}$ is able to reproduce the dependence of homogeneous freezing temperature on drop size V and water activity a_w of aqueous drops observed in a wide range of experimental studies for droplet diameter > 10 μm and a_w > 0.85, suggesting the effect of $\gamma_{cooling}$ and $N_{total\_droplets}$ may be secondary compared to the effect of V and a_w on homogeneous freezing temperatures in these size and water activity ranges under realistic atmospheric conditions. We use the $T_{N_c=1}$ approximation to argue that the distribution of homogeneous freezing temperatures observed in the experiments may be partly explained by the spread in the size distribution of droplets used in the particular experiment. It thus appears that the simplicity of this approximation makes it potentially useful for predicting homogeneous freezing temperatures of water droplets in the atmosphere.

Keywords: classical nucleation theory, homogeneous ice nucleation, freezing temperature

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1. Introduction

Since the summary article of McDonald (1953), it has been widely observed that ice nucleation of water droplets does not occur at the ice melting temperature (e.g. 273.15 K at 1atm), and liquid water is frequently observed in clouds as cold as to 238 K (Rosenfeld and Woodley, 2000; Hu et al., 2010). Laboratory observations of homogeneous ice nucleation in pure water generally show that all droplets do not freeze at exactly the same temperature, and that the fraction of droplets that freeze in a given time is a function of temperature and time (hereafter we refer to this type of experiment as a *fraction experiment*) (e.g. Bigg 1953; Carte 1956; Broto and Clausse, 1976; Earle et al., 2010; Riechers et al., 2013). Here, experimental data of the freezing temperatures of pure water droplets from 15 independent studies over the past 60 years are collected (Fig. 1 and Table 1), showing a clear dependence of freezing temperature upon drop volume across different experiments. Over the investigated size interval (1-1000 μm diameter), observed freezing temperatures range from 232 K to 240 K. The range of freezing temperatures and the volume dependence in Fig. 1 are consistent with the experimental data reviewed in Pruppacher (1995).

On the other hand, solutes, at sufficiently high concentrations, can suppress the homogeneous freezing temperature of water droplets. Koop et al. (2000) showed that the depression of freezing temperature strongly depends on the water activity a_w of the solution droplet, which has been confirmed in several independent experimental studies (e.g. Knopf and Lopez, 2009; Knopf and Rigg, 2011). In this paper, two aforementioned features of homogeneous ice nucleation observed in the experimental data are examined – (1) the volume and water activity dependence of homogeneous

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freezing temperatures of water droplets $T_f(V, a_w)$; (2) the distribution of homogeneous freezing temperatures observed in fraction experiments $f(T_f)$. In this paper, we describe only volume-based nucleation and do not include the droplet surface effects on homogeneous ice nucleation as there remains considerable uncertainty about the importance of surface nucleation (Kay et al., 2003; Duft and Leisner, 2004). The unified explanations of the observed dependencies 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). In our study, based on a cornerstone of classical nucleation theory (CNT), namely that a critical embryo existing in a droplet triggers ice crystal formation, we explore a simple approximation for the homogeneous freezing temperature, and seek a simpler parameterization to describe homogeneous ice nucleation process in the atmosphere. Section 2 describes the approximation; Section 3 gives the comparisons between the theoretical estimates and the experimental data; Section 4 is the discussion; Section 5 is the summary.

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2. Background

2.1 The approximation $T_{N_c=1}(V,a_w)$

According to CNT, the formation of a critical embryo inside a droplet can trigger the freezing process in the droplet. The critical embryo defined as the i-mers having the highest formation energy is formed by the critical fluctuation in orientation of hydrogen bonds (e.g. density fluctuation) (Baker and Baker 2004), which is large enough to provide the formation energy of the critical embryo $\Delta F_c(T,a_w)$ and remove metastability of supercooled water. The probability of occurrence of the critical fluctuation is $\exp(\frac{-\Delta F_c(T,a_w)}{k_B T})$ (Landau and Lifshitz, 1980, P.472-473; Pruppacher and Klett, 1997), and thus the *mean number* of the critical embryos inside a water droplet in thermal equilibrium can be predicted by a Boltzmann distribution (Landau and Liftshitz, 1958, P.107; Vali, 1999),

$$N_{c\_mean}(V,a_w,T) = V\rho\exp(\frac{-\Delta F_c(T,a_w)}{k_B T}) \quad (1)$$

where V is the volume of the droplet, ρ is the number density of water molecules, k_B is Boltzmann's constant, T is the temperature of the droplet, and $\Delta F_c(T,a_w)$ is the formation energy of the critical embryo in the droplet with water activity a_w at T, which will be discussed in detail in Sect. 2.2. The Boltzmann distribution form of the critical embryo is derived from the partitioning function of the grand canonical ensemble, and it should be noted that the derived particle number of the Boltzmann distribution function is not a "constant" but is a "mean" number (detailed derivation and explanations can be found in Landau and Liftshitz, 1958, P.107 and Sadovskii, 2012, Chapter 3.1).

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The total freezing time $\tau_{freezing}$ of a water droplet can be split conceptually into three stages – (1) $\tau_{meta\_remove}(\sim \frac{1}{J})$ the time needed for the occurrence of the critical fluctuation (2) $\tau_{formation}$ the time needed to form a critical embryo and (3) $\tau_{growing}$ the growing time for the critical embryo expanding to the whole droplet body. These depend on V, a_w and T of the droplet (Pruppacher and Klett 1997; Bauerecker et al., 2008). To observe freezing of droplets with volume V and water activity a_w occurring at temperature T, the residence time of freezing experiments $\tau_{residence}$ at T has to be longer than $\tau_{freezing}(V, a_w, T)$, resulting in a dependence of the homogeneous freezing temperature on the cooling rate $\gamma_{cooling}$ of droplets in principle. According to the theoretical estimates (see Pruppacher and Klett 1997, P.678), the time scale of $\tau_{formation} + \tau_{growing}$ for the size of the droplets investigated here is short compared with the typical residence times in the laboratory studies. Thus, the dominant factor determining the homogeneous freezing temperatures is τ_{meta_remove}. 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 larger droplet with more molecules $V\rho$ or at lower temperature when the fluctuation probability $\exp(\frac{-\Delta F_c(T, a_w)}{k_B T})$ is higher; $\tau^{-1}_{meta\_remove} \propto N_{c\_mean}(V, a_w, T)$. Embryo interaction is a stochastic process and $N_{c\_mean}(V, a_w, T)$ simply expresses the 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

