Response to Comments

1 Referee 3

Reviewer: *This paper proposes a new theoretical model for immersion nucleation, by investigating the thermodynamic and kinetic impact of the solid particle on near-by water molecules and its consequences for ice nucleation within the liquid droplet. Although immersion freezing is one of the main pathways of ice formation in the atmosphere, it is still poorly understood and the topic addressed in the paper is of great relevance for cloud physics. Furthermore, the paper puts together an important number of previous works in an attempt to make progress on our understanding of immersion nucleation. It is overall rather clearly written and the reasoning is supported by high quality figures and schematics. This paper could hence be an appropriate contribution to ACP. However, I believe there are shortcomings in the theoretical derivation and its presentation that should be resolved before the paper can be considered for publication. I therefore recommend major revisions of the current manuscript. In the following I will explain my concerns in more detail.*

Response: The comments by the reviewer are greatly appreciated. Please find detailed responses below.

Major Points

Reviewer: *1) Presentation of the theoretical development: I am not a specialist of ice nucleation and the related thermodynamics and kinetics. However, this will be the case for other ACP readers who would like to use the results presented in the paper. Since the theoretical derivation mainly consists in chemical physics, one possibility would be that the author submits this study to another journal, such as "The Journal of Chemical Physics". If the author chooses to present this work in ACP, I think some significant efforts should be spent in order to make the paper more accessible to the bulk of ACP readers. In particular, I think the organization of the derivation could be improved in that regard:.*

Response: Investigations on the subject of ice nucleation, either from the experimental or the theoretical point of view are within the scope of ACP. Many haven been published in the journal during the last decade. Understandably most studies are experimental. Theoretical investigations are however of great importance to the atmospheric community, particulalry as many authors many not often consult fundamental physics journals like JCP. Most concepts discussed in this work are also basic physical chemistry and therefore within the grasp of the broad atmospheric science community. I agree that the organization could be improved and the revisited paper has been reorganized to make

it more readable.

Reviewer: *Indeed, most ACP readers will be interested in the derived nucleation rate for immer- sion nucleation. Thus, I would start the theoretical section with the general expres- sion for the nucleation rate, i.e. the product of the concentration of critical clusters $cg = C0\ exp(-\Delta G/kB\ T)$, corrected by the Zeldovich factor times the flux of water molecules towards those clusters Fw : Jhet = Zcg Fw Thermodynamic effects of the particle on vicinal water affect cg and Z (through ΔG, the nucleation barrier for critical germ size) while kinetic effects affect Fw (the flux of water molecules towards the ice germs). After stating this, I would then elaborate on how expressions for the different factors are obtained in the new theory. This is mainly a change in presentation: most of the content is already present in the paper, but it should be made clearer where the derivation is going, e.g. when reading section 2.3 the reader sometimes misses the goal of the development which is only made clear in section 2.4.*

Response: This is an excellent suggestion. In the revisited paper I have made the calculation of the nucleation rate the central theme of the paper, starting as teh reviewer suggest with the broad definition of J_{het} as suggested then followed by Eq. (32). The firts paragrpahs of sections of 2.3.3, 2.4 have now been moved to a new broad introduction before Section 2.1. It mut be noted however that the distiction between "kinetic" and "thermodhyamic" effects is not as clear in the proposed model since the flux of water molecules to the nascent ice germ is controlled by the thermodynamic driving force Barahona (2015).

Reviewer: *2) Comparison with the classical theory of nucleation: The main point of the paper is to take into account the change in the thermodynamic and "dynamic" properties of vicinal water near the immersed solid particle and the impact on ice nucleation. In that sense, it differs from the classical nucle- ation theory (CNT) which rather considers the influence of the solid particle- liquid water interface directly. Although the CNT expression for the nucleation rate is recalled in section 2.2, it is not really contrasted with the new theory. I miss a more thorough discussion comparing the different expressions and hy- potheses between the theory introduced here and CNT. In particular, a table comparing the CNT and new theory expressions for the different factors in Jhet would be useful. I would suggest to add a dedicated section on that point in the discussion (and remove section 2.2).*

Response: This becomes much clearer with the reorganizatin of the paper. Since now a broad formulation of J_{het} is introduced earlier in the work it is easier to refer to how the different theories define each of the relevant terms (nucleation work, molecular flux). The suggested table although seeminlgy a good idea is actually more confusing since the equations involved are quite long. It is worth mentioning that the theory presented here builds upon previous work Barahona (2014, 2015) and therefore does not only differs on the effect of the particle on the vicinal water but also on how other terms are defined. This has been made clearer in the revisted work. The comparison against CNT was partially addressed in Figure 7. Following the reviewer's suggestion a new, separate Section has been introduced.
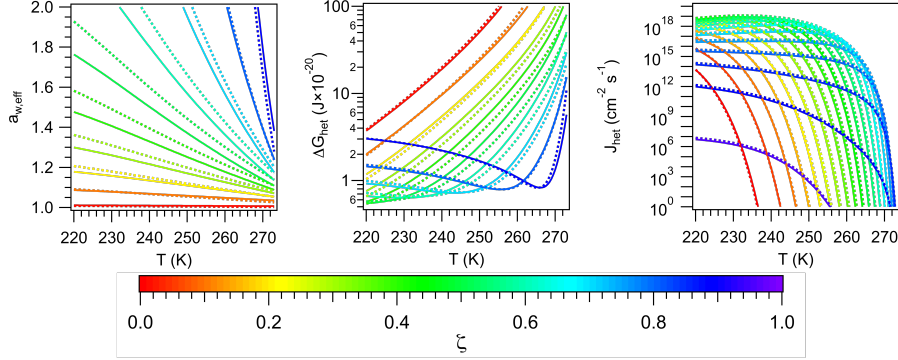
Figure 1: Comparison between the effective water activity, the nucleation work, and the nucleation rate between the original (dashed) and the corrected (solid) formulations of $a_{\mathrm{w,eff}}$.

Reviewer: *3) Contents: This is another reason for my reservations. On several instances, I have noticed algebra mistakes which are repeated in several formulas. This casts some doubts on the whole theoretical derivation and it is unclear without repeating all the work whether the related figures are correct or not. Since the theoretical derivation is central to the paper, it is essential that the author makes sure all the formulas are correct (and convinces the reviewer). References to previous studies should also be made as explicit as possible, to make the argument easier to follow. I list below the main two mistakes I have noticed:*

Response: The reviewer rightly points out an error in the derivation of the theory, as well as a number of typos. As shown below the effect of this error is limited and does not change the conclusion of the study. The corrected derivation is shown at the end of this document and it is now included in the the revisited paper. All the Figures are corrected in the revisited paper as well.

Reviewer: *page 7, Eq. (17): I have:* $a_w = a_{w,\,eff}^{\frac{1}{1+\zeta}} a_{w,eq}^{\frac{\zeta}{1+\zeta}} \exp\left(\Lambda_E \frac{1-\zeta}{1+\zeta}\right)$ *instead of the formula of the author. This formula is used in many instances, for example in Eqs. (19), (20), (21), (22), and (45)*

Response: This is a typo. $\Delta\mu_{\mathrm{S}}$ should be calculated at $a_{\mathrm{w,\,eff}}$, hence Eq. (14) of the original paper should read:

$$\Delta\mu_{\mathrm{S}} = -k_{\mathrm{B}}T \ln\left(\frac{a_{\mathrm{w,\,eff}}}{a_{\mathrm{w,\,eq}}}\right), \tag{1}$$

After introducing this equation into Eq.(13) it can be readily seen that Eq. (17) of the original paper is correct. The derivation of Eq. (8) is shown at the end of this document (Eq. 16).

Reviewer: *page 6, eq (7), (8) and (10): if the g^E term represents an excess energy imposing a penalty to mixing (and representing the tendency of IL and LL regions to clus ter), it should be positive:* $g^E = +A_w\zeta(1-\zeta)$ *with* $A_w = \frac{2k_B T c}{N}$.

3

In the current formulation the first part of Eq. (9), i.e. $\frac{\partial^2 \mu \eta c}{\partial \zeta^2} = 0$ does not hold at $\zeta = 0.5$. Some of the following equations build on this result (among which Eqs (12), (13), ...). 2 In Eq. (17) Λ_E should be $\Lambda_E = -\frac{2}{N}\frac{T_c}{T}$. Because of this error, the current Eq. (12) disagrees with Eq. (8) in Holten et al. (2013).

Response: This is indeed an error. Since A_w is a phenomenological parameter it can in principle have any value and sign. However this conflicts with the notion of A_w as a function of the critical temperature, T_c, and it is a mistake. In the appendix of this document the full derivation the equation of state of vicinal water has been reworked to (i) correct errors and typos, and (ii) to make it more readable stating clearly all the assumptions involved. The new expression is very close to the original expression. Both lead to the same general form for $a_{w,\,eff}$, i.e.,

$$a_{w,\,eff} = \left(\frac{a_w}{a_{w,\,eq}^\zeta}\right)^{\frac{1}{1-\zeta}} \exp\left(-\frac{\Lambda_{mix}}{\zeta - 1}\right). \tag{2}$$

In the original version (Eq. 19 of the original paper, with slightly different nomenclature) :

$$\Lambda_{mix} = -\frac{2}{N}\frac{T_c}{T}\zeta(1-\zeta) \tag{3}$$

In the corrected version (Eq. 24 of this document):

$$\Lambda_{mix} = \frac{1}{N}\left[\zeta\ln(\zeta) + (1-\zeta)\ln(1-\zeta)\right] + \frac{2}{N}\frac{T_c}{T}\zeta(1-\zeta) \tag{4}$$

The mixing term is only significant when $\zeta \sim 0.5$, since the energy of mixing vanishes for pure components. In the Figure 1 the effective water activity, the work of nucleation and the nucleation rate are drawn for $a_w = 1$ for different temperatures and ζ. For $\zeta = 0.5$ there is about a factor of two difference in ΔG_{het} leading to about two orders of magnitude difference in J_{het}. Athough these are significant differences, $a_{w,eff}$, ΔG_{het} and J_{het}, are otherwise very similar. This shows that Λ_{mix} only plays a secondary role, and the main conclusions of the study remain valid.

Specific Comments

Reviewer: *1. suggest to change the title from "On the Thermodynamic and Dynamic Aspects of Immersion Ice Nucleation" to "On the Thermodynamic and Kinetic Aspects of Immersion Ice Nucleation"; the "dynamic" aspects that the author refers to are related to the diffusion of water molecules in the fluid and in that sense could be referred to as "kinetic" (dynamic brings fluid dynamics to mind).*

Response: Dynamic was used as "kinetics" and "thermodynamics" start to blend in the new theory. However I agree that it may be confusing. The title has been changed.

Reviewer: *2. p 4, Eq (1) differs from the common expression in Prupaccher and Klett, which also includes N_c, Ω, the number of water molecules in contact with the cluster*

Response: The form of Eq.(1) has been used by several authors e.g., Marcolli et al. (2007), and is shown Eq. 9-37 of Pruppacher adn Klett (1997), although the correct equation does not include Z. This has been corrected in the revisited paper.

Reviewer: *3. p 5, Eqs (4), (5) and (6): it is more common to define an increasing entropy upon mixing. Thus, in both equations (4) and (5) it might be clearer to add a minus sign in front of $T\Delta S_{mix}$ in Eq. (4) and (5) and after "=" in Eq (6). This has no impact on the subsequent equations, but would be more consistent with the usual conventions.*

Response: In the revisited paper ΔG_{mix} is written directly from Eq. 16 of Holten et al. (2013). The expression is then explained as a combination of an ideal entropy of mixing and an empirical form for the enthalpy of mixing. This allows the readers to follow directly Holten et al. (2013) derivation. The derivation is also found in several textbooks (e.g., Prausnitz et al. (1998)). The goal is to limit the number of definitions in the derivation.

Reviewer: *4. p 10, Eq (24): I am not convinced that with that definition, $\Delta \mu_i$ should be referred to as supersaturation.*

Response: The sentence now reads "where $\Delta \mu_I$ represents the driving force for nucleation".

Reviewer: *5. p 10, line 9: unit of s should be $molec^{1/3}$ so that the units match in Eqs (23) and (25). 6. p 10, Eq 27: should be $n^{-4/3}$ rather than $n^{-1/3}$. 7. p 11, line 2: specify here again the condition for mechanical equilibrium.*

Response: Corrected.

Reviewer: *8. p 12, Eq (22) and l 25: here C_0 seems to be the monomer concentration per surface unit of the particle (and not in a volume of fluid), but this is only mentioned after Eq (44) where it is specified that $C_0 = 1/a_0$ is the cross-sectional area of of a water molecule. This should already be written line 25. The numerical value of a_0 should be mentioned.*

Response: As the reviewer points out C_0 is the concentration of molecules suceptible to grow into ice germs (i.e., the monomer concentration). Defining it as $1/a_0$ would limit the scope of the equation. To address the reviewer's concern the following line was added: "C_0 is defined either per-area or per-volume basis". For teh calculations $a_0 = \pi d_0^2$ with $d_0 = \left(\frac{6*v_w}{pi}\right)^{1/3}$ being v_w the molecular volume of water (See table 1). This has been added to Table 1.

