Response to comments

Donifan Barahona

Referee # 1

We thank the reviewer for his/her feedback on the manuscript. Answers to the comments are provided below.

“It should be made much clearer that this new approach/framework/ concept is a novel extension of CNT. In principle, the derivation follows exactly CNT ending with similar equations and terms (nucleation rate, Gibbs free energy etc.). . . .”

Nucleation rate and Gibbs free energy are general concepts not exclusive of classical nucleation theory (CNT). One of the central tenets of CNT is that the curvature of the germ determines the work of nucleation. The proposed thermodynamic framework does not employ that assumption and therefore is fundamentally different from CNT. However the reviewer is correct in that the kinetic framework of CNT is used. This is emphasized in the revised paper. It is also now mentioned explicitly in the abstract that “the new thermodynamic framework is incorporated within the kinetic framework of classical nucleation theory”.

“ ... except that the energy for making an interface between the ice and surrounding liquid has been modified by a potentially better model.”

Not only the new framework calculates explicitly the mass and energy excesses of the interface, but also the contribution of the energy of mixing to the work of nucleation. The latter arises from the finite size of the liquid phase and is neglected in CNT.

“However, this new model of the interface has similar weaknesses as the capillary approximation of CNT. For example, can the Gibbs interfacial model be indeed applied to a cluster of a few molecules in size that makes the critical ice germ? I am not disagreeing with this new concept, in fact I like it, but also in this case one has to wonder if the physics of a “bulk interface” are the same as for a tiny molecular cluster. This is the same issue with assuming that bulk parameters describing the ice-water interface can be applied to the critical ice germ. I think this caveat should be mentioned and I feel this does not render the conclusions of this study.”

There is no reason to believe that the Gibbs model cannot be applied to the ice germ with about 300 molecules. It has been shown that local equilibrium is a valid assumption for domains as small as 32 molecules [17]. Furthermore, the capillarity assumption is mostly critical for estimating the surface tension since the nucleation rate is very sensitivity to σ_{iw}, but it is safer for other properties (i.e., specific volume and latent heat) [12]. Since surface tension is not used in the new approach, it does not have similar weaknesses as CNT.

"**p. 1526, l. 9: Change "theory" with "approach".**"
Done

"**p. 1528, l. 22: References: Wang and Knopf did not study homogeneous ice nucleation. The better choices would be: Knopf and Lopez, PCCP, 2009 and Alpert et al., ACP, 2011.**"

Corrected

"**p. 1529, l. 4: Define K00.**"

It is defined in page 1528.

"**p. 1529, l. 2-6: "However in these studies σ_{iw} is typically modified to adjust CNT to K00, and the results obtained in this way are not independent of Koop et al. (2000) ... These statements are misleading do not accurately reflect the work of K00 nor does it support the author's work. K00 is based on several independent measurements and since then, many other studies have reproduced and supported the K00 approach. Homogeneous freezing data can be expressed by either the K00 approach or by CNT when interfacial tension is dependent on water activity. Clearly, both approaches are independent of each other even so they are based off of the same theory. The observed temperature or aw trend of freezing data suggest to modify CNT, not K00.**"

The referred statement indeed suggests that CNT must be adjusted not K00. It is not the goal of this work to evaluate K00. Following the reviewers' suggestion the statement has been modified to: However in these studies σ_{iw} is typically modified to adjust CNT to K00. In fact, Koop et al. (2000) suggested that CNT and K00 can be reconciled if σ_{iw} is allowed to vary with a_w (also shown by Alpert et al., 2011).

"**It is very obvious that when allowing interfacial tension to be dependent on aw that CNT can reproduce the data as shown in Alpert et al., PCCP, 2011. No one would expect that the interfacial tension between ice and water is the same as for ice and an aqueous organic or inorganic solution.**"

Although it might seem very obvious that σ_{iw} depends on water activity it would be just as obvious that such dependency must vary with the nature of the solute, which is however contrary to observations.

“**While K00 did not give a framework for σ_{iw}, it is clear that theory exists to describe the change in surface tension, for example the Gibbs-Thomson equation recently reviewed by Kaptay, J. Nanosci. Nanotech. (2011).**”

The referred work by Kaptay, J. (2011) [11] does not address the dependency of σ_{iw} on a_w.