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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*. Based on above-mentioned principles, the homogenous freezing temperature of water droplets and τ_{meta_remove} can each be written as a function of V, a_w, $\gamma_{cooling}$ and $N_{total\_droplets}$, namely $T_f(V, a_w, \gamma_{cooling}, N_{total\_droplets})$ and $\tau_{meta\_remove}(V, a_w, \gamma_{cooling}, N_{total\_droplets})$.

Koop et al. (1998) reported that observed homogeneous freezing temperatures do not significantly depend on $\gamma_{cooling}$ of the droplets for $\gamma_{cooling}$ smaller than 20 K min^{-1} (corresponding to vertical velocities 33.3 m s^{-1} in clear air). The results of Koop et al. (1998) actually indicate that the slope of $\frac{\partial \tau_{meta\_remove}}{\partial T}$ is very steep at the temperature when the scale of τ_{meta_remove} is close to $\tau_{residence}$ in most practical experiments and realistic atmospheric conditions, resulting in the small dependence of T_f on $\gamma_{cooling}$ as suggested by Brewer and Palmer (1951). Based on that, in most of the practical freezing experiments and realistic atmospheric conditions ($\gamma_{cooling}$ < 20 K min^{-1}), the observed homogeneous freezing temperatures can be considered as a threshold temperature when $\frac{\partial \tau_{meta\_remove}}{\partial T} \rightarrow \infty$. In this study, we intend to find this threshold temperature directly from the information given by $N_{c\_mean}(V, a_w, T)$. 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

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To simplify the ice nucleation model, CNT assumes that

To simplify the ice nucleation model, CNT assumes that the adsorption/desorption process of molecules can represent the formation process of the embryo, and the embryo can only grow via bonding with monomolecules (Defour and Defay, 1963). The activation energy for the transfer of a water molecule across the water–ice boundary ΔG_a is required for the calculation of adsorption flux, which is a highly uncertain parameter (Ickes et al., 2015), and the agreements between the observed freezing temperatures and the theoretical estimates derived by CNT always rely on the fitting of ΔG_a to data such as that in Fig. 1 (e.g.

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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). Nevertheless, since the formation of one critical embryo is required to trigger the ice nucleation process in a droplet, $T_{N_c=1}$ may be a good approximation for the threshold temperature, the temperature at which the mean number of the critical embryos inside a droplet is unity, which can be given by

$$N_{c\_mean} = 1 = V\rho \exp\left(\frac{-\Delta F_c(T_{N_c=1}, a_w)}{k_B T_{N_c=1}}\right) \qquad (2)$$

According to the formula of $\Delta F_c(T, a_w)$, $T_{N_c=1}$ is determined by V and a_w of the droplet, namely $T_{N_c=1}(V, a_w)$. Figure 2 shows the mean number of critical embryos inside a pure water droplet ($a_w = 1$) at different temperatures using Eq. (1) (see next section for details of $\Delta F_c(T, a_w)$ used in the calculation). It indicates that smaller droplets require lower temperatures to reach the state that $N_{c\_mean} = 1$, showing the volume dependence of $T_{N_c=1}(V, a_w)$. Figure 3 shows the mean number of critical embryos inside a solution droplet with different values of water activity. The result indicates that more concentrated solution droplets (lower a_w) need lower temperature to reach the state that $N_{c\_mean} = 1$. This represents the solution effect on $T_{N_c=1}(V, a_w)$. The sensitivity of $T_{N_c=1}(V, a_w)$ to the variation of diameter δd and water activity δa_w of droplets can be written as

$$\delta T_{N_c=1} = \frac{\partial T_{N_c=1}}{\partial a_w}\delta a_w + \frac{\partial T_{N_c=1}}{\partial \log_{10} d}\delta \log_{10} d \qquad (3)$$

where d is the diameter of droplet (μm). As shown in Fig. 1, the dependence of $T_{N_c=1}$ on $\log_{10} d$ is nearly linear, so the decadal log is used here to simply derive the

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linear dependence. The values of $\frac{\partial T_{N_c=1}}{\partial a_w}$ and $\frac{\partial T_{N_c=1}}{\partial \log_{10} d}$ are about 216 K and 2.5 K respectively over the investigated interval of water activity and drop size, which are derived numerically from Eq. (2).

2.2 Formation energy of the critical embryo $\Delta F_c(T, a_w)$

The formation energy of the critical embryo $\Delta F_c(T, a_w)$ can be written as

$$\Delta F_c = \frac{1}{3} s \sigma_{i/w}(T, a_w) r_c^2 \qquad (4)$$

$$r_c = \frac{2\sigma_{i/w}(T, a_w) v_1^{water}}{k_B T \ln(\frac{e_{sw} a_w}{e_{si}}) + k_B T \ln(a_w)} \qquad (5)$$

where $\sigma_{i/w}(T, a_w)$ is the interfacial energy between liquid water and solid ice, s is the shape factor of the embryo (~ 21 by assuming the shape is hexagonal prism), r_c is the radius of the critical embryo, v_1^{water} is the volume of single water molecule, e_{sw} and e_{si} are the saturation vapor pressures over water and ice respectively (Murphy and Koop, 2005), and a_w is the water activity of the solution droplet (see detailed derivations of Eq. (4) in Defour and Defay, 1963 and Pruppacher and Klett, 1997). It should be noted that the term $k_B T \ln(a_w)$ in r_c (Eq. (5)) is the *entropy of unmixing* which originates from the change of the Gibbs free energy of the bulk solution during freezing, and is usually neglected in the previous theoretical studies (Bourne and Davey, 1976; Black 2007). Barahona (2014) pointed out that although this term is small for dilute solution, it should not be neglected when applying to high concentration solution droplets (see Eq. (8) in Barahona (2014)).

