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.* $\overline{n_k}=a\exp(-\varepsilon_k/T)$ *(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* $\overline{n_k} = kT\partial \log Z_k/\partial\mu$ *"*, 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 $V\rho$ 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”

References

Abbatt, J. P., Benz, S., Cziczo, D. J., Kanji, Z., Lohmann, U. and Mohler, O.: Solid ammonium sulfate aerosols as ice nuclei: a pathway for cirrus cloud formation, Science, 313, 1770-1773, 1129726 [pii], 2006.

Dufour, L. and Defay, R.: Thermodynamics of clouds, Academic Press, New York, USA, 1963.

Knopf, D. A. and Lopez, M. D.: Homogeneous ice freezing temperatures and ice nucleation rates of aqueous ammonium sulfate and aqueous levoglucosan particles for relevant atmospheric conditions, Physical Chemistry Chemical Physics, 11, 8056-8068, 2009.

Knopf, D. A. and Rigg, Y. J.: Homogeneous ice nucleation from aqueous inorganic/organic particles representative of biomass burning: Water activity, freezing temperatures, nucleation rates, J. Phys. Chem. A, 115, 762–773, 2011.

Koop, T., Luo, B., Tsias, A. and Peter, T.: Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, Nature, 406, 611-614, 2000.

Landau, L. D. and Lifshitz, E.: Statistical physics, part I, 5, 468, 1980.

Pruppacher, H. R. and Klett, J. D.: Microphysics of Clouds and Precipitation, Springer Science & Business Media, 1997.

Riechers, B., Wittbracht, F., Hütten, A. and Koop, T.: The homogeneous ice nucleation rate of water droplets produced in a microfluidic device and the role of temperature uncertainty, Physical Chemistry Chemical Physics, 15, 5873-5887, 2013.

Sadovskii, M. V.: Statistical Physics. De Gruyter Studies in Mathematical Physics. Berlin: De Gruyter, 2012.

Townsend, P. K.: Statistical physics and cosmology Part IIA Mathematical Tripos, University of Cambridge

Vali, G.: Ice Nucleation-Theory: A Tutorial, in: NCAR/ASP 1999 Summer Colloquium, 1999.