Reviewer: *Furthermore, it is surprising that the author takes $C_0 = 1/a_0$. This implies that only the molecules in direct contact with the particle are considered as vicinal water susceptible to grow into ice germs. This contradicts the motivation for the development expressed, e.g. p3, l13-14: "In a groundbreaking work, Anderson (1967) found strong evidence of ice formation several molecular diameters away from the clay-water interface." The author should at least comment on that.*

Response: It is more appropiate to write as C_0 proportional to the volume of the vicinal layer. Unfortunately this would bring confusion since historically heterogeneous nucleation rates are defined using the particle surface area as

5

basis. Thus $C_0 = 1/a_0$ is more consistent with current literature and avoids a formal definitin of the volume of the vicinal layer which could be quite challenging.

However this does not mean that only the molecules in direct contact with the particle are considered vicinal water. Rather that the density of the water does not vary within the droplet, and remains constant even within the vicinal water. Thus, anywhere in the liquid the per-area molecular density should be the same as in the vicinal layer, and J_{het} can be scaled with respect to the immersed particle surface area. This only an approximation since under the proposed model low density regions are precursors to ice. But the density difference between ice and liquid is relatively small and such discrepancy should play a minor role.

The explanation above has been added after Eq.(44).

Reviewer: *9. p 12, Eq (33): It is not clear to me how the author comes up with that expression for the Zeldovich factor in this case, especially with $n^* = n_{hom} + 2$. I would rather obtain:*

$$Z = \left[-\frac{\left(\frac{\partial^2 \Delta G}{\partial n^2}\right)_{n=n^*}}{2\pi k_{\text{B}} T} \right]^{1/2} = \left[\frac{\Delta G_{\text{het}}}{3\pi k_{\text{B}} T n_{hom}(n_{hom} + 2)} \right]^{1/2} \tag{5}$$

The derivation should be briefly explained.

Response: It seems that in his/her derivation the reviewer calculated $\left(\frac{\partial^2 \Delta G}{\partial n^2}\right)_{n=n_{hom}}$ instead of $\left(\frac{\partial^2 \Delta G}{\partial n^2}\right)_{n=n_{hom}+2}$. The original expression, Eq. (33) was obtained assuming that the form of Zeldovich factor from homogeneous ice nucleation holds for the heterogeneous case. This is exact for the germ forming regime, but only an approximation for the spinodal regime. The correct expression for Z is

$$Z = \left[\frac{\Delta G_{\text{het}} n_{\text{hom}}^{1/3}}{3\pi k_{\text{B}} T (n_{\text{hom}} + 2)^{7/3}} \right]^{1/2} \tag{6}$$

for $n^* > 3$, $\frac{n_{\text{hom}}^{1/3}}{(n_{\text{hom}}+2)^{7/3}} \approx \frac{1}{(n^*)^2}$, with $n^* = n_{\text{hom}} + 2$. Indeed the discrepancy is only 30% at $n^* = 3$ and much smaller for larger clusters. Therefore the assumption made in Eq.(33) is largely valid.

However for $n^* = 2$ the exact expression cannot be used since $Z = 0$; for this regime Eq.(33) is only an approximation. The issue is rather fundamental. As explained by Kashchiev (2000), Chapter 13, the Zeldovich method consists in approximating $\Delta G(n)$ with a second order taylor expansion around n^*, which then is used to simplify the cluster population balance. As least two assumptions are involved (i) the cluster size distribution is at equilibrium and (ii) each germ grows by addition of a single molecule at a time. Both assumptions break in the spinodal regime. Unfortunately solving this issue requires a complete shift in the way cluster growth is modelled and it is beyond the scope of this work.

This caveat is now acknowledged and the explanation above has been added to the revisited paper.

Reviewer: *10. Section 2.4: please be more specific in this section regarding which assumptions have been previously made in the literature and which are introduced in this paper. Beyond the suggestions above for Sect.2, the presentation of this subsection on kinetics could be improved; e.g. I would put the text from l 24 p13 to l 1 p14 before Eq (35) since it provides some justification for the linear scaling introduced in Eq. (35)*

Response: The revisited paper expands this Section (and Section 2) to clarify the approach. Much of the justification to this Section is explained in Barahona (2015) and it is now is briefly summarized in this work. The Section has also been reorgnized following the reviewer's sugestion.

Reviewer: 11. p 16, l 28-32: Section 3.1 Please give a mathematical definition of the freezing temperature . The current definition is not very clear, the term "equilibrium temperature" suggests thermodynamic equilibrium between ice and liquid water. whereas nucleation is a kinetic process. I am not convinced, given the information in the next paragraph, that this $T_{\mathrm{f,eq}}$ can be referred to as an equilibrium temperature. In the legend and ylabel of Fig. 4, please add the symbol $T_{\mathrm{f,eq}}$.

Response: Thanks for pointing this out. The concept of thermodynamic freezing temperature refers to the pesudo equilibrium (i.e., metastable) temperarure between liquid and ice, for a given a_w. Qualitatively it must be the temperature at which freezing is observed if no kinetic limitations exist, hence freezing is only dictated by thermodynamics (hence it must be tha highest observable freezing temperature).

In the framework proposed in this work, this can be understood as the value of T for which $a_{\mathrm{w,het}} = a_{\mathrm{w}}$ in Eq. (20) which does not depend on the kinetics of the system. This definition however depends on selecting a value for $a_{\mathrm{w,hom}}$. A more fundamental definition may be achieved by using the spinodal separation of pure water instead of $a_{\mathrm{w,hom}}$? as reference.

The explanation above has been added to the Section. The symbol has been changed to T_{ft} and added to the caption of Figure 4.

Reviewer: 12. p 21 l 22: "regular solution" -¿ mixture ?.
Response: It is a solution. This is now more clear in the new derivation.

Reviewer: Table 1: when relevant, the numerical values (or the expressions) of the quantities corresponding to the symbols should be added there, and the books/papers from which the estimates are taken should be referenced. For instance, the value of a0 is not given. The units should always be specified (e.g. the cooling rate has no units). Also note that the unit "mol" is different from molecule and one should rather write "molec"
Response: Corrected.

2   Referee 1

Reviewer: *In this manuscript the role of different ordered structures of water close and far from an immersed particle is investigated. A theory of immersion*

freezing based on these different states is derived. The theoretical investigations are compared to real measurements of heterogeneous nucleation rates in different experiments. Since ice nucleation in general, and especially heterogeneous nucleation is not well understood and the theoretical investigations are not convincing at the moment, a theory based on thermodynamics of water is a very interesting step for improving our knowledge of heterogeneous ice nucleation. Thus, in general this is a valid contribution for Atmospheric Chemistry and Physics. However, before the manuscript can be accepted, some issues has to be clarified. Therefore I recommend major revisions of the manuscript. In the following I will explain my concerns in details.

Response: I thank the reviewer for the comments on the manuscript. They are addressed in detail below.

Major Points

Reviewer: *1. Representation of the theory: The topic of ice nucleation is quite complicated and usually only classical nucleation theory or some additional topics are well known in the ice cloud community, whereas the more detailed thermodynamic basis is usually hidden in many discussions. In this study, the author has to present details for the development of the theory but also has to make sure that the reader can follow his line of arguments. It would be very helpful if the author would present a kind of roadmap at the very beginning to describe what he wants to derive finally and which steps will be necessary in order to do so. Otherwise the reader is really lost in details, which stem either from standard thermodynamic arguments or are of phenomenological type.*

Response: The revisited paper has been reorganized to clarify the approach. More specifically the calculation of the nucleation rate has been made the central topic of the derivation introducing a general definition firts and the constrasting how each term is aborded in the classical approach and what is new in the proposed theory. The derivation of the equation of state of vicinal water has also been reworked to make it clearer and correct errors/typos. Finally the Section on kinetics has been reorganized contrasting introducing general concepts first. This has made the revisited paper much more readable.

Reviewer: *Derivation of equation (17). I could not reproduce the central equation (17) in the form the author did, I ended with the expression*

$$a_w = a_{w,\,\mathrm{eff}}^{\frac{1}{1+\zeta}} a_{w,eq}^{\frac{\zeta}{1+\zeta}} \exp\left(\Lambda_E \frac{1-\zeta}{1+\zeta}\right) \tag{7}$$

This is crucial, since the equation is often used in the following derivation.

Response: I thank the reviewer for pointing this out. . This is a typo. $\Delta\mu_{\mathrm{S}}$ should be calculated at $a_{\mathrm{w,\,eff}}$, hence Eq. (14) of the original paper should read:

$$\Delta\mu_{\mathrm{S}} = -k_{\mathrm{B}}T \ln\left(\frac{a_{\mathrm{w,\,eff}}}{a_{\mathrm{w,\,eq}}}\right), \tag{8}$$

After introducing this equation into Eq.(13) it can be readily seen that Eq. (17) of the original paper is correct. The derivation of Eq. (8) is shown at the end of this document (Eq. 16).

Reviewer: *For instance, I have several reservations about equation (19), since the limit $\zeta \to 1$ is not well defined. The author has to check his derivation of equation (17) and, if necessary also the derivation of the subsequent theory. In section 2.3.3 the model is extended to the spinodal limit and the limit $\zeta \to 1$ is investigated, which is unbounded in the current representation, but probably not for the derivation I have found. Thus, it is not clear to me if the discussion in this section still holds.*

Response: The new derivation at the end of this document shows more clearly that $a_{\text{w, eff}}$ is in fact bounded for $\zeta \to 1$. From Eq.(24),

$$a_{\text{W}} = a_{\text{W, eff}} \left(\frac{a_{\text{w, eq}}}{a_{\text{w, eff}}} \right)^{\zeta} \exp(\Lambda_{\text{mix}}) \tag{9}$$

and from Eq.(**??**)

$$a_{\text{w, eff}} = \left(\frac{a_{\text{w}}}{a_{\text{w, eq}}^{\zeta}} \right)^{\frac{1}{1-\zeta}} \exp\left(-\frac{\Lambda_{\text{mix}}}{\zeta - 1} \right). \tag{10}$$

Since $\Lambda_{\text{mix}} = 0$ for $\zeta = 1$, then Eq.(9) implies that $a_{\text{w}} = a_{\text{w, eq}}$. Hence for $\zeta = 1$, $a_{\text{w}} = a_{\text{w, eq}} = a_{\text{w, eff}} = 1$, indicating thermodynamic equilibrium.

Minor Points

Reviewer: *Could you explain the sign of the excess energy $g^E = -A_w\zeta(1-\zeta)$? What is the thermodynamic reason for this choice?*

Response: The choice was made simply to obtain a positive T_c. However as pointed out by other reviewers there is an error in the derivation of the mixing/excess term. Motivated by this I have reworked the derivation correcting errors and making it more readable. Since the excess term only plays a minor role, the correction only resulted in about up one order of magnitude difference in J_{het}. The new derivation is presented at the end of this document and it is now included in the revised paper.

Reviewer: *What are the thermodynamic conditions for the derivation of the critical temperature, i.e. where do the conditions $\frac{\partial^2 \mu_{\text{VC}}}{\partial \zeta^2} = 0$, $\frac{\partial^3 \mu_{\text{VC}}}{\partial \zeta^3} = 0$ come from? Please explain this shortly in the text.*

Response: A solution would split into two phases if by doing so lowers its Gibbs free energy (Prausnitz et al. (1998), c.f. Section 6.12). For a metastable solution μ_{VC} must be minimal, hence $\frac{\partial \mu_{\text{VC}}}{\partial \zeta} = 0$. The condition $\frac{\partial^2 \mu_{\text{VC}}}{\partial \zeta^2} < 0$ indicates that any increase in ζ increases μ_{VC} (i.e., the curve μ_{VC} vs. ζ becomes concave downward) such that it is thermodynamically more favorable for the solution to split into disticnt phases than to increase its concentration; $\frac{\partial^2 \mu_{\text{VC}}}{\partial \zeta^2} = 0$ thus limits the metastable region. The last condition, $\frac{\partial^3 \mu_{\text{VC}}}{\partial \zeta^3} = 0$, indicates that the metastable region reduces to a single point and there is a single critical temperature T_c for a regular solution.

The explanation above has been introduced in the text.

Reviewer: *In section 2.3.2 the water activity shift for heterogeneous nucleation is derived from the theory. Could you compare this results also numerically with the use of a constant shift in actual parameterisations and comment this? How large is ζ for the usual parameterisations?*

Response: Since the mixing term is typically small, $\zeta \sim 1 - \dfrac{\Delta a_{\text{w, het}}}{\Delta a_{\text{w, hom}}}$, hence $0 < \zeta <\sim 1$ (the upper limit is somwhere around .96 due to mixing effects). This relationship is true only in the germ-forming regime where J_{het} is mainly dictaed by thermodynamics. Kärcher (2003) suggested teh approximation $J_{\text{het}} \approx J_{\text{hom}}(\Delta a_{\text{w, het}})$. This of course resembles the definition of the nucleation work derived in Section 2.3.1. The revisited paper discusses this in further detail. As expected the two approaches considerable differ for the spinodal regime. It must be noted Knopf and Alpert (2013) parameterized J_{het} as a function of $\Delta a_{\text{w, het}}$ however since their coefficients are material specific comparison against their work is left for future works.