The value of interfacial energy between liquid water and solid ice $\sigma_{i/w}(T, a_w)$ is needed for our calculation of Eq. (4) and (5). As most studies suggest that the

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temperature dependence of $\sigma_{i/w}(T,a_w)$ should be linear (Ickes et al., 2015), and that increasing the concentration of the solution droplet increases the value of $\sigma_{i/w}(T,a_w)$ (Jones and Chadwick, 1971; Alpert et al. 2011), $\sigma_{i/w}(T,a_w)$ can be written as

$$\sigma_{i/w}(T,a_w) = \sigma_{i/w,e} + \frac{\partial\sigma_{i/w}}{\partial T}(T - T_0) + \frac{\partial\sigma_{i/w}}{\partial a_w}(1 - a_w) \quad (6)$$

where $\sigma_{i/w,e}$ is the interfacial energy at the equilibrium temperature of pure ice-water, and T_0 is the equilibrium temperature. The direct measurement of $\sigma_{i/w}(T,a_w)$ is extremely difficult, so most of the estimations are based on combinations of CNT and laboratory measurements of T_f and observed freezing rate to retrieve the values of $\sigma_{i/w}(T,a_w)$ (e.g. Zobrist et al., 2007; Murray et al., 2010). These studies have shown considerable diversity in the reported estimations of $\sigma_{i/w}(T,a_w)$ (Ickes et al., 2015). Instead, we use values of $\sigma_{i/w,e}$ and $\frac{\partial\sigma_{i/w}}{\partial T}$ derived from a state-of-the-art molecular dynamics model that explicitly simulates the molecular configurations under supercooling conditions. Benet et al. (2014) gives values of $\sigma_{i/w,e}$ from the TIP4P water model ($\sigma_{i/w,e}$=26.5×10^{-3} J m^{-2}), TIP4P/2005 water model ($\sigma_{i/w,e}$=27×10^{-3} J m^{-2}), and TIP4P-Ew water model ($\sigma_{i/w,e}$=27.5×10^{-3} J m^{-2}), and these three values will all be used in our calculations. 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. Regarding $\frac{\partial\sigma_{i/w}}{\partial T}$, Espinosa et al. (2014) provided an average value of 0.25 × 10^{-3} (J m^{-2} K^{-1}) from three different water molecular models (TIP4P/ICE, TIP4P and TIP4P/2005) down to a supercooling of about 30K. Regarding $\frac{\partial\sigma_{i/w}}{\partial a_w}$, Barahona (2014) proposed a new thermodynamic framework approximating the interfacial energy of ice-solution by assuming the interface between solid ice and liquid water is

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made of liquid molecules trapped by the solid matrix, which gives the relationship between $\sigma_{i/w}$ and a_w. Based on this approximation, the solution effect on the interfacial energy can be written as

$$\frac{\partial \sigma_{i/w}}{\partial a_w} = -\frac{\Gamma_w^2 s_{area} k_B T \frac{1}{a_w}}{(36\pi (v_1^{water})^2)^{1/3}} \qquad (7)$$

where Γ_w is the surface excess of water (~1.46) (Spaepen 1975) and s_{area} is the surface area parameter (~1.105 $mol^{2/3}$) (see Barahona 2014 for details). The values of $\sigma_{i/w}(T, a_w)$ estimated from above studies are used to derive the numerical result $T_{N_c=1}(V, a_w)$ presented here.

3. Results – Comparison between the approximation and the experimental data

3.1 Volume and water activity dependence of $T_f(V, a_w)$

To test our approximation, we aim to compare the observed $T_f(V, a_w)$ and $f(T_f)$ with $T_{N_c=1}(V, a_w)$ derived using the constraint in Eq. (2). First, $T_{N_c=1}(V, a_w = 1)$ of pure water droplet is derived. Figure 1 shows the comparison between the experimentally determined homogeneous freezing temperatures $T_f(V, a_w = 1)$ (details of the experiments are provided in Table 1) and the approximations $T_{N_c=1}(V, a_w = 1)$. For droplet diameters > 10μm, the theoretical values of $T_{N_c=1}(V, a_w = 1)$ 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 about 1~2 K of $T_{N_c=1}(V, a_w = 1)$. There is one study regarding the time dependence should be

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mentioned. The laboratory observation of Murray et al. (2010) (black triangle in Fig. 1) showed that varying of cooling rate from 2.5 K min^{-1} to 10 K min^{-1} corresponds to a shift of 0.5 K to 1 K in observed freezing temperatures of pure water droplets, and our best agreement estimates $T_{N_c=1}(V, a_w = 1)$ can only explain the experimental data with slowest cooling rate (2.5 K min^{-1}). The finding of Murray et al. (2010) will be discussed in Sect. 4. For droplets smaller than 10 μm (diameter), there are obvious deviations of observed freezing temperatures among the experimental studies. These studies do not provide enough information regarding $\gamma_{cooling}$, $N_{total\_droplets}$ and the spread in drop size, so we cannot evaluate what causes the disparity. We suggest that freezing experiments of pure droplets smaller than 10 μm (diameter) need more refinement and should report the potentially important dependencies such as applied cooling rate, size distribution of droplets and number of observed droplets used in experiments.