“ **In fact, this manuscript does not give any new theoretical framework for σ_{iw} either, as the author’s approach makes only an assumption that there exists an interfacial phase and follows CNT closely.**”

Not true. A main point of this manuscript is the development of a new theoretical framework for σ_{iw} in the context of ice nucleation. The interfacial tension can be obtained by dividing the energy of the interface, $\Delta h_{\mathrm{w,ls}}$, by a reference area (in CNT the surface area of the ice germ). The assumption of an interfacial phase is not introduced in this work. It was proposed by Gibbs [7]) as a mathematical construct to calculate interfacial properties. This is now explicitly discussed in the revised paper.

“ **p. 1529, l. 19-21: “In this work a new theoretical approach is proposed to describe ice formation by homogeneous nucleation. The new model relies on a novel picture of the solid-liquid transition placing emphasis on the entropy changes across the interface.” With regard to the general comments, this should be reworded to “In this work a new approach to CNT is proposed to describe ice formation by homogeneous nucleation, which relies on a novel picture . . . ”**”

As explained above, this work is not necessarily an extension of CNT. The statement has been modified to: “In this work a new thermodynamic framework is proposed to describe ice formation by homogeneous nucleation. The new model relies on a novel picture of the solid-liquid transition placing emphasis on the entropy changes across the interface. The thermodynamic framework is introduced within CNT to study the effect of water activity on ice nucleation rate.”

“ **p. 1533, l. 15: The factor 1.46 is reported from an older study. The results will crucially depend on this factor which is in the exponent and raised to the 3rd power. So, small variation will have a significant effect on the Gibbs free energy. It would be very beneficial to show how Jhom depend on variation of this factor. A sensitivity analysis could be conducted.**”

The factor of 1.46 is not an arbitrary parameter. It represents the surface coverage, Γ_w, and its value results from explicit construction of the interface following the rules: (i) maximize the density, (ii) dissalow octahedral holes and (iii) preference for tetrahedral holes [19]. The factor will not change in newer studies as long as the same construction rules are followed. Spaepens’ classic model has been confirmed by experimental observations and molecular simulations [2, and references therein].

However the reviewer is correct in pointing that even small deviations from Spaepen's model may have an appreciable effect on the nucleation rate; fortunately Γ_w can be well constrained by the underlying physics without recurring to nucleation rate measurements. Variation Γ_w may originate from crystal defects in the germ, and from significant order beyond the second interfacial layer. The former may be rare since defects will be energetically unfavored. The latter is more difficult to assess, however the percentage of molecules that would display order beyond the second layer is expected to be small. Assuming that 10% of the molecules adsorbed on the second layer exhibit order will increase Γ_w to 1.51 leading to a decrease in the nucleation rate between one and two orders of magnitude. This discussion has been introduced in the revised paper.

" **p. 1535, l. 6: The ΔG_{act} term should be better explained at this point in the manuscript. This term is discussed at several later places in the manuscript and only there one gets an idea what is meant by this term and why it is different from derived ΔG_{nuc} . I recommend to elaborate here and save space at the places of discussion below. Also, the studies e.g. by Zobrist et al., 2007, Alpert et al., 2011, Knopf and Forrester, 2011 explicitly treat ΔG_{act}.**

Further discussion has been added to clarify the meaning of ΔG_{act}. In must be noticed that in this study ΔG_{act} is also explicitly treated by using the correlation of Zobrist et al. (2007) [21].

"**p. 1536, l. 23: ". . .although no parameterization was reported." If I understand the paper by Alpert et al. (2011) correctly, Jhom is taken from K00 and using parameterizations of Zobrist et al. (2007), σ_{iw} can be determined analytically. Therefore, no parameterization is needed to be reported as it could be found from previous studies. The author should remove this statement.**."

Alpert et al. (2011) [1] described a method to obtain σ_{iw} from nucleation measurements, not an explicit expression for σ_{iw}. Their results are not easily reproducible since custom expressions were used to describe the activation energy and the equilibrium concentration of water molecules. Also the method of Alpert et al. (2011) is not rigorous since an analytical expression for σ_{iw} can only be obtained under the assumption that the Zeldovich factor does not depend on ΔG_{nuc}. Moreover, following the method of Alpert et al. (2011), σ_{iw}, is only defined where K00 is applicable. In this work instead an empirical expression for σ_{iw} is found by fitting CNT freezing temperatures to K00. Linear dependencies of σ_{iw} on T and a_w are used to extrapolate σ_{iw} outside the range of validity of K00. The statement has been removed.