Reviewer: *In figure 4 different curves of water activity are shown. As far as I understand, the colors (dark red to yellow) indicate different versions of the new theory (aw,het). Thus, the label aw,het as red in the diagram is misleading*

Response: Corrected.

3 Corrected derivation of the equation of state of vicinal water

The vicinal layer is defined as a solution of hypothetical ice-like (IL) and liquid-like (LL) regions, with Gibbs free energy given by

$$\mu_{\text{vc}} = (1 - \zeta)\hat{\mu}_{\text{LL}} + \zeta\hat{\mu}_{\text{IL}} \tag{11}$$

where $\hat{\mu}_{\text{LL}}$ and $\hat{\mu}_{\text{LL}}$ are the chemical potentials of the LL and IL species within the solution, respectively, and ζ is the fraction of IL regions in the layer. Equation (11) can also be written in terms of the chemical potentials of the "pure" LL and IL species, μ_{LL} and μ_{IL}, respectively, in the form,

$$\mu_{\text{vc}} = (1 - \zeta)\mu_{\text{LL}} + \zeta\mu_{\text{IL}} + \Delta G_{\text{mix}} \tag{12}$$

where $\Delta G_{\text{mix}} = (\hat{\mu}_{\text{IL}} - \mu_{\text{IL}})\zeta + (1 - \zeta)(\hat{\mu}_{\text{LL}} - \mu_{\text{LL}})$ is the Gibbs energy of mixing. For a mixture of pure LL and IL species $\Delta G_{\text{mix}} = 0$, whereas for and ideal solution ΔG_{mix} is determined by the ideal entropy of mixing. Reorganizing Eq. (12) we obtain,

$$\mu_{\text{vc}} = \mu_{\text{LL}} + \zeta\Delta\mu_{\text{il}} + \Delta G_{\text{mix}} \tag{13}$$

where $\Delta\mu_{\text{il}} = \mu_{\text{IL}} - \mu_{\text{LL}}$. $\Delta\mu_{\text{il}}$ can be approximated by using the equilibrium between bulk liquid and ice as the reference state and introducing the definitions

$$\mu_{\text{IL}} = \mu_{\text{eq}} + k_{\text{B}}T\ln(a_{\text{IL}}), \tag{14}$$

and

10

$$\mu_{\text{LL}} = \mu_{\text{eq}} + k_{\text{B}}T \ln \left(\frac{a_{\text{w, eff}}}{a_{\text{w, eq}}} \right), \tag{15}$$

where $a_{\text{w, eff}}$ is termed the "effective water activity" and it is the value of a_{w} associated with the LL regions in the vicinal water, and a_{IL} is the water activity in the IL regions. Similarly to bulk ice the solute does not significanlty partition to the IL phase and $a_{\text{IL}} \approx 1$. With this, and combining Eqs.(14) and Eqs.(15) and rearranging we obtain,

$$\Delta\mu_{\text{il}} = -k_{\text{B}}T \ln \left(\frac{a_{\text{w, eff}}}{a_{\text{w, eq}}} \right), \tag{16}$$

The central assumption behind Eq. (16) is that $a_{\text{w, eq}}$ corresponds to the equilibrium water activity between liquid and ice, or in other words that near equilibrium $\Delta\mu_{\text{il}} \approx \Delta\mu_{\text{S}}$, being $\Delta\mu_{\text{S}}$ the excess energy of solidification of water.
In reality $\Delta\mu_{\text{S}}$ corresponds to actual liquid and ice instead of the hypothetical LL and IL substances. In principle this difference can be accounted for by selecting a proper functional form for ΔG_{mix}, for which several empirical and semiempirical interaction models with varying degrees of complexity exist Prausnitz et al. (1998). In this work it is going to be assumed that the vicinal water can be described as a regular solution. This is the simplest model that accounts for the interaction between solvent and solute during mixing and that is flexible enough to include corrections for the difference between $\Delta\mu_{\text{S}}$ and $\Delta\mu_{\text{il}}$. Holten et al. (2013) have shown some success in describing the chemical potential of supercooled water. Moreover the authors also showed that taking into account clustering of water molecules upon mixing led to a better description of the thermodynamics of supercooled water.
According to the regular solution model, modified by clustering (Holten et al., 2013, c.f. Eq. 16),

$$\Delta G_{\text{mix}} = \frac{k_{\text{B}}T}{N} \left[\zeta \ln(\zeta) + (1-\zeta)\ln(1-\zeta) \right] + A_w\zeta(1-\zeta) \tag{17}$$

The first term on the right hand side corresponds to the usual definitioin of the ideal entropy of mixing, i.e., random ideal mixing and a weak interaction between IL and LL regions, modified to account for clustering in groups of N molecules. From Holten et al. (2013) $N = 6$ corresponds to clustering in hexamers and is near the optimum fit between MD simulations and the solution model. It must be noted that Holten et al. (2013) recommended an alternative model termed "athermal solution", where nonideality is ascribed to entropy changes upon mixing. In vicinal water some evidence points at nonideality originating from enthalpy changes near the particle Etzler (1983), hence a regular solution is more appropiate in this case. Furthermode Holten et al. (2013) showed that for $N = 6$ the two models were almost equivalent.

The second term on the right hand side of Eq. (17) is an empirical functional form used to approximate the enthalpy of mixing selected so that ΔG_{mix} becomes negligible for $\zeta = 0$ and $\zeta = 1$. A_w is a phenomenological interaction parameter and typically must be fitted to experimental observations. Here it is assumed A_w implicitly acts as a correction factor to the approximation $\Delta\mu_{\text{il}} \approx \Delta\mu_{\text{S}}$.

A important aspect of the regular solution model is that it predicts that ΔG_{mix} has a critical temperature, T_c, at $\zeta = 0.5$, defined by the conditions,

$$\frac{\partial^2 \Delta G_{\text{mix}}}{\partial \zeta^2} = 0 \ , \ \frac{\partial^3 \Delta G_{\text{mix}}}{\partial \zeta^3} = 0. \tag{18}$$

Using Eq. (17) into Eq. (18) and solving for A_w gives for $T = T_{\text{c}}$,

$$A_w = \frac{2k_{\text{B}} T_{\text{c}}}{N}. \tag{19}$$

Physically, T_c represents the stability limit of the vicinal water, at which it spontaneously separates into IL and LL regions. Hence Eq. (19) provides a an opportunity to determine A_w, since T_c should also correspond to the temperature at which the work of nucleation becomes negligible. This is explored in Section 3.2.

Collecting Eqs. (16), (17), and (19), into Eq. (13) we obtain,

$$\mu_{\text{vc}} = \mu_{\text{LL}} - \zeta k_{\text{B}} T \ln\left(\frac{a_{\text{w, eff}}}{a_{\text{w, eq}}}\right) + \frac{k_{\text{B}} T}{N} \left[\zeta \ln(\zeta) + (1 - \zeta) \ln(1 - \zeta)\right] + \frac{2k_{\text{B}} T_{\text{c}}}{N} \zeta (1 - \zeta) \tag{20}$$

Making

$$\Lambda_{\text{mix}} = \frac{1}{N} \left[\zeta \ln(\zeta) + (1 - \zeta) \ln(1 - \zeta)\right] + \frac{2}{N} \frac{T_{\text{c}}}{T} \zeta (1 - \zeta) \tag{21}$$

Equation (20) can be written in the form,

$$\mu_{\text{vc}} = \mu_{\text{LL}} - \zeta k_{\text{B}} T \ln\left(\frac{a_{\text{w, eff}}}{a_{\text{w, eq}}}\right) + k_{\text{B}} T \Lambda_{\text{mix}} \tag{22}$$

Equation (22) is the equation of state of vicinal water. It describes the properties of vicinal water in terms of the material-specific parameter ζ, and the interaction parameters N and T_{c}. MD simulations indicate that $N \sim 6$ Bullock and Molinero (2013); Holten et al. (2013). T_{c} is thus the only remaining unknown in Eq. (22) and it is calculated Section 3.3.

In immersion freezing the particle remains within the droplet long enough that equilibrium is established. This condition is mathematically expressed by the equality, $\mu_{\text{VC}} = \mu_{\text{W}}$, where μ_{W} is the chemical potential of water in the bulk of the liquid, i.e., away from the particle. Using Eq. (22) this implies,

$$\mu_{\text{W}} = \mu_{\text{LL}} - \zeta k_{\text{B}} T \ln\left(\frac{a_{\text{w, eff}}}{a_{\text{w, eq}}}\right) + k_{\text{B}} T \Lambda_{\text{mix}} \tag{23}$$

Using again the equilibrium between bulk liquid and ice as the reference state, so that $\mu_{\text{W}} = \mu_{\text{eq}} + k_{\text{B}} T \ln(a_{\text{W}})$, and using Eq. (14), Eq. (23) can be written in terms of the water activity in the form

$$a_{\text{W}} = a_{\text{w, eff}} \left(\frac{a_{\text{w, eq}}}{a_{\text{w, eff}}}\right)^{\zeta} \exp(\Lambda_{\text{mix}}) \tag{24}$$

From Eq. (24) $a_{\text{w, eff}}$ can be readily obtained in the form,

$$a_{\text{w, eff}} = \left(\frac{a_{\text{w}}}{a_{\text{w, eq}}^{\zeta}} \right)^{\frac{1}{1-\zeta}} \exp\left(-\frac{\Lambda_{\text{mix}}}{\zeta - 1} \right). \tag{25}$$

References

Barahona, D.: Analysis of the effect of water activity on ice formation using a new thermodynamic framework, Atm.Chem. Phys., 14, 7665–7680, https://doi.org/10.5194/acp-14-7665-2014, URL `http://www.atmos-chem-phys.net/14/7665/2014/`, 2014.

Barahona, D.: Thermodynamic derivation of the activation energy for ice nucleation, Atm. Chem. Phys., 15, 13 819–13 831, https://doi.org/10.5194/acp-15-13819-2015, URL `http://www.atmos-chem-phys.net/15/13819/2015/`, 2015.

Bullock, G. and Molinero, V.: Low-density liquid water is the mother of ice: on the relation between mesostructure, thermodynamics and ice crystallization in solutions., Faraday Discuss., https://doi.org/10.1039/C3FD00085K, 2013.

Etzler, F. M.: A statistical thermodynamic model for water near solid interfaces, J. Coll. Interf. Sci., 92, 43–56, 1983.

Holten, V., Limmer, D. T., Molinero, V., and Anisimov, M. A.: Nature of the anomalies in the supercooled liquid state of the mW model of water, J. Chem. Phys., 138, 174 501, 2013.

Kärcher, B.: Simulating gas-aerosol-cirrus interactions: Process-oriented microphysical model and applications, Atmos. Chem. Phys. Discuss., 3, 1645–1664, 2003.

Kashchiev, D.: Nucleation: basic theory with applications, Butterworth Heinemann, 2000.

Knopf, D. A. and Alpert, P. A.: A water activity based model of heterogeneous ice nucleation kinetics for freezing of water and aqueous solution droplets, Faraday disc., 165, 513–534, 2013.

Marcolli, C., Gedamke, S., Peter, T., and Zobrist, B.: Efficiency of immersion mode ice nucleation on surrogates of mineral dust, Atmos. Chem. Phys., 7, 5081–5091, 2007.

Prausnitz, J. M., Lichtenthaler, R. N., and de Azevedo, E. G.: Molecular thermodynamics of fluid-phase equilibria, Prentice Hall, Upper Saddle River, NJ, USA, 3rd edn., 1998.

On the Thermodynamic and ~~Dynamic~~ Kinetic Aspects of Immersion Ice Nucleation

Donifan Barahona[1]

[1]NASA Goddard Space Flight Center, Greenbelt, MD, USA

Correspondence to: Donifan Barahona (donifan.o.barahona@nasa.gov)

Abstract.

Heterogeneous ice nucleation initiated by particles immersed within droplets is likely the main pathway of ice formation in the atmosphere. Theoretical models commonly used to describe this process assume that it mimics ice formation from the vapor, neglecting interactions unique to the liquid phase. This work introduces a new approach that accounts for such interactions by linking the ability of particles to promote ice formation to the modification of the properties of water near the particle-liquid interface. It is shown that the same mechanism that lowers the thermodynamic barrier for ice nucleation also tends to decrease the mobility of water molecules, hence the ice-liquid interfacial flux. Heterogeneous ice nucleation in the liquid phase is thus determined by the competition between thermodynamic and kinetic constraints to the formation and propagation of ice. At the limit, ice nucleation may be mediated by ~~the dynamics of vicinal water~~ kinetic factors instead of the nucleation work. This new ice nucleation regime is termed spinodal ice nucleation. Comparison of predicted nucleation rates against published data suggests that some materials of atmospheric relevance may nucleate ice in this regime.