Second, the solution effect on homogeneous freezing temperature $T_f(V, a_w)$ is explored by changing the water activity in Eq. (5) and (6) to derive the approximation $T_{N_c=1}(V, a_w)$, which will be compared with the experimental data collected in Koop et al. (2000), Knopf and Lopez (2009) and Knopf and Rigg (2011). Size of the droplets used in the collected experimental data ranges from 1 μm to 10 μm in Koop et al. (2000), from 10μm to 80μm in Knopf and Lopez (2009) and from 20μm to 80μm in Knopf and Rigg (2011), and these sizes are included to calculate the approximation $T_{N_c=1}(V, a_w)$. Figure 4 shows the comparison between the experimental data and the approximation $T_{N_c=1}(V, a_w)$. 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

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feature (i.e. $N_{total\_droplets}$), the result shows that the approximation $T_{N_c=1}(V, a_w)$ is in good agreement with the experimental data for $a_w > 0.85$. The scattering of the experimental data between the theoretical estimates for $a_w > 0.85$ (i.e. $T_{N_c=1}$ 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. For the solution droplets with high concentration ($a_w < 0.85$), the observed freezing temperatures show considerable spread. Abbatt et al. (2006) suggests that the disparity of the experimental data for low a_w can be partly attributed to a variety of heterogeneous process, which can result in the higher observed freezing temperatures. In addition, as suggested by knopf and Lopez (2009), the deviations at low water activity may be most likely due to our incomplete understanding of a_w for certain aqueous solutions and the corresponding uncertainties. Future experimental study is suggested to focus on the freezing process of solution droplets with high solute concentration ($a_w < 0.85$) to clarify the causes of the disparity.

Regarding the experimental uncertainty, Knopf and Lopez (2009) reported that the value of a_w for supercooled aqueous solutions has the experimental uncertainty δa_w of about ± 0.01, which can results in the variation in $T_{N_c=1}$ of about ± 2 K based on Eq. (3). Riechers et al. (2013) reported that the size of droplets produced by the microfluidic device used in their experiment has three standard deviations (99.7%) of about 18 μm to 33 μm in diameter, which can cause the variation in $T_{N_c=1}$ of about ± 0.2 K to ± 0.5 K based on Eq. (3). Therefore, the variation in $T_{N_c=1}$ caused by the experimental uncertainties δa_w and δd can be both substantial and should not be

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neglected. We suggest future experimental studies should provide detailed information regarding experimental uncertainties δa_w and δd for the purpose of better constraining the observed freezing temperatures.

3.2 Fraction of frozen pure water droplets as a function of temperature $f(T_f)$

To further examine the application of $T_{N_c=1}(V, a_w)$ in homogeneous ice nucleation, $T_{N_c=1}(V, a_w)$ is compared to the experimental data of the fraction experiment of Riechers et al. (2013). 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 $f(T_f)$. In other words, the size distribution of droplets used in a given experiment may be an important factor governing the observed spread of freezing temperatures (i.e. dotted line shown in Fig. 1). To test this, we incorporate the reported droplet size distribution width into the numerical calculation. Unique among such studies, Riechers et al. (2013) report both the spread of homogeneous freezing temperatures and the mean μ and standard deviation σ of droplet size. According to Eq. (3), the spread in the size distribution of water droplets will result in a spread in the fraction of frozen droplets because larger droplets have higher $T_{N_c=1}(V, a_w)$ (i.e. require less supercooling to freeze). Given the droplet size width, the distribution of the approximations $T_{N_c=1}(V, a_w)$ of droplets can be derived from Eq. (2). Given a

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Gaussian distribution of drop sizes, we estimate the fraction of drops that will freeze at a given temperature *solely by assuming that the spread in freezing temperatures arises from the spread in droplet sizes* based on Eq. (3). For example, we estimate $T_{N_c=1}(V,a_w)$ of the droplets with size of μ+3σ (~ the largest 0.15% of the drops) as the theoretical onset freezing temperature T_f^{onset}, $T_{N_c=1}(V,a_w)$ of the droplets with size of μ+1.64σ (≈ the largest 10% of the drops) as the theoretical estimates $T_f^{10\%}$, $T_{N_c=1}(V,a_w)$ of the droplets with mean size as the theoretical estimates $T_f^{50\%}$, and $T_{N_c=1}(V,a_w)$ of the droplets with size of μ-1.64σ (≈ the smallest 10% of the drops) as the theoretical estimates $T_f^{90\%}$, and $T_{N_c=1}(V,a_w)$ of the droplets with size of μ-3σ (≈ the smallest 0.15% of the drops) as the theoretical estimates T_f^{end}. The results presented in this section only use the value of $\sigma_{i/w,e}$ from the TIP4P water model, which has the best agreement with the experimental data shown in Sect. 3.1 (Fig. 1).

There are five experimental results from Riechers et al. (2013), each with different μ and σ. The comparisons (Fig. 5 and Table 2) show that our estimates match the experimental data fairly well. The slope of the freezing fraction versus temperature in the theoretical results is driven entirely by the reported spread in the size distribution of drops and matches fairly well with the observed slope, although across the experiments the theoretical slope is somewhat greater (observed values are shifted to the right of the blue curve at the higher temperatures but mostly to the left at the lower temperature), which might be attributable to the stochastic feature of the ice nucleation process. That said, the observational uncertainties in the experimental values of T_{on-set}, $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ more or less span the theoretical values derived from Eq. (2). Riechers et al. (2013) also reported that during cooling, the

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majority of the droplets are frozen over a temperature interval of 0.84-0.98 K, which is consistent with the range between the theoretical estimates T_f^{onset} and T_f^{end} derived here, namely 0.42-1.06 K from five different droplet size distributions, 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.