"**p. 1536, l. 24: ". . .shows reasonable agreement." Jhom depends very strongly on σ_{iw} and so agreement between Eq. 27 and results by Alpert et al. should be quantified and not vaguely described as reasonable. Even if σ_{iw} differs by a few percent, this may cause changes in J_{hom} by orders of magnitude.**."

Any difference between the value of σ_{iw} reported by Alpert et al. (2011) and the correlation reported here only shows the effect of different assumptions in the implementation of CNT and highlights the caveats of obtaining σ_{iw} from nucleation measurements rather than by independent methods.

To address the reviewers' concern the approach to describe σ_{iw} has been modified to give a better picture of current estimates. Values of σ_{iw} extracted from the supplementary Figure 1 of Alpert et al. (2011) were included in a new Figure and compared against other published data and the values obtained in this work.

" p. 1537, 1st paragraph: If the author could perform a sensitivity analysis on applied parameters, this would elevate the quality of this manuscript."

Besides the heat of fusion, the NNF model depends on two constants: the surface coverage, Γ_w, and the geometric constant defining the crystal lattice, s. It is clear that variation in physical properties, particularly the heat of fusion, will affect nucleation rates. However physical properties can be obtained from independent methods and it is out of the scope of this work to evaluate their accuracy.

Since they are elevated to the third power in the expression for the work of nucleation, nucleation rates are sensitive to Γ_w and s. However they can be obtained independently without using nucleation rate measurements. Furthermore, their plausible range of variation is well-constrained by the underlying physics. As explained above Γ_w is expected to be close to 1.46 and very likely below 1.51. The factor, s, is 1.09 for hcp crystals and 1.12 for bcc crystals [9], which represents a variation in nucleation rates of about an order of magnitude. Thus, the combination of variability in Γ_w and s within plausible values would result in 2-3 orders of magnitude variability in J_{hom}

To address the reviewer's concern sensitivity of the results to the value of s has been included in Figure 5. A new subsection has been added discussing sources of uncertainty.

"Also here and later on, it seems K00 is applied to values outside suggested water activity criterion range. So, some of the comparison may not be appropriate/fair."

The correlation obtained for σ_{iw} was extrapolated assuming linear tendencies on T and a_w. However only freezing temperatures within the interval where K00 is applicable were used in its derivation.

" p. 1537-1538: Discussion of Murray et al. and Riechers et al. data: Riechers et al. have a unique dynamic temperature calibration. It very likely represents a very accurate Jhom measurement in terms of temperature. The study by Knopf and Rigg group achieves similar values and thus corroborate Riechers et al. If one would have to bet on the best value, it will most likely be Riechers et al. Also Riechers et al. do not predict any Jhom , they determine it experimentally. Thus, please omit "although no independent works have corroborated

their conclusions." A lower Jhom for pure water would also shift the K00 freezing line accordingly."

It is out of the scope of this work to weight on the accuracy of a recently developed experimental technique. The experimental range of variability in freezing temperatures is explicitly shown in the gray area of Figure 5. The statement has been removed.

" **p. 1537-1538: Be consistent in using R13 or Riechers et al. (2013) here and in the whole manuscript. I suggest to write it out in the text. Figure legend can be different.**"

Corrected.

"**p. 1538, l. 4 and following until end of page: First, K00 can only be applied to maximum J_{hom} rates of about $10^{18}\mathrm{cm}^{-3}\mathrm{s}^{-1}$ as stated in their publication. Any extrapolation beyond this is a false representation as K00 only applies to a defined range of Δa_w values. If this is appropriately represented then there is much less deviation between formulations.**"

Calculations with K00 have been limited to $0.26 < \Delta a_w < 0.34$ [13]. All the Figures have been modified accordingly.

"**Also, the temperature and water activity range of the results using this new approach has to be discussed as well (see comments above on uncertainties). K00 is based on independent experiments whereas this framework is not based on experiments. So, comparison and discussion of Fig. 2 as done, I feel, may not be appropriate.**"

It is not a claim of this work that the NNF model is based on experiments. NNF is a first-principles, theoretical model. As such, it is validated by comparing its predictions against independent experimentally-based results, represented by K00. Such exercise is not only appropriate but also required for the objectives of this work. The temperature and water activity for the comparison were selected as relevant for atmospheric conditions.