1 Introduction

Ice nucleation in cloud droplets and aerosol particles leads to cloud formation and glaciation at low temperature. It is often initiated by certain aerosol species known as ice nucleating particles (INP) (**???**). These include dust, biological particles, metals, effloresced sulfate and sea salt, organic material and soot (**??**). Background INP concentrations may be influenced by aerosol emissions (**?**). Anthropogenic activities may thus alter the formation and evolution of ice clouds leading to an indirect effect on climate. The assessment of the role of INP on climate is challenging due to the complexity of the atmospheric processes involving ice and the limited understanding of the ice nucleation mechanism of INP (**?**). Ice nucleation promoted by a particle completely immersed within the liquid phase, referred as "immersion freezing", is likely the most common ice formation pathway in the atmosphere (**??**). Immersion freezing is involved in the initiation of precipitation and determines to a large extent the phase partitioning in convective clouds (**????**).

The accurate representation of immersion ice nucleation is critical for the correct modeling of cloud processes in ~~atmospheric models~~ the atmosphere (**???**). Field campaign data have been used to develop empirical formulations relating the INP concentration to the cloud temperature, T, and saturation ratio, S_i (e.g, **???**), and more recently to the ambient aerosol size and composition (e.g., **???**). Empirical formulations provide a simple way to parameterize ice nucleation in atmospheric models

(e.g., **??**). However they may not be valid outside the conditions used in their development, particularly as different experimental techniques may result on a wide range of measured ice nucleation efficiencies (**?**). Alternatively, the ice nucleation efficiency can be empirically parameterized using laboratory data, although with similar caveats (**??**).

Molecular dynamics (MD) simulations and direct kinetic methods have been used to study ice nucleation (e.g., **????**). However, the classical nucleation theory (CNT) is nearly the only theoretical approach employed to describe immersion freezing in cloud models (e.g., **????**). According to CNT, nucleation is initiated by the growth of a cap-shaped ice germ on the surface of the immersed particle ~~which grows by random collision of water molecules~~ (**??**). The geometry of the ice germ is defined by a force balance at the particle-ice-liquid interface, ~~described~~ and characterized by the contact angle, θ. In this sense, the ice germ is assumed to "wet" the immersed particle in the same way a liquid droplet wets a solid surface (**?**). Low values of θ indicate a high affinity of the particle for ice and a low energy of formation of the ice germ.

Direct application of CNT in immersion freezing is thwarted by uncertainty in fundamental parameters of the theory~~as for example~~, i.e., the ice-liquid interfacial energy, σ_{iw}, and the activation energy. Moreover, using a single θ to describe the nucleation efficiency of dust and other materials typically leads to large discrepancy between CNT predictions and experimental measurements (e.g., **????**). ~~More fundamentally, CNT neglects important interactions near the immersed particle that may influence the nucleation rate.~~ MD simulations show that an ice germ formed near a surface tends to have a complex geometry instead cap-shaped assumption of CNT (e.g. **???**). ~~Also~~For example, in a liquid the ice germ ~~would~~ may not "wet" the particle but rather exert stress on the substrate (**??**)~~. It~~, and it is not clear that ~~such force balance can be expressed in terms of a contact angle~~ this can be described as a simple function of θ (**?**). It has also been shown that σ_{iw} obtained by fitting CNT to measured nucleation rates tends to be biased high to account for mixing effects neglected in common formulations of the theory (**?**).

~~Another fundamental assumption used in CNT is~~ More fundamentally, CNT neglects important interactions near the immersed particle that may influence the nucleation rate. It is assumed that ice nucleation solely depends on the local geometry of the absorbed molecules on the immersed particle (**?**). This implies that the particle influences the formation of the ice germ but does not influence the adjacent water. The viscosity and density of water in the vicinity of the particle and in contact with the ice germ are assumed similar to those in the bulk (**?**). This is at odds with evidence of a strong effect of immersed particles on the vicinal water (**??**). In fact, such an effect may be responsible for the enhancement of ice nucleation near immersed solids (**?**).

~~To analyze how these interactions may affect immersion ice nucleation this work introduces a new approach to link the enhancement of the ice nucleation efficiency by immersed particles to the properties of vicinal water.~~

2 ~~Theoretical development~~

1.1 Evidence for the formation of ordered structures near the liquid-particle interface

There is considerable evidence of the modification of the properties of vicinal water (i.e., the water immediately adjacent to the particle) by immersed surfaces. It has been known for some time that water near interfaces displays physicochemical properties different from those of the bulk (e.g., **???**). By examining a wealth of available observations **?** concluded that vicinal water

may exist in a ordered state near the solid-liquid interface and that such ordered structures may propagate over considerable

60   distance, of the order of hundreds to thousands of molecular diameters. More recent experiments showing that hydrophilic surfaces have a long-range impact further support this conclusion (e.g., **?**). The interaction between the particle and the vicinal water becomes more significant as the temperature decreases and the viscosity increases (**?**). Recent studies have shown the presence of ordered water near ~~interfaces in~~ the interface of biological (**??**), metallic (**?**) and clay (**??**) particles, a notion that is also supported by molecular dynamics simulations (**??**). In a groundbreaking work, **?** found strong evidence of ice formation

65   several molecular diameters away from the clay-water interface. The author concluded that ice formation does not require an ice germ attached to the substrate, but rather the nascent ice germ is stabilized by ordering in the interfacial zone. To date no quantitative theory has been developed exploiting such a view of ice nucleation.

The description of the properties of vicinal water is still under investigation. Early studies concluded that ordered water near immersed surfaces does not resemble a caltrate-like orientation of water molecules (**?**). Rather, in the supercooled region

70   the presence of structured low-density regions near solid surfaces (termed "ice-like") has been reported for different materials (e.g., **?????**). In this region **?** parameterized the density and enthalpy of vicinal water as ~~an ideal~~ a mixture of ice-like and bulk-like water. Additional experimental observations show the modification of the mobility of vicinal water near interfaces; i.e., the vicinal water typically has a higher viscosity when compared to the bulk (**????**). In some cases, clays and biological systems exhibit a viscous layer of water at the particle-liquid interface that remains liquid even if the bulk has already frozen

75   (**?**). These effects are typically characterized as non-equilibrium, since they affect the flux of molecules to the nascent ice germ rather than the thermodynamics of ice nucleation. **?** found experimentally that the viscosity of interfacial water regulates the ice nucleation activity, giving support to the idea that the work of nucleation and the enhancement of the viscosity of the vicinal water are tightly linked. In fact, increased viscosity may be a necessary condition for ice nucleation since structural ordering is not possible in a fluid with low viscosity (**?**).

80   These considerations are largely missing in the theoretical description of ice nucleation. There is currently no theory that can account for the thermodynamic and ~~dynamic~~ kinetic effects of an immersed particle on the surrounding water, hence on ice nucleation. ~~To this end, an approach to describe~~ Such a task is undertaken in this work. Section **??** presents the theoretical description of a new approach, accounting for the thermodynamics of vicinal water ~~is introduced in Section ??. Then in Sections ?? and ??~~ (Section **??**) and their relation to the work of nucleation (Section **??**) and the nucleation rate (Sections **??** and **??**).

85   These new relations are analyzed and applied to specific cases of atmospheric relevance in Section **??**.

2   Theoretical development

The new approach is developed within the scope of the kinetic treatment of nucleation, when cluster formation is the limiting step to ice formation (**??**). The central result of this theory is the well-known general expression for the nucleation rate in steady state (e.g., **?**, Cf. Eq. 13-33),

90   $$J = Z f^* C^*, \tag{1}$$

3

where Z is the Zeldovich factor, f^* is the attachement frequency (also called the impingement factor) and C^* is the concentration of supercritical clusters. Z corrects for the detachment of monomers from the cluster during nucleation. It can also be interpreted as the probability that a molecule reaches the ice germ following a thermally activated "random walk". Generally,

$$Z = \left[-\frac{\left(\frac{\partial^2 \Delta G^*}{\partial n^2} \right)_{n=n^*}}{2\pi k_{\mathrm{B}} T} \right]^{1/2} \tag{2}$$

95 where ΔG^* is the work of critical germ formation and n^* is the number of water molecules in the ice germ. If the molecular cluster size distribution can be assumed to be near equilibrium, which is the case for the immersion freezing, then

$$C^* = C_0 \exp\left(-\frac{\Delta G^*}{k_B T} \right) \tag{3}$$

where C_0 is the monomer concentration adjacent to the surface of the growing ice germ impliying that interface transfer is the dominant mechanism of cluster growth.

100 These expressions can be applied directly to model ice nucleation as follows. For homogeneous ice nucleation, $\Delta G^* = \Delta G_{\mathrm{hom}}$, ~~it is used to develop quantitative models for the thermodynamics and dynamics of ice nucleation~~ $f^* = f^*_{\mathrm{hom}}$, and $C_0 = v_w^{-1}$ being v_w the molecular volume of water (**?**),

$$J_{\mathrm{hom}} = \frac{Z f^*_{\mathrm{hom}}}{v_w} \exp\left(-\frac{\Delta G_{\mathrm{hom}}}{k_B T} \right), \tag{4}$$

and for heterogeneous ice nucleation, $\Delta G^* = \Delta G_{\mathrm{het}}$, $f^* = f^*_{\mathrm{het}}$, respectively, $C_0 = a_0^{-1}$ being a_0 the average cross-sectional
105 area of a water molecule, i.e.,

$$J_{\mathrm{het}} = \frac{Z f^*_{\mathrm{het}}}{a_0} \exp\left(-\frac{\Delta G_{\mathrm{het}}}{k_B T} \right). \tag{5}$$

Using $C_0 = a_0^{-1}$ is advantageous because J_{het} is typically normalized to the particle surface area (**??**). It however involves the assumption that the density of water does not vary within the droplet, remaining constant even at the particle-water interface. In other words, anywhere within the liquid the per-area molecular density should be the same. This assumption however does
110 not lead to significant error since the effect of the particle on the water density is small (e.g., **?**) and J_{het} is lineraly related to C_0.

Equation (**??**) provides the basis for this work. It shows that to predict the effect of the immersed particle on ice formation it is neccesary to understand how the presence of the particle affects ΔG_{het} and f^*_{het}. Such a task is undertaken in this section. Section **??** provides an overview of the main assumptions of CNT, which are then constrasted with the Negentropic Nucleation

4

115 Framework (NNF) in Section ??. Sections ?? and ?? analyze the thermodynamic aspects of immersion ice nucleation, and formulate a new expression for ΔG_{het}. Section ?? develops an expression for f^*_{het} accounting for the effect of the particle on the mobility of water molecules. In Section ?? a new expression for the nucleation rate is formulated.

2.1 Classical Nucleation Theory

Since CNT is the most widely used theoretical approach in atmospheric models we start
120 by highlighting its main characteristic. Common CNT expressions use several assumptions to simplify the description of the interaction between water and the immersed particle (e.g., ???). Typically the particle is assumed to have a negligible effect on the mobillity and the thermodynamics of the vicinal water, impliying that $f^*_{\text{het}} \approx f^*_{\text{hom}}$. The later is calculated assuming that the formation of clusters within the liquid phase mimics a first order reaction in an ideal gas where every molecule that randomly jumps the ice-liquid interface is incorporated within
125 the ice lattice. Thus f^*_{hom} is the product of the frequency factor (derived from transition state theory) and the monomer concentration at the ice-liquid interface. This leads to (??),

$$J = \frac{k_{\text{B}}TZ}{a_0 h} f^*_{\text{hom, CNT}} = \frac{\Omega d_0}{v_w} \frac{k_{\text{B}}T}{h} \exp\left[-\frac{\Delta G_{\text{act}} + g(\theta)\Delta G_{\text{hom, CNT}}}{k_B T} \right], \tag{6}$$

130 where ΔG_{act} is the activation energy, i.e., the energy required for a water molecule to leave its equilibrium position in the bulk towards the vicinity of the ice germ (??), h is Plank's constant, Ω the surface area of the ice germ and d_0 is the molecular diameter of water.
135 The work of ice nucleation results from the assumption that the ice germ has a hemi-spherical shape. Other assumptions include no surface stress (?) and negligible mixing effects during the germ formation (?). These considerations lead to the expression (?),

$$\Delta G_{\text{het,CNT}} = g(\theta)\Delta G_{\text{hom, CNT}}, \tag{7}$$

where $\Delta G_{\text{hom, CNT}}$ is the homogeneous nucleation work, given by

140
$$\Delta G_{\text{hom,CNT}} = \frac{16\pi \sigma_{\text{iw}}^3 v_{\text{w}}^2}{3\left(k_{\text{B}}T \ln S_{\text{i}}\right)^2}, \tag{8}$$

where σ_{iw} is ~~th~~ the ice-water interfacial energy ~~. Typically σ_{iw} is empirically fitted to match measured nucleation rates~~ and S_i is the supersaturation. The effect of the immersed particle on $J_{het, CNT}$ depends on the adsorption of water molecules on individual sites, and ~~it~~ is characterized by the contact angle, θ, in the form,

$$g(\theta) = \frac{1}{4}(2 + \cos\theta)(1 - \cos\theta)^2. \tag{9}$$

Equation (**??**) can be extended to account for line tension, curvature and misfit effects (e.g., **?**). Those are however neglected in this study. Introducing Eqs. (**??**) and (**??**) into Eq. (**??**) we obtain the known expression,

~~It is clear that the~~

$$J_{het, CNT} = \frac{Z\Omega d_0}{a_0 v_w}\frac{k_B T}{h} \exp\left[-\frac{\Delta G_{act} + g(\theta)\Delta G_{hom, CNT}}{k_B T}\right], \tag{10}$$

where $\Omega = 4\pi r_g^2$ being $r_g = \left(\frac{3n^* v_w}{4\pi}\right)^{1/3}$ the ice germ radius. Other symbols are defined in Table 1.