The comparison made in Sect. 3.1 to 3.2 shows that the distribution of the freezing temperatures among the data can mostly be explained by the dependence of $T_{N_c=1}(V,a_w)$ on V and a_w for droplet diameter > 10 µm and a_w > 0.85 without considering the dependence of homogeneous freezing temperature on $N_{total\_droplets}$ and $\gamma_{cooling}$ in the calculations. It suggests that in most of the practical experiments and for most atmospheric conditions, the time scale of $\tau_{residence}$ is shorter than τ_{meta_remove} at the temperatures higher than $T_{N_c=1}(V,a_w)$ (i.e. $\tau_{residence} < \tau_{meta\_remove}$, when $T > T_{N_c=1}(V,a_w)$), and when the temperature of the droplets is close to $T_{N_c=1}(V,a_w)$, the time scale of τ_{meta_remove} decreases strongly with temperature decreases and becomes shorter than $\tau_{residence}$ of the experiments (i.e. $\tau_{residence} > \tau_{meta\_remove}$ when $T < T_{N_c=1}(V,a_w)$). This leads to the result that most of the homogeneous ice nucleation process can only be observed at temperatures close to $T_{N_c=1}(V,a_w)$ even though in principle, droplets can be frozen at any temperature.

4. Discussion

As mentioned in Sect. 2, the observed freezing temperatures with $\gamma_{cooling}$ ~ 2.5 K min^{-1} reported in Murray et al. (2010) can be well described by $T_{N_c=1}(V,a_w)$, but it

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also showed there is a shift of 0.5 K to 1 K in observed freezing temperatures when varying the cooling rate from 2.5 K min^{-1} to 10 K min^{-1}. One possibility is that the total freezing time $\tau_{freezing}$ needed to freeze a droplet at $T_{N_c=1}(V,a_w)$ is longer than the time scale of $\tau_{residence}$ when $\gamma_{cooling}$ is higher than 2.5 K min^{-1}, which may be attributed to τ_{meta_remove}, $\tau_{formation}$ or $\tau_{growing}$. Without considering the experimental uncertainty associated with the thermal equilibrium time $\tau_{thermal}$, these 0.5K to 1K shifts corresponds to 3s to 6s shifts (for $\gamma_{cooling}$ = -10 K min^{-1}), which may be partly caused by $\tau_{formation}+\tau_{growing}$. Bauerecker et al. (2008) (hereafter Ba08) explored an advanced method providing time series of water droplet temperature during the entire cooling and freezing process (from supercooled water to completely freezing) using an infrared camera. The results of Ba08 showed that for the droplet sized 3mm (diameter), $\tau_{growing}$ is around 20s and $\tau_{thermal}$ is around 60s. The droplet used in Ba08 is much larger than the size normally used in the freezing experiments because of the limitation of IR camera sensitivity. If $\tau_{growing}$ linearly depends on drop radius, we may expect it to be several tenths of a second for the drops sized 10-100 μm in diameter. We suggest that the infrared camera technique should be used more widely in the future experimental studies of ice nucleation with smaller droplets, which can add significant insights into the time dependence study of ice nucleation, and clarify the importance of τ_{meta_remove}, $\tau_{formation}$ and $\tau_{growing}$ observed in the experiments. On the other hand, Koop et al. (1998) suggested that when the cooling rate is smaller than about 2K min^{-1}, mass transport of water can take place between the frozen ice particles and supercooled droplets, but if the cooling rate is too large, it can cause an offset between the measured temperature and the actual temperature of the drops,

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which can both cause a bias of the observed freezing temperatures. Therefore, we suggest that in future experimental studies, in order to precisely measure $\frac{\partial T_f}{\partial \gamma_{cooling}}$, potential biases at high cooling rate and the shift caused by $\tau_{formation} + \tau_{growing}$ should be better constrained. Since Koop et al. (1998) and Murray et al. (2010) showed different dependencies of homogeneous freezing temperatures on $\gamma_{cooling}$, future experiments should reexamine and perform the same experiments for $\gamma_{cooling} >$ 2.5 K min^{-1}. 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 <10μm), and future experiments are suggested to emphasize these droplet size and water activity ranges.

5. Summary

The limitation of our method proposed here is that the time dependence and the stochastic feature of homogeneous freezing temperature cannot be considered because the Boltzmann distribution applied here is a average distribution and does not provide any information regarding time. Combining the well-known Boltzmann distribution function for the mean number of critical embryos $N_{c\_mean}(V, a_w, T)$ and their formation energy $\Delta F_c(T, a_w)$ from CNT formulae, $T_{N_c=1}(V, a_w)$ is derived as a function of volume and water activity of water droplets. With the comparison made in Sect. 3.1 to 3.2, it can be summarized that under most atmospheric conditions, homogeneous freezing temperatures can be well described by the new approximation $T_{N_c=1}(V, a_w)$ proposed here without considering information of the applied cooling

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rate (i.e. time dependence) and the number of droplets used in the experiment (i.e. stochastic feature) for d > 10μm and a_w > 0.85. Future experimental study is suggested to focus on the homogeneous freezing process of droplets with high solute concentration ($a_w < 0.85$) and small volume (d < 10μm). The experimental spread in homogeneous freezing temperatures of water droplets may be partly explained by the size distribution of droplets used in the experiments. The advantage of our approximation in the cloud modeling is "the temperature history" of droplets is not required to calculate the homogeneous freezing temperature as it is when using the ice nucleation rate (i.e. Eq. (7-71) in Pruppacher and Klett, 1997). When using the ice nucleation rate $J(T(t))$, the complete temperature history of droplets is needed to calculate the integration of $J(T(t))$ with respect to time in order to consider the time dependence and the stochastic feature, which can introduce considerable complexity in cloud modeling. However, based on the experimental studies of homogeneous freezing temperature collected and discussed in our study, we suggest in most of the practical experiments and realistic atmospheric conditions (i.e. $\gamma_{cooling} <$ 20 K min^{-1}), the time dependence and the stochastic feature of homogeneous freezing temperature may be a secondary factor compared to the effect of volume and water activity for droplet diameter > 10 μm and a_w > 0.85. The approximation proposed here is relatively simpler to be implemented into cloud models and may improve the representation of homogeneous ice nucleation in the atmosphere.

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Acknowledgements

The authors gratefully appreciate helpful discussion with Marcia Baker, Daniel Cziczo and Sarvesh Garimella who provided important insight and guidance for this study. Two anonymous reviewers are thanked for providing important feedback that helped to improve the paper. The authors thank Thomas Koop for his help in supplying the data in Figure 4.