"**p. 1538, l. 14-29: The discussion of experiments and frozen fractions is not correct. The experiments end when all droplets have frozen, i.e. $f = 1$. Of course, $f > 1$ is impossible. Therefore, I assume, for regions of $f > 1$, it is meant a lower temperature and corresponding higher Jhom ? To observe Jhom at lower temperatures, much smaller droplets have to be applied, which then freeze at lower temperatures and higher J_{hom} values. Homogeneous ice nucleation studies performed as a function of water activity are performed at atmospherically relevant temperature ranges and thus ranges in Jhom . Therefore, it is not necessary to extrapolate to higher Jhom from the experimentally derived data. There seems to be a misconception of how the experiments are conducted and analyzed. Furthermore, K00 is falsely represented, yet again, as the parameterization is extended**

up to 10^{36}cm^{-3}s^{-1} when limits are directly stated in K00. Frankly speaking, this entire section should be discarded. In particular, if K00 is applied to suggested range, there is no need for this discussion.

Agreed. Limiting calculations with K00 to $0.26 < \Delta a_w < 0.34$ makes the referred discussion irrelevant. The paragraph has been removed.

" **p. 1539, l. 9: As mentioned above, no one would expect σ_{iw} to be independent of the type of aqueous solution and thus aw. CNT does not state anywhere that σ_{iw} should not depend on aw. However, most ice nucleation studies are performed in pure water and this is the likely reason why the dependence of σ_{iw} on aw is not found much discussed.**"

Further analysis of the work of Kashchiev (2000) indicates that independence of σ_{iw} from a_w is not a requirement of Eq. (30). The statement has been rewritten in the form: "where it is assumed that the molecular excess of solute at the interface is negligible".

"**p. 1540, l. 5: Does the EDS work fine for these tiny molecular clusters? See comments above. And how much does it depend on the parameters defining EDS?**"

Yes it does. The "tiny" molecular clusters are big enough (about 260 moecules) so that an interface can be defined and local equilibrium applies. The EDS is not a physical object. As introduced by Gibbs, it is an abstract construct that allows the calculation of the properties of a diffuse interface. Therefore it finds its place very well in ice nucleation.

"**p. 1541, l. 20 and following: There are uncertainties in K00 and this approach. I assume within both their uncertainties included, no statements can be made about any differences besides that the scatter in the data is too large to judge which approach is more accurate.** "

It is mentioned explicitly that the difference between K00 and NNF is within the range of experimental observations. A greater scatter in freezing temperatures than presented in the gray area of Figure 5 is not supported by experiments.

"**p. 1545, l. 19-21: I do not understand how the new approach will reduce the uncertainty in Jhom associated with the parameterization of iw in theoretical models. Since this is in the conclusions, it should be discussed in detail earlier in the manuscript, but it is not. ... This statement is not necessary and unsupported and should be removed.**

The statement is not unsupported. Comparison of the model developed against experiments (as represented by K00) indeed suggests that the assumptions are reasonable. The assumptions of the model are also supported by previous work. The model presented obviates the need of introducing the interfacial energy as a parameter that needs to be customized to fit different experimental conditions.

To address the reviewer's concern the scope of the statement has been clarified as follows: [the framework] provides an independent estimate of the nucleation work not derived from nucleation rate data, and obviates the usage of the interfacial tension as defining parameter.

“ **... There is no uncertainty estimate discussed in this model. Also, how could the author be certain that the assumptions of the interfacial phase are correct?** ”

The expected range of variability in the model results was discussed in the answers to the comments above and is now incorporated in the revised paper. The model assumptions are based on observations reported in the literature and from well-known approximations to the structure the interface. However the validity of the assumptions can only be assessed by comparing against independent experiments, as done extensively in this work.

“**p. 1545, l. 11-16: The association with the formation of glasses comes somehow out of the blue. As mentioned above, I think the uncertainty of the models is too large to make any claim that there is a significant discrepancy between these two approaches. Nothing is gained with these statements and thus should be omitted.**

As is shown in Figure 5, the experimental uncertainty is not as large as the reviewer suggests. The NNF model is not used to evaluate K00; K00 is considered the benchmark for comparison. However it is clear that places where K00 and the NNF model deviate may indicate that the assumptions of NNF may not completely hold. Thus the sentences do not come out of the blue as glass formation has been shown to be a factor at low temperature and is not included in NNF, but may be represented in K00. Still, the statements have been removed since they are speculative.

Referee # 2

We thank the reviewer for his/her feedback on the manuscript. Answers to the comments are provided below.