Due in part to the assumption of a negligible effect of the particle on the adjacent water the CNT framework does not provide a way to link the properties of the vicinal water to the ~~liquid-ice interfacial diffusion rate~~ nucleation rate. Another caveat is that fundamental parameters like ΔG_{act}, σ_{iw} and θ do not have a clear definition outside of the context of the theory. For example, ΔG_{act} is typically assumed the same as in bulk water, hence it represents a barrier to "bulk" diffusion instead of interfacial transfer (**??**). Similarly σ_{iw} is not well defined for a diffuse interface and it is difficult to measure away from equilibrium. Moreover, θ relies on a droplet-like picture of the nascent ice germ, which may not be appropiate for a germ forming within a denser phase (**?**). Due to this most studies treat ΔG_{act}, σ_{iw} and ~~the nucleation work, hence the nucleation rate. Accounting for such effects therefore requires a different approach, introduced in the next sections.~~ θ as empirical parameters, fitted to match measured nucleation rates. Many times this results in complex functional forms of T and S_i that may not be easily expanded to account for the modified properties of water near the immersed particle.

2.2 ~~Thermodynamics of ice formation near the liquid-particle interface~~

2.2 Negentropic Nucleation Framework

~~The discussion presented in Section **??** suggests that~~ Some of the caveats of CNT are addressed in the negentropic nucleation framework (NNF) (**??**). In NNF simple thermodynamic arguments are used to approximate ΔG_{hom} and f_{hom} in terms of water properties that could in principle be independently estimated. This obviates the need for parameters that should be fittted to measured nucleation rates. At the same time, NNF is a relatively simple framework that can be easily implemented in large scale atmospheric models and that has been shown to reproduce homogeneous freezing temperatures down to 180 K (**??**). Hence NNF provides a suitable framework that can be extended to link the ~~immersed particle enhances order near the particle-liquid interface, lowering the energy required to nucleate ice. Hence the first step towards linking immersion freezing to the~~ properties of ~~vicinal~~ the vicinal water to the thermodynamic and kinetic aspects of ice nucleation. This section presents the main results of NNF for homogeneous ice nucleation.

In NNF the energy of formation of the interface, Φ_s, is a explicit function of the water activity and temperature in the form,

$$\Phi_s = \Gamma_w s \left(\Delta h_f - \Gamma_w k_B T \ln a_w \right), \tag{11}$$

where the constants $\Gamma_w = 1.46$ and $s = 1.105$ molec$^{1/3}$ define the coverage of the ice-water interface and the lattice geometry of the ice germ, respectively, and Δh_f is the latent heat of fusion of water ~~is to develop a thermodynamic description of the~~

175 ~~latter~~. Other symbols are defined in Table **??**. Equation (**??**) results from accounting for the finite character of the ice-liquid interface and from the assumption that in joining the ice lattice the water molecules lose most of their entropy (**?**). The driving force for ice nucleation $\Delta \mu_i$ is given by,

~~The vicinal water differs from the bulk in that it contains a larger fraction of four-bonded, low density regions. Therefore it can be represented as a solution of ice-like~~

180 $$\Delta \mu_i = k_B T \ln \left(\frac{a_w^2}{a_{w,eq}} \right), \tag{12}$$

where $a_{w,eq}$ is the equilibrium water activity. Equation (**??**) accounts for the work of "unmixing" affecting the bulk of the liquid when the ice germ is formed, which is proportional to $\ln(a_w)$ (**?**). Using Eqs. (**??**) and ~~liquid-like "species". In reality it is likely that vicinal water , just as bulk water, is made of a complex mixture of different water configurations (??). However two-state models have shown success in parameterizing the properties of supercoooled water and are favored for their simplicity (??).~~

185 ~~Within this framework it is assumed that Ice-Like (IL) and Liquid-Like (LL) species with chemical potentials μ_{IL} and μ_{LL}, respectively, are mixed from their pure state forming a solution. During mixing some of~~ (**??**), the critical germ size, n_{hom}^*, is simply obtained from the condition of mechanical equilibrium, $\frac{\partial \Delta G}{\partial n_{hom}^*} = 0$ (**?**),

$$n_{hom}^* = \left(\frac{2\Phi_s}{3\Delta \mu_i} \right)^3 \tag{13}$$

from where ΔG_{hom} is readily written in the form,

190 $$\Delta G_{hom,\,NNF} = \frac{1}{2} n_{hom}^* \Delta \mu_i. \tag{14}$$

In more recent work the kinetics of homogeneous ice nucleation have been reexamined in NNF to account for molecular rearrangement during the transfer of water molecules across the ice-liquid interface (**?**). Within this approach f_{hom}^* is determined by the liquid-ice diffusion coefficient for interfacial transfer, D, in the form (**??**),

$$f^* = \frac{D\Omega}{v_w d_0} \tag{15}$$

where Ω is the surface area of the ice germ. D represents contributions from purely diffusive process and from structural transformations required to incorporate water molecules into the ice germ. The latter originates because random jump of water molecules across the interface is no a sufficient condition for ice crystal growth. Neighboring molecules need to be rearranged to accommodate new ones into the ice lattice. This process generates entropy, hence it can be characterized by the work dissipated when each molecule is incorporated to the ice-lattice. Using considerations from non-equilibirium thermodynamics this leads to the result,

$$D = D_\infty \left[1 + \exp\left(\frac{W_d}{k_B T} \right) \right]^{-1} \tag{16}$$

where D_∞ the bulk self-diffusion coefficient of water, and W_d is the average dissipated work during interface transfer. The latter is proportional to the ~~thermodynamic configurations available to each substance are lost due to the presence of the other solute, resulting in the entropy of mixing, ΔS_{mix}. The enthalpy and total entropy of each substance in solution may differ from their corresponding values in the pure state, leading to an~~ excess free energy ~~, g^E. If we denote by ζ the fraction of IL regions, then adding these contributions results in a equation of state for the vicinal water in the form,~~ of solidification of water, i.e., $W_d = -n_t \Delta\mu_s$, being $n_t = 16$, the number of possible trajectories in which individual water molecules can make four-bonded water. Equation (**??**) shows explicitly that bulk diffusion (i.e., D_∞) as well a structural rearragement are required for ice germ growth. Introducing Eq. (**??**) into Eq. (**??**) we obtain,

~~$$\mu_{\text{vc}} = (1-\zeta)\mu_{\text{LL}} + \zeta\mu_{\text{IL}} + T\Delta S_{\text{mix}} + g^E,$$~~

$$f_{\text{hom}}^* = \frac{D_\infty \Omega}{v_w d_0} \left[1 + \exp\left(-n_t \Delta\mu_s \right) \right]^{-1} \tag{17}$$

~~The parameter ζ describes how efficiently~~ Application of Eq. (**??**) in homogeneous ice nucleation shows agreement of J_{hom} with experimental data at very low T, where kinetic processes dominate the formation ice (**?**).

NNF provides explicit dependencies of D and Φ_s on thermodynamic properties withouth depending on nucleation rate measurements. Thus it provides a suitable basis to study how vicinal water affects the thermodynamics and kinetics of ice formation in the vicinity of immersed particles. Doing so requires first building a model to describe the thermodynamics of vicinal water.

2.3 Thermodynamics of the liquid-particle interface

The discussion presented in Section **??** suggests that the immersed particle enhances ~~the~~ order near the particle-liquid interface, lowering the energy required to nucleate ice. To represent this the vicinal layer is described as a solution of hypothetical ice-

like behavior on the adjacent water, hence it acts as a "templating" factor. The limiting values $\zeta = 0$ (IL) and liquid-like (LL) regions, with Gibbs free energy given by

$$\mu_{\rm vc} = (1-\zeta)\hat{\mu}_{\rm LL} + \zeta\hat{\mu}_{\rm IL}, \tag{18}$$

where $\hat{\mu}_{\rm LL}$ and $\zeta = 1$ imply that vicinal water behaves as liquid-like or ice-like, respectively. Note that even for $\zeta = 0$ vicinal water likely has some IL configurations (which is the case for bulk supercooled water) and Eq. (??) merely represents a relative increase in the ice-like character near the immersed particle rather than absolute fraction of low density regions $\hat{\mu}_{\rm LL}$ are the chemical potentials of the LL and IL species within the solution, respectively, and ζ is the fraction of IL regions in the layer. Increased ordering is thus represented by a higher fraction of IL regions, hence higher ζ.

Equation (??) can be reorganized in the the also be written in terms of the chemical potentials of the "pure" LL and IL species, $\mu_{\rm LL}$ and $\mu_{\rm IL}$, respectively, in the form,

$$\mu_{\rm vc} = (1-\zeta)\mu_{\rm LL} + \zeta(\mu_{\rm IL} - \mu_{\rm LL}) + T\Delta S_{\rm mix} + g^E . G_{\rm mix} \tag{19}$$

To express $\mu_{\rm vc}$ in terms of measurable properties, two approximations are introduced. First $\Delta S_{\rm mix}$ is given where $\Delta G_{\rm mix} = (\hat{\mu}_{\rm IL} - \mu_{\rm IL})\zeta + ($ is the Gibbs energy of mixing. For a mechanical mixture of pure LL and IL species, $\Delta G_{\rm mix} = 0$, whereas for an ideal solution $\Delta G_{\rm mix}$ is determined by the ideal entropy of mixing modified by a clustering factor, N, i. e.(?). Reorganizing Eq. (??) we obtain,

$$\Delta S_{\rm mix}\mu_{\rm vc} = \frac{k_{\rm B}}{N}\zeta\ln(\zeta)\mu_{\rm LL} + (1-\zeta)\ln(1-\zeta).\Delta\mu_{\rm il} + \Delta G_{\rm mix} \tag{20}$$

This approximation results from assuming random mixing and a weak interaction between IL and LL regions, which tend to cluster in groups of N molecules. Deviations from this behavior are in principle corrected by the excess energy, g^E, provided a suitable expression is available. Since g^E must be negligible for $\zeta = 0$ and $\zeta = 1$ the simplest model describing this behavior takes the form, where $\Delta\mu_{\rm il} = \mu_{\rm IL} - \mu_{\rm LL}$. $\Delta\mu_{\rm il}$ can be approximated using the equilibrium between bulk liquid and ice as reference state (?). Making,

$$\mu_{\rm IL} = \mu_{\rm eq} + k_{\rm B}T\ln(a_{\rm IL}), \tag{21}$$

and

$$g^E \mu_{\rm LL} = -A_w\zeta(1-\zeta)\mu_{\rm eq} + k_{\rm B}T\ln\left(\frac{a_{\rm w,\,eff}}{a_{\rm w,\,eq}}\right), \tag{22}$$

where A_w is a phenomenological interaction parameter, and the negative sign accounts for the tendency of IL and LL regions to cluster (?). Using Eq. (?? $a_{w,\text{eff}}$ is termed the "effective water activity" and it is the value of a_w associated with the LL regions in the vicinal water, and a_{IL} is the water activity in the IL regions. It is assumed that similarly to bulk ice the solute does not significanlty partition to the IL phase, so that $a_{\text{IL}} \approx 1$. With this, and combining Eq.(??) and Eq. (??) within Eq. (??) (??) and rearranging we obtain,

$$\Delta\mu_{\text{vcil}} = \mu_{\text{LL}} + \zeta(\mu_{\text{IL}} - \mu_{\text{LL}}) + \frac{k_B T}{N}\zeta - k_B T \ln(\zeta) + (1-\zeta)\ln(1-\zeta) - A_w\zeta(1-\zeta), \left(\frac{a_{w,\text{eff}}}{a_{w,\text{eq}}}\right). \tag{23}$$

This expression corresponds to a regular solution approximation to the properties of vicinal water. It has been previously used with success in describing the The central assumption behind Eq. (??) is that $a_{w,\text{eq}}$ corresponds to the equilibrium water activity between liquid and ice, or in other words that near equilibrium $\Delta\mu_{\text{il}} \approx \Delta\mu_s$. In reality $\Delta\mu_s$ corresponds to actual liquid and ice instead of the hypothetical LL and IL substances. This difference can be accounted for by selecting a proper functional form for ΔG_{mix}, for which several empirical and semiempirical interaction models, with varying degrees of complexity exist (?). In this work it is going to be assumed that the vicinal water can be described as a regular solution. This is the simplest model that accounts for the interaction between solvent and solute during mixing and that is flexible enough to include corrections for the difference between $\Delta\mu_s$ and $\Delta\mu_{\text{il}}$. Using this model ? were able to approximate the chemical potential of supercooled water(?). To use . The authors also showed that taking into account clustering of water molecules led to better agreement of the estimated water properties with MD simulations and experimental results.