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References	Diameter (µm)	T_f (K)	Diameter Range (µm)	Range of freezing temperatures (K)	Cooling rate	Uncertainty (K)
Pound et al. (1953)	30[+]	233.15[a]	[10 50]	[231.15 235.15]	n/a	n/a
Mossop (1955)	530[+]	238.65[a]	[220 840]	[238.65 242.15]	0.5K/ min	0.2
Carte (1956)	15[+]	236.25[a]	[10 20]	[235.15 237.15]	1K/min	0.2
	231.3[d]	238.45[b]	n/a	n/a	0.5K/min	0.2
	279.4[d]	238.55[b]	n/a	n/a	0.5K/min	0.2
	292.9[d]	238.35[b]	n/a	n/a	0.5K/min	0.2
	321.9[d]	238.45[b]	n/a	n/a	0.5K/min	0.2
	362.2[d]	238.55[b]	n/a	n/a	0.5K/min	0.2
	427.3[d]	238.65[b]	n/a	n/a	0.5K/min	0.2
	469.7[d]	238.55[b]	n/a	n/a	0.5K/min	0.2
	498.2[d]	238.95[b]	n/a	n/a	0.5K/min	0.2
	567.3[d]	238.95[b]	n/a	n/a	0.5K/min	0.2
	623.6[d]	238.85[b]	n/a	n/a	0.5K/min	0.2
	718.5[d]	238.85[b]	n/a	n/a	0.5K/min	0.2
	818.1[d]	238.95[b]	n/a	n/a	0.5K/min	0.2
	965.2[d]	239.15[b]	n/a	n/a	0.5K/min	0.2
	1179.8[d]	239.45[b]	n/a	n/a	0.5K/min	0.2
	1408.4[d]	239.65[b]	n/a	n/a	0.5K/min	0.2
Langham and Mason (1958)	66.1[d]	237.35[a]	n/a	n/a	0.33K/min	n/a
	92.3[d]	237.65[a]	n/a	n/a	0.33K/min	n/a
	115.3[d]	238.15[a]	n/a	n/a	0.33K/min	n/a
	144[d]	238.25[a]	n/a	n/a	0.33K/min	n/a
	171.8[d]	238.15[a]	n/a	n/a	0.33K/min	n/a
	270.5[d]	238.55[a]	n/a	n/a	0.33K/min	n/a
Hoffer (1961)	110[+]	236.55[a]	[100 120]	[235.65 238.15]	1K/min	0.5
	130[+]	237.25[a]	[125 145]	[235.65 238.15]	1K/min	0.5
Kuhns and Mason (1967)	1[d]	233.05[a]	n/a	n/a	6K/min	0.1
	5[d]	234.65[a]	n/a	n/a	6K/min	0.1
	8[d]	235.15[a]	n/a	n/a	6K/min	0.1
	10[d]	235.45[a]	n/a	n/a	6K/min	0.1
	20[d]	236.15[a]	n/a	n/a	6K/min	0.1
	30[d]	236.75[a]	n/a	n/a	6K/min	0.1

	40[d]	237.05[a]	n/a	n/a	6K/min	0.1
	50[d]	237.25[a]	n/a	n/a	6K/min	0.1
	60[d]	237.35[a]	n/a	n/a	6K/min	0.1
	70[d]	237.45[a]	n/a	n/a	6K/min	0.1
	80[d]	237.55[a]	n/a	n/a	6K/min	0.1
	90[d]	237.65[a]	n/a	n/a	6K/min	0.1
	100[d]	237.65[a]	n/a	n/a	6K/min	0.1
	120[d]	237.65[a]	n/a	n/a	6K/min	0.1
Broto and Clausse (1976)	3[d]	234.35[a]	n/a	n/a	1.25K/min	0.5
Cziczo and Abbatt (1999)	0.35[d]	234.15[d]	n/a	n/a	n/a	n/a
Bertram et al. (2000)	8.3[+]	235[a]	[5.6 11.0]	n/a	10k/min	1.5
Prenni et al. (2001)	0.6[+]	234.95[d]	n/a	n/a	1K/increment	0.2
Larson and Swanson (2006)	40[+]	237.15[a]	[30 50]	n/a	n/a	n/a
Stan et al. (2009)	80 [d]	236.25[a]	n/a	[235.35 237.15]	2~100K/sec	0.21
Earle et al. (2010)	2[+]	236.35[a]	[0.8 4]	[236 236.75]	n/a	n/a
	3.4[+]	236.35[a]	[1.2 10]	[236 236.75]	n/a	n/a
	5.8[+]	236.15[a]	[2 14]	[235.5 236.75]	n/a	n/a
Murray et al. (2010)	25[+]	236.25[a]	[10 40]	[235.9 236.7]	2.5K/min	0.6
	25[+]	236.05[a]	[10 40]	[234.75 237.75]	5K/min	0.6
	25[+]	235.75[a]	[10 40]	[236.45 237.75]	7.5K/min	0.6
	25[+]	235.51[a]	[10 40]	[234.45 237.75]	10K/min	0.6
Riechers et al. (2013)	53[m]	236.65[c]	[35 71]	[236.55 237.44]	1K/min	0.3
	63[m]	236.65[c]	[33 93]	[236.49 237.5]	1K/min	0.3
	82[m]	236.85[c]	[58 106]	[236.67 237.63]	1K/min	0.3
	85[m]	237.15[c]	[67 103]	[236.93 237.77]	1K/min	0.3
	96[m]	237.35[c]	[63 129]	[236.89 237.91]	1K/min	0.3

Table 1. Information regarding the details of the homogeneous ice nucleation experiments used in the comparison, including the size, the freezing temperature, as well as the cooling rate and uncertainty of the experiments. Homogeneous freezing temperature T_f, <a>: freezing temperature when half of the water droplets freezing $T_{50\%}$, <b>: freezing temperature when 95% of the water droplets freezing $T_{95\%}$, <c>: freezing temperature when most of the droplets freezing (peak signal) T_{Mode}, and <d>: not defined or provided by the experiments. Diameter of water droplets used in the

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experiments, <+> median size, <m> mean size, and <d> not provided by the experiments.