"...However, calling this a new theoretical approach and new model of homogeneous nucleation oversells the finding. The title needs to be changed.

The title does not mention a new theoretical approach neither a new model of homogeneous nucleation. It specifically mentions a new thermodynamic framework, which is thoroughly justified in the manuscript. The thermodynamic framework for ice nucleation introduced in this work has not been proposed before and it has not been applied to homogeneous nucleation, therefore it is new.

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

The referred equation is correct. It is a well-known relation between the volume and the surface of a solid (e.g, Nagaev, 1991). For example, for a primitive cubic centered crystal it is known that $s = 1$ and $n_s = \mathrm{n}^{2/3}$ (e.g., Black 1996) , being n_s and n the surface and total number of atoms in the crystal, respectively. Notice that n does not exclude the surface atoms as being part of the crystal. This is further explained below. No corrections/modifications are required to the equation.

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

Although the work of Cziczo et al. 2013 [5] clearly shows a significant impact of heterogeneous ice nucleation on cirrus formation, the reviewer overstates the findings of Cziczo et al. (2013) as only limited field campaign data was used. As shown in Barahona et al.(2013) [4] such picture can be reconciled with strong and localized heterogeneous events but still with homogeneous ice nucleation being the dominant mechanism of cirrus formation around the globe.

"1527 line 2: What are the "significant gaps in the understanding" mentioned here? Is this statement at odd to the following statement (line 4ff.) that MD simulations lead to a fundamental understanding of homogeneous nucleation?

This statement refers to the limited understanding of the role and meaning of the interfacial tension at the microscopic scale and of the properties of the ice germ during the first stages of nucleation. However I agree that these are rather gaps in the modeling of ice nucleation that limit the theoretical prediction of nucleation rates. To avoid confusion the statement has been modified to: "These studies have led to a greater understanding of the mechanism of ice nucleation. Yet the role and meaning of the interfacial tension at the microscopic scale and the properties the ice germ during the first stages of nucleation remain unclear and difficult the theoretical prediction of nucleation rates."

"**1527 line 28: An explanation why the measurement of σ_{iw} is difficult and uncertain could be added here.**."

The following paragraph has been added: Challenges to the measurement of σ_{iw} are related to difficulties in maintaining equilibrium between a growing ice crystal and the liquid phase, particularly at supercooled temperatures. The presence of impurities and crystal defects and the large temperature gradients near the ice liquid interface also pose a challenge to the experimental determination of σ_{iw} [10].

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

Crystal defects, size, and anisotropy may modify the value of σ_{iw}. However the exact way in which these factors alter σ_{iw} is uncertain.

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

CNT introduces several assumptions to calculate the work of nucleation. Among them, a negligible excess of solute at the interface, an spherical ice germ, and capillarity. These assumptions cannot be independently tested by obtaining σ_{iw} from nucleation rate measurements. Different assumptions in the implementation of CNT will also result in different values of σ_{iw} when fitted against experimental measurements. On the other hand, using independent methods to estimate σ_{iw} typically results in large deviations from experiments. Thus as the reviewer suggests, the only way to reconcile CNT with observations is by untying σ_{iw} from its theoretical meaning. This however leads to a hole in CNT since it is not clear what σ_{iw} exactly represents and whether it is accesible by independent methods.

However the reviewer is right in that discrepancy with other theories does not necessarily indicate a flaw in CNT. One can only say that σ_{iw} is incommensurate with independent estimates, as for example those obtained from contact angle measurements (MacKenzie, 1997).

The paragraph has been modified introducing the discussion above.

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

This line refers specifically to the high uncertainty related to the estimation of σ_{iw} from independent methods. However the statement has been deleted since this is now explained in the previous paragraph.

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

The statement has been modified to:
For aqueous solutions empirical correlations of the nucleation rate were often developed based on $(NH_4)_2SO_4$ and H_2SO_4 model solutions [8,20]. However Koop et al. (2000) demonstrated that when parameterized in terms of the water activity, a_w, ...

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

The reference has been corrected.

“ **1528 line 26-27: It is mentioned that there is no information on the nucleation mechanism in Koop et al., (2000). But as you state in the following, Koop et al., (2000) report that by using $\sigma_{\mathrm{iw}}(a_w)$ and $\Delta G_{\mathrm{act}}(a_w)$ they are able to reconcile their result with CNT. This could be read as information on the mechanism.**

Fits of $\sigma_{\mathrm{iw}}(a_w)$ and $\Delta G_{\mathrm{act}}(a_w)$ incorporated in CNT only provide an empirical way to adjust CNT to observations. But they do not provide additional information on the mechanism of germ formation.