According to the regular solution model, modified by clustering (?, Cf. Eq. 16),

$$\Delta G_{\text{mix}} = \frac{k_B T}{N}[\zeta\ln(\zeta) + (1-\zeta)\ln(1-\zeta)] + A_w\zeta(1-\zeta) \tag{24}$$

The first term on the right hand side corresponds to the usual definition of the ideal entropy of mixing, i.e., random ideal mixing and a weak interaction between IL and LL regions, modified to account for clustering in groups of N molecules. $N = 6$ corresponds to clustering in hexamers and is near the optimum fit between MD simulations and the solution model (?). It must be noted that ? recommended an alternative model termed "athermal solution", where nonideality is ascribed to entropy changes upon mixing. In vicinal water some evidence points at nonideality originating from enthalpy changes near the particle (?), hence a regular solution is more appropiate in this case. For $N = 6$ the difference between the two models is negligible (?).

The second term on the right hand side of Eq. (??) , it must be casted in terms of measurable variables. For this we notice that ??) is an empirical functional form used to approximate the enthalpy of mixing, selected so that $\Delta G_{\text{mix}} = 0$ for both, $\zeta = 0$ and $\zeta = 1$. A_w is a phenomenological interaction parameter here assumed to implicitly correct the approximation $\Delta\mu_{\text{il}} \approx \Delta\mu_s$. Typically A_w must be fitted to experimental observations. In this work A_w is calculated using an alternative approach, as follows.

An important aspect of the regular solution model is that it predicts that μ_{vc} has a critical temperature, T_c, at $\zeta = 0.5$, defined by the conditions(?),

$$\frac{\partial^2 \mu_{\mathrm{vc}}}{\partial \zeta^2} = 0 \, , \, \frac{\partial^3 \mu_{\mathrm{vc}}}{\partial \zeta^3} = 0. \tag{25}$$

These conditions originate because $\frac{\partial^2 \mu_{\mathrm{vc}}}{\partial \zeta^2} = 0$ represents a stability limit for vicinal water. A solution would split into two phases if by doing so lowers its Gibbs free energy (?, Cf. Section 6.12). For a metastable solution μ_{vc} must be minimal, hence $\frac{\partial \mu_{\mathrm{vc}}}{\partial \zeta} = 0$. The condition $\frac{\partial^2 \mu_{\mathrm{vc}}}{\partial \zeta^2} < 0$ indicates that any increase in ζ increases μ_{vc} (i.e., the curve μ_{vc} vs. ζ becomes concave downward) such that it is thermodynamically more favorable for the solution to split into distinct phases than to increase its concentration. The last condition, $\frac{\partial^3 \mu_{\mathrm{vc}}}{\partial \zeta^3} = 0$, indicates that the metastable region reduces to a single point and there is a single critical temperature, T_c, for a regular solution. Using Eq. (???) into Eq. (???) and solving for A_w gives for $T = T_c$,

$$A_w = \frac{2k_{\mathrm{B}} T_c}{N}. \tag{26}$$

Physically, T_c represents the stability limit of the vicinal water, at which it spontaneously separates into IL and LL regions. ~~To further simplify Eq. (??) we introduce the approximation,~~

~~$\zeta(\mu_{\mathrm{IL}} - \mu_{\mathrm{LL}}) + T\Delta S_{\mathrm{mix}} \approx \zeta \Delta\mu_s,$~~

~~where $\Delta\mu_s$ is the free energy of solidification of water.~~ Equation (??) ~~is obtained by taking into account that the difference $\mu_{\mathrm{IL}} - \mu_{\mathrm{LL}}$, plus the energy of mixing, must approximate the energy released during freezing, hence its must be of the order of $\Delta\mu_s$. In reality $\Delta\mu_s$ corresponds to actual liquid and ice instead of the hypothetical LL and IL substances. Thus~~ ??) thus provides an opportunity to theoretically determine A_w ~~plays the role of a semi-empirical correction factor accounting for, (i) the non-ideality originated from the mixing between the IL and the LL regions, and, (ii) the deviation of their chemical potentials from bulk ice and water, respectively.~~, since T_c should also correspond to the temperature at which the work of nucleation becomes negligible. This is explored in Section ??.

Introducing Eqs. ~~(??), (??)and (????)~~, (??), and (??), into Eq. ~~(??) gives~~ ??) we obtain,

$$\mu_{\mathrm{vc}} = \mu_{\mathrm{LL}} - \zeta k_{\mathrm{B}} T \ln\left(\frac{a_{\mathrm{w, eff}}}{a_{\mathrm{w, eq}}}\right) + \frac{k_{\mathrm{B}} T}{N}\left[\zeta \Delta\mu_s - \frac{2 k_{\mathrm{B}} T_c}{N}\ln(\zeta) + (1-\zeta)\ln(1-\zeta)\right] + \frac{2 k_{\mathrm{B}} T_c}{N}\zeta(1-\zeta). \tag{27}$$

Making,

$$\Lambda_{\mathrm{mix}} = \frac{1}{N}\left[\zeta \ln(\zeta) + (1-\zeta)\ln(1-\zeta)\right] + \frac{2}{N}\frac{T_c}{T}\zeta(1-\zeta), \tag{28}$$

Equation (**??**) can be written in the form,

$$\mu_{\text{vc}} = \mu_{\text{LL}} - \zeta k_{\text{B}} T \ln\left(\frac{a_{\text{w, eff}}}{a_{\text{w, eq}}}\right) + k_{\text{B}} T \Lambda_{\text{mix}} \tag{29}$$

Equation (**??**) is the ~~expression sought~~equation of state of the vicinal water. It describes the properties of the vicinal water in terms of the material-specific parameter ζ, and the interaction parameters N and ~~T_c~~T_c. MD simulations indicate that $N \sim 6$ (**??**). ~~T_c~~T_c is thus the only remaining unknown in Eq. (**??**) and it is calculated ~~at the point where the work of nucleation becomes negligible, as detailed in Section ??~~Section **??**.

2.3.1 ~~Work of germ formation~~

2.4 Work of germ formation

The equation of state of vicinal water can be used to link ΔG_{hom} and ΔG_{het} as follows. In immersion freezing the particle remains within the droplet long enough that equilibrium is established. This condition is mathematically expressed by the equality, $\mu_{\text{vc}} = \mu_{\text{w}}$, where μ_{w} is the chemical potential of water in the bulk of the liquid, i.e., away from the particle. Using Eq. (**??**) this implies,

$$\mu_{\text{w}} = \mu_{\text{LL}} + \zeta \Delta \mu_s - \frac{2 k_{\text{B}} T_c}{N} \zeta(1 - \zeta) k_{\text{B}} T \ln\left(\frac{a_{\text{w, eff}}}{a_{\text{w, eq}}}\right) + k_{\text{B}} T \Lambda_{\text{mix}}. \tag{30}$$

This expression indicates that the effect of the particle on its vicinal water can be understood as an enhancement of the chemical potential of the LL regions, a consequence of the tendency of the particle to lower μ_{vc}. Since ~~$\Delta \mu_s < 0$~~$\Delta \mu_{\text{jl}} < 0$, μ_{LL} must increase to maintain equilibrium. Using again the equilibrium between bulk liquid and ice as reference state, so that $\mu_{\text{w}} = \mu_{\text{eq}} + k_{\text{B}} T \ln(a_{\text{w}})$, and using Eq. (**??**), Eq. (**??**) can be written in terms of the water activity in the form,

~~Equation (??) also~~

$$a_{\text{w}} = a_{\text{w, eff}} \left(\frac{a_{\text{w, eq}}}{a_{\text{w, eff}}}\right)^{\zeta} \exp(\Lambda_{\text{mix}}). \tag{31}$$

This expression suggests that thermodynamically immersion freezing can be described as homogeneous ice nucleation occurring at an enhanced water activity. This is because it is possible to create a path including homogeneous ice nucleation with the same change in Gibbs free energy than for heterogeneous freezing~~, as shown in Figure ??. This fact is used to develop an expression for the work of germ formation in immersion freezing, ΔG_{het}. To this end it is useful expressing Eq. (??) in terms of the water activity. Using the equilibrium between bulk liquid and ice as the reference state, $\Delta \mu_s$, can be written in the form (??),~~

$$\Delta\mu_s = -k_{\mathrm{B}}T\ln\left(\frac{a_{\mathrm{w}}}{a_{\mathrm{w,eq}}}\right),$$

where $a_{\mathrm{w,eq}}$ is the equilibrium water activity between liquid and ice. Similarly, introducing the definitions,

$$\mu_{\mathrm{w}} = \mu_0 + k_{\mathrm{B}}T\ln(a_{\mathrm{w}}),$$

and

$$\mu_{\mathrm{LL}} = \mu_0 + k_{\mathrm{B}}T\ln(a_{\mathrm{w,\ eff}}),$$

Equation (??) can be written in the form,

$$a_{\mathrm{w}} = a_{\mathrm{w,\ eff}}\left(\frac{a_{\mathrm{w,\ eq}}}{a_{\mathrm{w,\ eff}}}\right)^{\zeta}\exp[\Lambda_{\mathrm{E}}\zeta(1-\zeta)]$$

where $\Lambda_{\mathrm{E}} = -\frac{2}{N}\frac{T_c}{T}$, and $a_{\mathrm{w,\ eff}}$ is termed the "effective water activity" and it is the value of a_{w} associated with the LL regions in the vicinal water. Figure ?? shows that for a particle-droplet system in equilibrium, $a_{\mathrm{w,\ eff}}$ satisfies the condition,:

$$\Delta G_{\mathrm{het}}(a_{\mathrm{w}}) = \Delta G_{\mathrm{hom}}(a_{\mathrm{w,\ eff}}). \tag{32}$$

Equation (??) represents a thermodynamic relation between ΔG_{het} and ΔG_{hom}. It has the advantage that ΔG_{het} can be obtained without invoking assumptions on the mechanistic details of the interaction between the particle and the ice germ, which are parameterized by ζ. Since a_{w} is typically the controlled variable in ice nucleation, $a_{\mathrm{w,\ eff}}$ can be readily obtained by solving Eq. (??),

$$a_{\mathrm{w,\ eff}} = \left(\frac{a_{\mathrm{w}}}{a_{\mathrm{w,\ eq}}^{\zeta}}\right)^{\frac{1}{1-\zeta}}\exp\left(-\Lambda_{\mathrm{E}}\zeta\right)\frac{\Lambda_{\mathrm{mix}}}{\zeta-1}\right). \tag{33}$$

Although ascribing ice nucleation to the LL fraction of vicinal water agrees with the decisive role of free water in the formation of ice (?), caution must be taken in considering this to be the actual mechanism of ice nucleation, which could be quite complex. Equation (??) however establishes a thermodynamic constrain for ΔG_{het} that should be met by any ice nucleation mechanism.

2.4.1 Water activity shift

When thermodynamics is the controlling factor in ice nucleation, Eq. (**??**) also represents a direct relationship between J_{hom}
345 and J_{het}. Such relationship have been proposed in several works and confirmed experimentally (**????**). This is related to the water activity criterion (**??**), the condition that for a given material the water activity at which heterogeneous ice nucleation is observed, $a_{\text{w, het}}$, is related by a constant to $a_{\text{w, eq}}$ (**??**). Here it is shown that the two-state thermodynamic model proposed in Section **??** implies the water activity criterion.

By definition the thermodynamic path shown in Fig. **??** operates between two equilibrium states. The relation between
350 ΔG_{het} and ΔG_{hom} is therefore independent of the way the system reaches $a_{\text{w, eff}}$. One can imagine two separate experiments in which the environmental conditions are set to either a_{w} or $a_{\text{w, eff}}$, the former resulting in heterogeneous freezing and the latter in homogeneous ice nucleation. Equation (**??**) implies that in any condition when heterogeneous ice nucleation is observed at $a_{\text{w, het}} = a_{\text{w}}$ there is a corresponding homogeneous process that would occur at $a_{\text{w, hom}} = a_{\text{w, eff}}$. Thus we can write an equivalent expression to Eq. (**??**), but relating the observed homogeneous and heterogeneous ice nucleation thresholds in two separate
355 experiments,

$$a_{\text{w, het}} = a_{\text{w, hom}} \left(\frac{a_{\text{w, eq}}}{a_{\text{w,hom}}} \right)^{\zeta} \exp[\Lambda_{\text{E}} \zeta (1 - \zeta)] \exp(\Lambda_{\text{mix}}), \tag{34}$$

This expression is only valid at the thermodynamic limit, that is when the flux of water molecules to the nascent ige germ is very large and ice nucleation is controlled by the nucleation work. The limits of such approach are analyzed in Section **??**.