Diameter μ±σ	96±11(μm)		85±6 (μm)		82±8 (μm)	
	Experiment values (K)	$T_{N_c=1}$ (K)	Experiment values (K)	$T_{N_c=1}$ (K)	Experiment values (K)	$T_{N_c=1}$ (K)
T_f^{onset}	237.91± 0.2	237.74	237.77± 0.2	237.53	237.63± 0.2	237.55
$T_f^{10\%}$	237.87± 0.2	237.59	237.76± 0.2	237.43	237.63± 0.2	237.42
$T_f^{50\%}$	237.4± 0.3	237.46	237.28± 0.3	237.34	237.13± 0.3	237.31
$T_f^{90\%}$	236.89± 0.3	237.31	236.93± 0.3	237.25	236.67± 0.3	237.18
T_f^{end}	N/A	237.05	N/A	237.11	N/A	236.97
Diameter μ±σ	63±10 (μm)		53±6 (μm)			
	Experiment values (K)	$T_{N_c=1}$ (K)	Experiment values (K)	$T_{N_c=1}$ (K)		
T_f^{onset}	237.50± 0.2	237.43	237.44± 0.2	237.17		
$T_f^{10\%}$	237.46± 0.2	237.23	237.40± 0.2	237.02		
$T_f^{50\%}$	236.94± 0.3	237.05	236.94± 0.3	236.88		
$T_f^{90\%}$	236.49± 0.3	236.83	236.55± 0.3	236.72		
T_f^{end}	N/A	236.4	N/A	236.46		

Table 2. Comparison between the experimental results of the fraction experiment

from Riechers et al. (2013) and the theoretical estimates $T_{N_c=1}$ derived here.

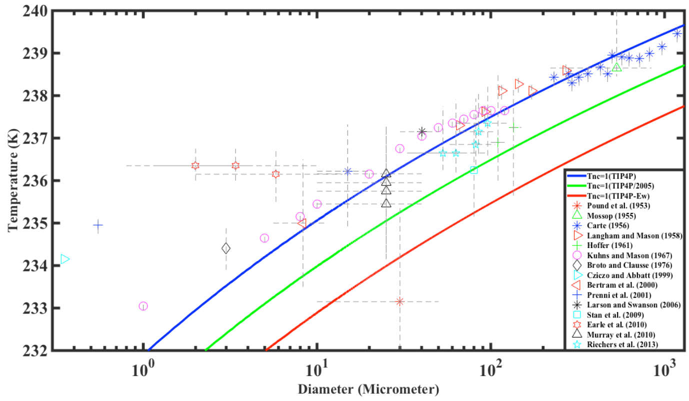

Figure 1. Freezing temperatures of pure water droplets: comparison between the approximations $T_{N_c=1}(V, a_w = 1)$ and the collected experimental data. Experimental data: the uncertainties and ranges of the drop size and the freezing temperatures are presented by the dotted line if information is provided by the studies (details in Table 1). The approximations $T_{N_c=1}(V, a_w = 1)$: blue line - $\sigma_{i/w,e}$ from TIP4P model, green line - $\sigma_{i/w,e}$ from TIP4P/2005 model and red line - $\sigma_{i/w,e}$ from TIP4P- Ew model.

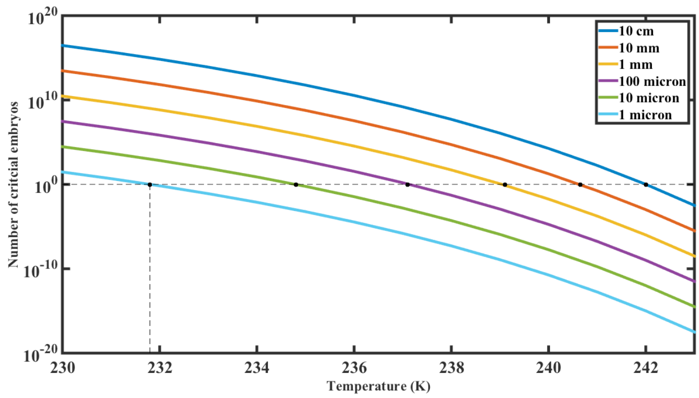

Figure 2. Mean number of critical embryos N_{c_mean} (by Eq. (1)) in a pure water droplet ($a_w = 1$) with different size (diameter) as a function of temperature. Solid circle: the approximations $T_{N_c=1}(V, a_w)$ derived by Eq. (2) (using $\sigma_{i/w,e}$ from TIP4P model).

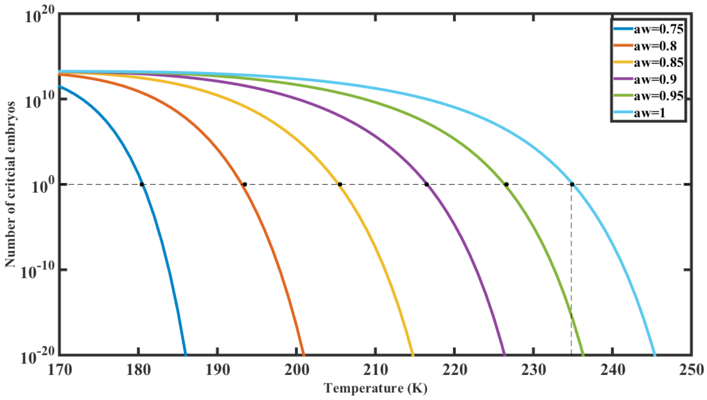

Figure 3. Mean number of critical embryos N_{c_mean} (by Eq. (1)) in a solution droplet (diameter=1μm) with different water activity as a function of temperature. Solid circle: the approximations $T_{N_c=1}(V, a_w)$ derived by Eq. (2) (using $\sigma_{i/w,e}$ from TIP4P model).