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

As written, the statement refers specifically to a formulation that is independent of the nature of the solute. Such formulation has not been presented in the literature.

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

The last part of the statement has been modified to: By adjusting the parameters of CNT to reproduce observed nucleation rates, CNT will by design reproduce the observed water activity dependency of J_{hom}. This however does not imply that CNT can independently explain the water activity criterion.

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

nucleation oversells the finding.”

The thermodynamic framework introduced in this work is fundamentally different from CNT in that it does not consider the curvature of the ice germ the dominant factor in ice nucleation. It rather emphasizes the entropic cost of the formation of the new phase. Moreover, the effect of changes in the bulk composition of the solution upon nucleation are accounted form, but neglected in CNT. However the reviewer is correct in that the kinetic framework of CNT is used. The statement has been modified to:

“In this work a new thermodynamic framework is proposed to describe the work of germ formation by homogeneous nucleation. The new model relies on a novel picture of the solid-liquid transition placing emphasis on the entropy changes across the interface. The thermodynamic framework is incorporated with the kinetic framework of classical nucleation theory and used to analyze the effect of water activity on ice formation and ice nucleation rates.”

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

The solid does not provide a matrix different from the interface itself. There is little distinction between solid and liquid around the interface. If one moves from the interface towards the bulk of the liquid it is expected that the water properties will resemble more that of the bulk liquid, and viceversa when moving towards the bulk of the solid. In the approximation presented here, the outermost layer of the solid is considered part of the interface. This has been clarified in the revised paper.

“**1533 line9: Should the number of molecules at the surface not be $sn_s^{2/3}$? If as suspected, the number of molecules at the surface depends on the total number of atoms in the bulk of the germ instead of the total number (which includes the number of molecules at the surface), all formulas starting with Eq. (16) have to be corrected. Please check that your formula $n_{ls} = sn^{2/3}$ is correct and explain why it should not read $n_{ls} = sn_s^{2/3}$.**”

In this work, the outermost layer of the solid is considered part of the interface. Applying the equation as suggested by the reviewer will exclude the molecules of the outermost layer of the solid from its volume and would be incorrect.

“**1534 Eq. (18) Can n^* be derived if $n_{ls} = sn_s^{2/3}$?**”

In principle it may be possible to consider a different approximation to calculate the number of molecules at the interface, as long as expressions for the surface excess consistent with such approximation can be written explicitly. The convention used in this work facilitates the calculation of Δh_{ls} and it is therefore preferred.

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

Besides the heat of fusion, the NNF model depends on two constants: the surface coverage, Γ_w, and the geometric constant defining the crystal lattice, s. It is clear that variation in physical properties, particularly the heat of fusion, will affect nucleation rates. However they can be obtained by independent methods. It is out of the scope of this work to evaluate the accuracy of current estimates of the physical properties of water.

Since they are elevated to the third power in the work of nucleation, nucleation rates are also sensitive to Γ_w and s. In principle their variation would have a similar effect on nucleation rates as variation in σ_{iw} in Eq. (23). However unlike σ_{iw}, Γ_w and s can be constrained independently without using nucleation rate measurements. Furthermore, their plausible range of variation is well-constrained by the underlying physics. From Spaepen’s model [19], Γ_w is expected to be close to 1.46 since order is rapidly lost when moving from the interface into the bulk of the liquid. Assuming that 10% of the third layer molecules belong to the interface (which is likely an upper limit of variability) will increase Γ_w to 1.51. The factor, s, is 1.09 for hcp crystals and 1.12 for bcc crystals [9], which represents a variation in nucleation rates of about an order of magnitude. Thus, the combination of variabillity in Γ_w and s would result in about 2-3 orders of magnitude variability in J_{hom}.

A section regarding the possible uncertainties in the model has been added to the revised paper.

“1535 Eq. (21) ΔG_{act} according to Zobrist et al., 2007 is used. What is the error made by not using a $\Delta G_{act}(a_w)$ as proposed by Koop et al., 2000?”.