~~Equation (**??**) is useful in deriving the so-called water activity criterion, i.e., the condition that the difference $a_{\text{w, het}} - a_{\text{w, eq}}$~~
360 ~~must be approximately constant for a given material (**??**).~~ Using the approximation $1 + \ln(a_{\text{w}}) \approx a_{\text{w}}$ $1 + \ln(x) \approx x$ for $x \sim 1$, Eq. (**??**) can be linearized in the form

$$-\zeta(a_{\text{w, hom}} \, {}_{\text{w, het}} - a_{\text{w, eq}}) \, {}_{\text{w, hom}} = \zeta(a_{\text{w, het}} \, {}_{\text{w, eq}} - a_{\text{w, hom}}) + \Lambda_{\text{E}} \zeta(1 - \zeta) \, {}_{\text{mix}}. \tag{35}$$

After rearranging we obtain,

$$\Delta a_{\text{w, het}} = (\Delta a_{\text{w, hom}} + \zeta \Lambda_{\text{E}})(1 - \zeta) + \Lambda_{\text{mix}}, \tag{36}$$

365 where $\Delta a_{\text{w, hom}} = a_{\text{w, hom}} - a_{\text{w, eq}}$ and $\Delta a_{\text{w, het}} = a_{\text{w, het}} - a_{\text{w, eq}}$ are the homogeneous and heterogeneous water activity shifts, respectively. $\Delta a_{\text{w, hom}}$ has been found to be approximately constant for a wide range of solutes (**?**); therefore Eq. (**??**) suggests that $\Delta a_{\text{w, het}}$ should be approximately constant since ~~$\zeta \Lambda_{\text{E}} \sim 0.01$~~ $\Lambda_{\text{mix}} \sim 0.02$ and only depends on T. Thus, ~~despite its simplicity~~ the two-state model presented in Section **??** implies the so-called water activity criterion (**?**) for heterogeneous ice nucleation, giving support to the hypothesis that increasing order near the particle surface drives ice nucleation.

370 ### 2.4.2 Extension of the homogeneous model to the spinodal limit

~~Equation (**??**) indicates that calculation of ΔG_{het} requires an expression for ΔG_{hom}, for which CNT will be used. Unlike in the case of heterogeneous freezing, CNT has shown considerable success in predicting homogeneous ice nucleation rates.~~

~~Recently the introduction of the negentropic nucleation framework (NNF) (**??**) relaxes some of the key assumptions of CNT. NNF accounts for the work of "unmixing" affecting the bulk of the liquid when the ice germ is formed (**?**), and, for the~~ finite character of the ice-liquid interface hence obviating the explicit parameterization of the ice-liquid interfacial energy. Furthermore, NNF also takes into account the fact that structural transformations are required to form ice, i.e., random clustering of water molecules is not a sufficient condition to form ice and molecular rearrangement is required (**??**). At the same time, NNF is still a simple framework that can be easily implemented in large scale atmospheric models and that has been shown to reproduce homogeneous freezing temperatures down to 180 K (**??**).

~~As $\zeta \to 1$, $a_{w,\,eff}$ may become very large (Eq. **??**). Thus, in~~ In applying a homogeneous model to the heterogeneous problem in the form ~~described~~ detailed in Section **??**, caution must be taken in describing the limiting condition where the size of the ice germ becomes exceedingly small, i.e., $n^*_{hom} \to 1$, representing the vanishing of the energy barrier to ice nucleation. ~~Since for such a limiting case~~ This is possible since as $\zeta \to 1$ $a_{w,eff}$ becomes large (Eq. **??**), and for $\zeta = 1$ it is only defined at thermodynamic equilibrium. Since for $n^*_{hom} \to 1$ thermodynamic potentials are not well defined it is necessary to ~~evaluate whether NNF is still valid~~test the validity of NNF at such a limit. Moreover, ~~since it is based on CNT,~~ in its original formulation (Section **??**) NNF predicts a positive ΔG_{hom} for $n = 1$, ~~leading to inconsistency, since the~~ at odds with the notion that the formation of a monomer-sized germ should carry no work.

At the limiting condition, $n^*_{hom} = 1$, the work of nucleation is smaller than the thermal energy of the molecules, and represents the onset of spontaneous phase separation (termed "spinodal decomposition") during nucleation. This hypothesis has been advanced by **?** within the framework of the two-step nucleation theory. Here it is argued that being a far-from-equilibrium process ice nucleation always carries energy dissipation. When accounted for, the apparent inconsistency in ~~CNT~~ NNF at $n^*_{hom} = 1$ vanishes, since as shown below such condition is not accessible. This approach differs from previous treatments where $n^*_{hom} = 1$ is associated with a negligible driving force for nucleation; Eq. (**??**) is then corrected so that $\Delta G_{hom} = 0$ when $n = 1$ (**?**).

To account for the finite, albeit small, amount of work dissipated from the generation of entropy during spontaneous fluctuation~~(?)~~, a simple approach is proposed. It involves writing the work of germ formation in the form,

$$\Delta G = -n\Delta\mu_i + n^{2/3}\Phi_s + W_{\underline{d}\,diss} \tag{37}$$

where $\underline{W_d}\,W_{diss}$ is the work lost during germ formation, assumed independent of the germ size since it results from spontaneous fluctuations occurring ~~within~~ in the liquid phase. ~~$\Delta\mu_i$ is the supersaturation given by~~

$$\Delta\mu_i = k_B T \ln\left(\frac{a_w^2}{a_{w,eq}}\right),$$

~~and Φ_s is the energy of formation of the interface, given by,~~

$$\Phi_{\mathrm{s}} = \Gamma_{\mathrm{w}} s \left(\Delta h_{\mathrm{f}} - \Gamma_{\mathrm{w}} k_{\mathrm{B}} T \ln a_{\mathrm{w}} \right),$$

where the constants $\Gamma_{\mathrm{w}} = 1.46$ and $s = 1.105 \ \mathrm{mol}^{2/3}$ define the coverage of the ice-water interface and the lattice geometry of the ice germ, respectively, and Δh_{f} is the latent heat of fusion. Other symbols are defined in Table ??. Equation (??) is the well-known CNT typical expression for ΔG (?, Cf. Eq. 15) with an additional term accounting for work dissipation. However instead of the common CNT definitions of $\Delta\mu_i$ and Φ_{s} (Section ??), the NNF approach is used (?).

W_d and W_{diss} and n_{hom}^* are obtained from the conditions,

$$\Delta G|_{n_{\mathrm{hom}}^*=1} = 0, \frac{\partial \Delta G}{\partial n_{\mathrm{hom}}^*} = 0, \frac{\partial^2 \Delta G}{\partial n^2}|_{n_{\mathrm{hom}}^*=1} = 0. \tag{38}$$

The first condition expresses the fact that the formation of monomer-sized germ carries no work. The second is the common CNT condition that a stable ice germ must be in mechanical equilibrium with its environment. Additionally, the third condition ensures that $n_{\mathrm{hom}}^* = 1$ also corresponds to the stability limit of the system where nucleation and spontaneous separation are analogous. This is referred as the spinodal point. From Eq. (??) we obtain,

$$\frac{\partial^2 \Delta G}{\partial n^2} = -\frac{2}{9} n^{-1/3 - 4/3} \Phi_{\mathrm{s}} = 0. \tag{39}$$

Since n only attains positive values, then only the trivial solution $\Phi_{\mathrm{s}} = 0$ satisfies Eq. (??). This means that the energy barrier to the formation of the ice germ vanishes at the spinodal. Using $\Phi_{\mathrm{s}} = 0$ and $\Delta G|_{n_{\mathrm{hom}}^*=1} = 0$ Eq. (??) can be solved for W_d W_{diss} in the form,

$$W_{d\,\mathrm{diss}} = \Delta\mu_i. \tag{40}$$

Thus the minimum amount of work dissipated during nucleation should correspond to a fluctuation relaxing $\Delta\mu_i$. Since W_d is independent of n, the critical germ size, n_{hom}^*, is simply obtained from the Replacing this expression within Eq. (??) and applying the condition of mechanical equilibrium, $\frac{\partial \Delta G}{\partial n_{\mathrm{hom}}^*} = 0$, in the form detailed in ?. Using Eqs. (??) and (??), this leads to,

$$k_{\mathrm{B}} T \ln \left(\frac{a_{\mathrm{w}}^2}{a_{\mathrm{w,eq}}} \right)^3.$$

$$($$

~~Replacing this expression within Eq. (??), and rearranging, gives~~ , gives after rearranging the work of germ formation by homogeneous ice nucleation,

$$\Delta G_{\text{hom}} = \frac{1}{2}\Delta\mu_i(n_{\text{hom}}^* + 2). \tag{41}$$

Equation (??) only differs from the ~~common CNT expression(?)~~ NNF expression, Eq. (??), on the right hand side, where it is implied that nucleation in solution requires the coordination of at least two molecules, a condition that has been observed experimentally in the crystallization of proteins (?). It also suggests that ~~non-equilibrium~~ dissipation effects are negligible for typical ~~conditions leading to homogeneous ice nucleation where~~ homogeneous nucleation conditions, i.e., $\Delta G_{\text{hom}} \approx \Delta G_{\text{hom, NNF}}$, since $n_{\text{hom}}^* \sim 200$ (?). Moreover, the fact that $\Delta G_{\text{hom}} > 0$ even when $n_{\text{hom}}^* \to 0$, implies that ice nucleation always requires some work. Using Eq. (??) the heterogeneous work of nucleation can be readily written as,

$$\Delta G_{\text{het}}(a_{\text{w}}) = \left[\frac{1}{2}\Delta\mu_i(n_{\text{hom}}^* + 2)\right]_{a_{\text{w, eff}}}. \tag{42}$$

The ~~result~~ results of Eqs. (??) and (??) ~~requires~~ require further explanation since in principle an ice germ with only two molecules does not exist. Thus Eq. (??) must be interpreted in a different way. As $\zeta \to 1$, or in deeply supercooled conditions, the fraction of ice-like regions in the vicinal water becomes large. Under such a scenario the reorientation of only two molecules may be enough to initiate ice nucleation. In other words, beyond the spinodal point ice nucleation is controlled by molecular motion within already formed ice-like regions~~(akin to pre-clustering)~~. For homogeneous ice nucleation this would require extreme supercooling ($T \sim 140$ K, Fig. ??). In immersion ice nucleation it may occur at higher T since the formation of a high fraction of ice-like regions in the vicinal water is facilitated by efficient INP. This aspect of the proposed theory is further explored in Section ??.

~~Even with the application of NNF , CNT~~ NNF carries the assumption that thermodynamic potentials can be defined for the ice germ. In other words n_{hom}^* should be large enough that it represents a statistical ensemble of molecules. Of course this is not the case for $n_{\text{hom}}^* = 1$, and it may cast doubt on the application of Eq. (??) to such limits. This possibility is however mitigated in two ways. Unlike CNT ~~implementations using~~ which is based on the interfacial tension, the NNF framework is robust for small germs. Size effects impact ΔG mostly through Φ_{s} since $\Delta\mu_i$ does not change substantially with the size of the system~~as long as microscopic reversibility can be assumed~~. In NNF the product $\Gamma_{\text{w}}s\Delta h_{\text{f}}$ in Eq. (??) remains ~~relatively constantfor a given T~~constant, and Φ_{s} is relatively insensitive to n. This is because Δh_{f} decreases with n as the total cohesive energy of the germ is inversely proportional to the number of molecules within the ice-liquid interfacial layer (??). At the same time, the product $\Gamma_{\text{w}}s$, i.e., the ratio of the number of surface to interior molecules in the germ (??) should increase for small ice germs offsetting the decrease in Δh_{f}. Such behavior is supported by MD simulations (?). Equation (??) thus remains valid for small germs. A second mitigating factor is discussed in Section ?? where it is shown that conditions leading to ~~$n^* \approx 1$~~ $n^* \to 1$ are rare in the atmosphere, and, J_{het} is largely independent of n^* for very small germs.

~~Finally, to~~

2.4.3 Critical temperature

455 To complete the thermodynamic description of ice nucleation near ~~a~~ the particle-liquid interface it is necessary to specify the critical separation temperature defined in Eq. (??). ~~The key to finding~~ T_c ~~, is recognizing that it corresponds to~~ represents the stability limit ~~defined by the condition $\frac{\partial^2 \Delta G}{\partial n^2} = 0$, which also defines a global minimum for~~ of vicinal water. Hence it must be given by the temperature that simultaneously satisfies the conditions described in Eqs. (??) and (??). In other words, T_c must lie near the minimun in ΔG_{het} ~~. This behavior~~ for $\zeta = 0.5$. This is analyzed in Fig. ??. As T decreases $\Delta\mu_i$ increases,

460 decreasing ~~n^*_{hom}~~ n^* and ΔG_{het}. However ~~for $n^*_{\text{hom}} < 2$,~~ around T_c, $n^* \to 2$ and the tendency is reversed since in this regime dissipative effects dominate and ΔG_{het} becomes proportional to $\Delta\mu_i$, and independent of n^*. ~~For a given T there is a critical value of $\zeta = \zeta_c$ around which ΔG_{het} is minimum. This indicates that T_c should correspond to the temperature at which ΔG_{het} has a minimum for $\zeta_c = 0.5$.~~ Figure ?? shows that this occurs around ~~$T \sim 220$ K. In fact,~~ $T \sim 211$ K for $\zeta = 0.5$. A better estimate can be found by combining Eqs. (??) and (??)~~it is possible to iterativelycalculate, $T_c = 219.802$~~. Since both ΔG_{het}

465 and $a_{\text{w, eff}}$ depend on T_c this must be done iteratively, resulting in $T_c = 211.473$ K. Figure ?? also suggests that ~~$\zeta = \zeta_c$ represents~~ when T remains constant there is a critical value of ζ that marks the transition between two thermodynamic regimes. This is analyzed in Section ??.