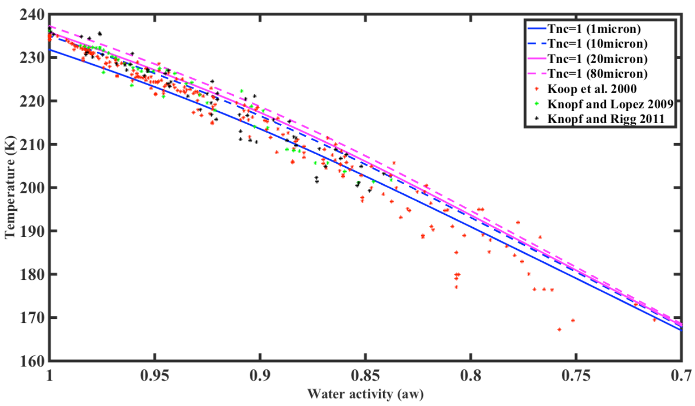

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Figure 4. Comparison between the experimental data of freezing temperatures of solution droplets (Koop et al. 2000; Knopf and Lopez, 2009; Knopf and Rigg, 2011) and the approximation $T_{N_c=1}(V, a_w)$.

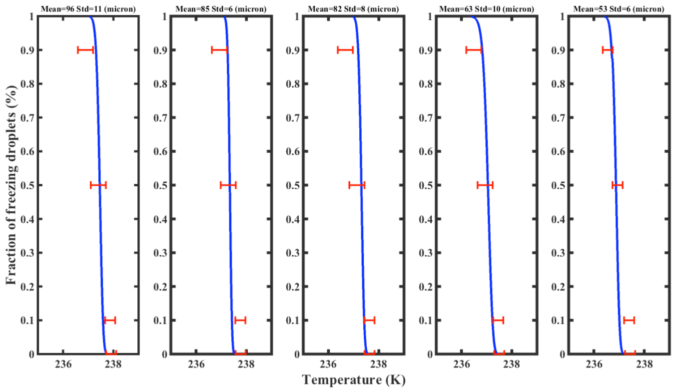

Figure 5. Comparison between the experimental results of the fraction experiment from Riechers et al. (2013) and the theoretical estimates derived here. Red: experimental results with uncertainties from Riechers et al. (2013). Blue: theoretical estimates ($\sigma_{i/w,e}$ from TIP4P model).

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Within CNT, to derive τ_{meta_remove} from $N_{c\_mean}(V,a_w,T)$, and thereby include the stochastic nature of ice nucleation process, the kinetic adsorption/desorption flux system of molecule is applied to derive the ice nucleation rate J_{ice}.

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To simplify the ice nucleation model, CNT assumes that the adsorption/desorption process of molecules can represent the formation process of the embryo, and the embryo can only grow via bonding with monomolecules (Defour and Defay, 1963). The activation energy for the transfer of a water molecule across the water–ice boundary ΔG_a is required for the calculation of adsorption flux, which is a highly uncertain parameter (Ickes et al., 2015), and the agreements between the observed freezing temperatures and the theoretical estimates derived by CNT always rely on the fitting of ΔG_a to data such as that in Fig. 1 (e.g. Pruppacher 1995).

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are about 1-2 K lower than the experimental data $T_f(V,a_w=1)$. The volume dependence of $T_{N_c=1}(V,a_w=1)$ derived by the values of $\sigma_{i/w,e}$ from three different water models all compare remarkably well with the experimental data (slope of Fig. 1), and different values of $\sigma_{i/w,e}$ only lead to a shift up and downward of the theoretical estimates $T_{N_c=1}(V,a_w=1)$. From the comparison made in Fig. 1, as suggested by Koop et al. (1998), the varying of $\gamma_{cooling}$ from 0.3 K min^{-1} to 10 K min^{-1} (corresponding to vertical velocities between 0.5 m s^{-1} and 16.6 m s^{-1} in clear air) among most of the collected data does not cause an significant variation in $T_f(V, a_w = 1)$ and after considering the uncertainty and the freezing ranges (dotted lines in Fig. 1) of the experiments, most of the data are in good agreement with $T_{N_c=1}(V, a_w = 1)$ .However,

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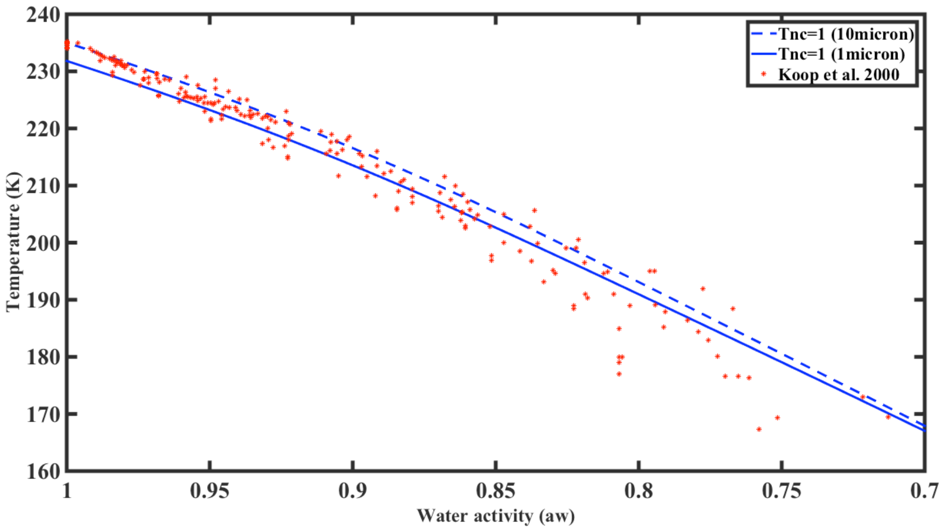

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