Koop et al. (2000) did not report an explicit expression for $\Delta G_{act}(a_w)$. Nucleation rates, and particularly freezing temperatures, are much less sensitive to moderate variation in $\Delta G_{act}(a_w)$ than to variation in σ_{iw}. Using a different expression for $\Delta G_{act}(a_w)$ from the one employed here does not represent error, but rather the effect of using a different parameterization to define a physical property. The effect of plausible variation in physical properties is now analyzed in the revised work.

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

The references have been corrected.

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

The reference has been corrected.

“1536 Eq. (26): The fit provided by Murray et al., (2010a) has a particularly weak temperature dependence. The more frequently

used parameterisations of σ_{iw} provided by Zobrist et al., 2007 or by Pruppacher and Klett, 1997 might change the comparison."

This is a good point. It was realized that to single out the Murray et al., (2010a) [15] correlation as representative of $\sigma_{\mathrm{iw}}(T)$ is incorrect. The approach to represent σ_{iw} has been modified in the revised paper including expressions from different sources, along with estimates of σ_{iw} derived from the NNF model. The section describing σ_{iw} has been expanded accordingly. However the correlations of Zobrist et al., (2007) [21] and Pruppacher and Klett (1997) [16] are not applicable over the whole range of temperature tested, therefore they have been omitted.

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

Although the value of Δa_w reported by K00 has been slightly modified in more recent works, none has invalidated the K00 approach. Furthermore, the updated correlation of Koop and Zobrist (2009) [14] for $a_{\mathrm{w,eq}}$ was used therefore more recent data is already incorporated in the discussion. Eq. (27) was obtained to make a fair comparison between CNT and K00 and it is not meant to provide the best estimate of σ_{iw}, which can only be obtained from independent methods, not fits of CNT to nucleation rate data.

" **1536 line 21: Digilov, 2004 cites one value for σ_{iw} C measured by Hobbs and Ketcham, 1969 and also Pruppacher and Klett, 1997 did not do their own measurements on σ_{iw}. Please check if the references are appropriate.**"

The references have been corrected.

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

The NNF model is not a fit. It a is first-principles model and does not include any nucleation rate data on its development. The fact that the NNF model agrees with the experimentally-based K00 model, is not trivial. It actually validates the proposed approach. The agreement of the NNF model with the K00 data does not result from fitting to K00 data. It results from the proper consideration of the effect of water activity on the formation of the interface and the entropy of unmixing during the formation of the ice germ.

The section has been expanded and clarified to avoid the confusion brought up by the reviewer. The first principles character of the NNF model is now emphasized in the paper.

" **1537 line 10-11: The experiments by Murray et al., 20010a and**

Riechers et al., 2013 were conducted in a much smaller temperature range than the data points shown in Fig.2.

The correlations have been restricted to their ranges of validity.

"**Generally, reporting nucleation rate coefficients higher than 10^{20}cm^{-3}s^{-1} is not meaningful as very little experimental data is available to compare to and it has no relevance for atmospheric ice formation.**"

The comparison is certainly meaningful since it shows theoretical predictions of nucleation rate where experimental data may not be available. They also show the limiting behavior and robustness of the NNF model, and should not be dismissed as irrelevant.

"**1537 line 26: Declare what "models" you refer to.**"

These lines refers to different experimental measurements of nucleation rate as studied by Murray et al (2010a). The statement has been expanded adding the appropriate references to the nucleation rate measurements.

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

Nucleation rate data were not used in the development of the NNF model, and there is no connection between experimental scattering in nucleation rate measurements and the NNF results. As discussed in previous comments, variability in the NNF results originates from variability in the model parameters and is now discussed in the revised paper. However for a given set of parameters there is no intrinsic error in the theoretical model, i.e., the same set of parameters always produces the same result. This is now discussed in the paper.

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

Clearly the main advantage of using the NNF model is its independence from nucleation rate data. As explained above, all the parameters of NNF can be constrained using either theoretical arguments or independent measurements. A section analyzing the possible variability in nucleation rates originated from variability in the model parameters is now included in the paper. The referred statement has been removed.

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

The K00 parameterization have been limited to $0.26 < \Delta a_w < 0.34$. All the figures have been modified accordingly.

“ **1538 line21-23: It is generally true that experiments are limited to a fraction frozen of 1. Thus taking about frozen fraction ¿ 1 does not make sense.**”

The paragraph has been removed since limiting K00 to low nucleation rates makes the referred discussion irrelevant.

“ **Experimental data showing the decrease in J at the predicted temperatures should be cited here to underline the validity of the calculations.**”

To the author’s knowledge no such experimental data is available. In the revised paper it is acknowledged that such behavior is a “theoretical prediction that needs to be confirmed by independent measurements.”

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

The analysis of Ford (2001) [6] was based on excess energies calculated from CNT and K00. However further review shows that σ_{iw} in the CNT expressions was based on Pruppacher and Klett (1997) [16] which is not applicable at low temperature. The statement has been removed and the above discussion has been introduced in the paper.

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

The statement has been corrected. The expression is in fact applicable even if σ_{iw} is dependent on a_w. Using the equation helps to highlight the differences between experimental calculations and the theoretical approaches. The expression is also commonly used in experimental analysis. The comparison also helps to show how the choice of the dividing surface affects the calculation of the germ size. This has been clarified and emphasized in the revised work.

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

The statement has been expanded to: For atmospheric conditions, the increased pressure at the interface will not result in destabilization of the water structure. This indicates that the picture of the interface presented here is physically plausible.

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

The sentence has been modified to: Finally we investigate whether the model presented in Sect. 2 is able to reproduce the constant shift in water activity between melting a nucleation, Δa_w, and explain the water activity criteria of

Koop et al. (2000).

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

The sentence has been modified as suggested.

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

Sections 2 and 3.2 showed that the surface excess of water at the interface is a function of water activity. Since the interface itself obeys the Gibbs-Duhem equation [18] the solute excess can be written in terms of the solute excess of water at the interface. It follows that for any solute, the solute excess at the interface must be a function of water activity. Thus the interface energy can be expressed in terms of water activity independently of the nature of the solute. Since the interface energy determines to great extent the nucleation rate, J_{hom} will at least to first order (since solutes can modify ΔG_{act}), be independent of the nature of the solute.
The above discussion has been added to the section.

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

In this work Eq. (28) is used to calculate the freezing temperature. Since Eqs. (33) and (28) are equivalent, Eq. (33) is also a solution to Eq. (28). This explanation has been added to the paragraph.

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

The freezing temperature as defined in Eq. (28), T_f, is less influenced by dispersion in the droplet volume than when using other definitions. For example, the temperature for which $f_f = 0.01$ is influenced by volume dispersion since large droplets freeze at slightly higher T [3]. This explanation has been included in the revised paper.

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

The section has been expanded and clarified. It was noticed that the freezing function is in fact only the left hand side of Eq. (33). This has been corrected. To explain the oscillating behavior of the freezing function, an additional plot has been added showing the contribution of kinetic, thermodynamic and interface energy terms to the freezing function. Essentially, the oscillating behavior results from the relative variation in the temperature derivative of the interfacial and thermodynamic terms defining the nucleation work.

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

The proposed framework framework does not only represents the interface but also the effect of the entropy of mixing on the nucleation work. The sentence has been modified to: “a new thermodynamic framework”.

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

This is discussed in detail in Sections 2 and 3. Additional details have been added, particularly to emphasize the first-principles character of the NNF model.

“**1544 line 24: I disagree that the missing dependency of σ_{iw} on a_w is a shortcoming of CNT itself, and rather a missing element in some widely used parameterisations of σ_{iw}.**”

An empirical expression for σ_{iw} can always be found to match CNT predictions and observations. However an expression for σ_{iw} that depends on water activity is incompatible with the assumption of CNT of a negligible excess of solute at the interface. The reviewer is right in that this point needs to be better articulated, and it is expanded in the revised paper.

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

This refers explicitly to the assumption that the surface excess of solute and solvent are simultaneously zero. Furthermore CNT assumes a negligible entropy of mixing during the formation of the ice germ, i.e., the term ΔG_{sln} in Eq. (4). This has been emphasized in the revised paper.

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

The K00 correlation is a fit to experimental measurement and as such it contains all the physics that may happen during freezing. The physics of the NNF model does not consider glass formation or non-equilibrium effects. The sentence speculates that neglecting these effects at low temperature may explain the deviation of the NNF model from K00. However since these statements are mostly speculative they have been removed.

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

As explained above the comparison is not invalid, since these are common methods to describe the ice germ size. The slight increase is n^* as temperature decreases results from a faster decrease in the interfacial term than in the thermodynamic term (i.e., the numerator and denominator of Eq. (18), respectively) as temperature decreases. At low water activity the tendency is reversed. This is now discussed in the paper. Grid lines have been added to the plot.

Technical Corrections

All technical corrections have been incorporated.

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