2.5 Kinetics of immersion freezing

Almost every theoretical approach to describe the effect of INP on ice formation focuses on the thermodynamics of ice nu-

470 cleation. However as discussed in Section ??, ~~the increased order and the no-slip condition near the surface of the particle, both of which increase the~~ increased molecular ordering increases the viscosity of vicinal water, ~~imply~~ implying that the immersed particle modifies the flux of water molecules to the nascent ice germ, hence the kinetics of ice ~~germ growth~~nucleation. This is believed to result from changes in the structure of water near the interface (??). Since these structural changes are also related to modifications in the chemical potential of the vicinal water, it is likely that the same mechanism that decreases

475 ΔG_{het} also controls the mobility of water molecules in the environment around the particle. Such a connection between the water thermodynamic properties and its molecular mobility is well established (???), but it is generally neglected in nucleation theory ~~(e.g., ???)~~(e.g., ??). In this section a heuristic model is proposed to account for such effects.

~~The heterogeneous ice nucleation rate is given by the product of the equilibrium concentration of supercritical clusters and~~ Kinetic effects modify the value of the impingement factor, f^*_{het}, which controls the flux of water molecules to the ice germ~~(?),~~

480 $$J_{\text{het}} = C_0 Z f^*_{\text{het}} \exp\left(-\frac{\Delta G_{\text{het}}}{k_B T}\right),$$

~~where C_0 is the monomer concentration, f^*_{het} is the impingement factor for heterogeneous ice nucleation, and Z is the Zeldovich factor given by (?),~~

$$Z = \left[\frac{\Delta G_{\text{het}}}{3\pi k_{\text{B}} T \left(n^*\right)^2} \right]^{1/2}.$$

~~where $n^* = [n^*_{\text{hom}} + 2]_{a_{\text{w, eff}}}$. Other symbols are defined in Table ??. In writing~~. In general the ice germ grows by diffusion and rearrangement of nearby water molecules across the ice-liquid interface, characterized by the interfacial diffusion coefficient, D. Increased ordering is characterized by a higher IL fraction, hence higher ζ. Thus, in immersion freezing D must be a function of ζ. Using Eq. (~~??) it is assumed that interface transfer is the dominant mechanism of~~ ??) this can be expressed in the form,

$$f^*_{\text{het}} = \frac{\Omega}{v_w d_0} D(\zeta), \tag{43}$$

Assuming that within the vicinal layer ice germ growth ~~,~~ follows a similar mechanism as in the bulk of the liquid, then Eq. (??) can be applied to the heterogeneous process in the form,

~~The impingement factor, f^*_{het}, is the frequency of attachment of water molecules to the ice germ. For homogeneous ice nucleation it~~

$$D(\zeta) = D_\infty(\zeta) \left\{ 1 + \exp\left[\frac{W_{\text{d}}(\zeta)}{k_{\text{B}} T} \right] \right\}^{-1} \tag{44}$$

The last expression indicates that ice-liquid interfacial transfer requires a diffusional and a rearragement component. The latter is controlled by the ~~bulk diffusion coefficient and the work dissipated during molecular transferacross the interface (?), i.e.,~~

$$f_{\text{hom}}^* = \frac{D_\infty \Omega}{v_w d_0} \left[1 + \left(\frac{a_w}{a_{\text{w,eq}}} \right)^{n_t} \right]^{-1},$$

~~where D_∞ the bulk self-diffusion coefficient of water, Ω the surface area of the germ, v_w and d_0 the molecular volume and diameter of water , respectively, and $n_t = 16$ is the number of possible trajectories in which water molecules incorporate~~ dissipated work during interfacial transfer, W_{d}, and results from molecular rearragement. Since only the transfering of molecules from the LL fraction of the vicinal water to the ice lattice ~~. Equation (??) differs from common CNT expressions in that it takes into account that molecular rearrangement is required tofacilitate the incorporation of water molecules to~~ would lead to rearragement, W_{d} is scaled by $1 - \zeta$. Using this into Eq. (??) and comparing against Eq. (??) leads to,

$$D(\zeta) = D_\infty(\zeta) \left[1 + \exp\left(\frac{-n_t \Delta \mu_{\text{s}}(1-\zeta)}{k_{\text{B}} T} \right) \right]^{-1} \tag{45}$$

This expression is consistent with the thermodynamic model presented in Section ??; as $\zeta \to 1$ the vicinal water would have a larger "ice" character and fewer molecules need to rearrange to be incoporated into the growing ice germ~~, leading to energy dissipation (?)~~.

As outlined in Section **??** it is likely that the same mechanism that facilitates ice nucleation also controls the dynamic behavior of the environment around the particle . Thus, for heterogeneous ice nucleation f_{het}^* must be a function of ζ. This is represented by scaling in f_{hom}^* the form,

2.5.1 Diffusion within the ice-liquid interface

$f_{\text{het}}^* = f_{\text{hom}}^* \Upsilon(\zeta).$

To derive an expression for $\Upsilon(\zeta)$ the The diffusional component of D corresponds to the random jump of water molecules across the ice-liquid interface. For $\zeta \to 0$ there is no interaction between the particle and the adjacent water, hence diffusion must proceed as in the bulk of the supercooled water. At the opposite limit, $\zeta \to 1$, $D_\infty(\zeta) \to 0$, which simply states that interfacial transfer vanishes when no driving force exists across the ice-liquid interface; i.e., the system is in equilibrium. To model this behavior the well-known relaxation theory proposed by **?** (hereinafter, AG65) is employed. According to AG65, relaxation and diffusion in supercooled liquids require the formation of cooperative regions (CRs). The probability of such a rearrangement (i.e., the transition probability) average transition probability determining the timescale of diffusion is deter-mined by the size of the smallest CR. Following a statistical mechanics treatment and assuming that each CR interacts weakly with the rest of the system, the authors derived the following expression for the average transition probability,

$$\bar{W} \propto \exp\left(-\frac{A}{TS_c}\right), \tag{46}$$

where A represents the product of the minimum size of a CR in the liquid and the energy required to displace water molecules from their equilibrium position in the bulk, and S_{c} is the configurational entropy. Since A is approximately constant, the mobility of water molecules is controlled by S_{c}. Such a behavior has been confirmed in molecular dynamics simulations and experimental studies (e.g., **??**).

Since f_{het}^* The self-diffusivity of water is proportional to the mobility of water molecules across the ice-liquid interface (**??**), hence to their transition probability, the scaling function introduced in Eq. (**??**) can be written and can be expressed in the form ,

$\Upsilon(\zeta) = \dfrac{\bar{W}_{\text{vc}}}{\bar{W}},$

where $\bar{W}_{\text{vc}}$ and $\bar{W}$ are the average transition probabilities in the vicinity of the particle and in the bulk of the liquid, respectively $D_\infty \sim D_0 \bar{W}$ where D_0 is a constant. Using Eq. (**??**) , Eq. (**??**) can be written as, this suggest the relationship,

$$\Upsilon(\zeta)\frac{D_\infty(\zeta)}{D_\infty} = \frac{\bar{W}(\zeta)}{\bar{W}(\zeta=0)} = \exp\left[-\frac{A}{TS_{\text{c},0}}\left(\frac{S_{\text{c},0}}{S_{\text{c}}}-1\right)\right], \tag{47}$$

20

where $D_\infty = D_\infty(\zeta = 0)$ and $S_{c,0}$ represents the value of S_c in the absence of an immersed particle (i.e., $\zeta = 0$). Equation (~~??~~??) implies that the flux of molecules to the ice germ during immersion freezing is controlled by the configurational entropy of vicinal water.

~~The usage~~ Usage of Eq. (~~??)~~ ??) thus requires developing and expression for S_c. ~~This is done under the assumption that the flux of water molecules to the nascent ice germ depends mostly on the fraction of LL regions in the vicinal water, that is, only molecules not participating in ice-like regions are~~ Using a similar model as in Section ?? we write,

$$S_c = (1-\zeta)S_{c,\mathrm{LL}} + \zeta S_{c,\mathrm{IL}}, \tag{48}$$

where $S_{c,\mathrm{LL}}$ and $S_{c,\mathrm{IL}}$ are the configurational entropies of the IL and LL fractions, respectively. It is expected that $S_{c,\mathrm{LL}}$ dominates S_c since diffusion is controlled by molecules mobile enough to ~~diffuse to the ice germ (?). This reduces the number of configurations available to the vicinal water, so that~~ be incoporated in CRs (?). On the other hand, $S_{c,\mathrm{IL}}$ may determine S_c ~~is scaled in the form $S_c \sim S_{c,0}(1-\zeta)$. Also, to be incorporated in the ice germ water molecules~~ when $\zeta \to 1$ since at such limit LL regions would have lost most of their mobility.

The regular model proposed in Section ?? suggests that the interaction between IL and LL regions is weak since the ΔG_{mix} is typically small compared to μ_w. Thus we can approximate $S_{c,\mathrm{LL}} \approx S_{c,0}$. Unfortunately such an assumption may not work for $S_{c,\mathrm{IL}}$. Making $S_{c,\mathrm{IL}}$ equal to the configurational entropy of bulk ice, which may be deduced from geometrical arguments (?), would violate the requirement that $D \to 0$ at thermodynamic equilibrium. Thus to estimate $S_{c,\mathrm{IL}}$ we use the fact that to be incorporated into the ice lattice water molecules in the IL regions should be displaced from their equilibrium position in the ~~vicinity of the immersed particle, i.e., they should be "unmixed" from the vicinal water. Adding these contributions we obtain,~~

$$S_c = S_{c,0}(1-\zeta) + s_w - s_{\mathrm{LL}}$$

~~where s_{LL} and s_w are the molar entropies of LL and water, respectively. Using Eq. (??), the last two terms of Eq. (??) can be written as,~~

$$s_w - s_{\mathrm{LL}} = -\zeta \frac{\Delta\mu_s}{T} + \frac{h_w - h_{\mathrm{LL}}}{T} - \frac{g^E}{T}.$$

~~where h_{LL} and h_w are the molar enthalpies of the bulk liquid and the LL regions , respectively. The last two terms on the right side of Eq. (??) should cancel out since in regular solutions the excess energy results mostly from enthalpy changes during mixing (?) (Section ??).~~ vicinal water gaining an amount of energy equal to $-\Delta\mu_s$, which should be returned to the system upon entering the ice-liquid interface. Assuming that such a energy change results mostly from configurational rearrangement (?) then the associated increase in configurational entropy must be equal to $-\Delta\mu_s/T$ (??). This must also be close to the configurational entropy "stored" in the IL regions controlling the rate of interface transfer. With this, and using ~~Eq. (??), the~~

~~configurational entropy of vicinal water molecules can be approximated as~~ $\Delta\mu_s = -k_B T \ln\left(\frac{a_w}{a_{w,eq}}\right)$, an approximation to S_c can be written in the form,

$$S_c = S_{c,0}(1-\zeta) + \zeta k_B \ln\left(\frac{a_w}{a_{w,eq}}\right).$$ (49)

Introducing this expression into Eq. (??) and rearranging we obtain,

$$\Upsilon(\zeta)\frac{D_\infty(\zeta)}{D_\infty} = \exp\left[-\frac{A}{TS_{c,0}}\frac{\zeta(1-\sigma_E)}{1-\zeta(1-\sigma_E)}\frac{\zeta\sigma_E}{(1-\zeta\sigma_E)}\right],$$ (50)

where $\sigma_E = S_{c,0}^{-1}k_B\ln\left(\frac{a_w}{a_{w,eq}}\right)$. ~~The self-diffusivity of water is proportional to the transition probability, and can be expressed in the form $D_\infty \sim D_0\bar{W}$ where D_0 is a constant. Thus~~ $\sigma_E = 1 - S_{c,0}^{-1}k_B\ln\left(\frac{a_w}{a_{w,eq}}\right)$. Using $D_\infty = D_0\bar{W}$ an equivalent expression to Eq. (??) can be written in the form,

$$\Upsilon D_\infty(\zeta) = D_\infty\left(\frac{D_\infty}{D_0}\right)^{\frac{\zeta(1-\sigma_E)}{1-\zeta(1-\sigma_E)}\frac{\zeta\sigma_E}{1-\zeta\sigma_E}},$$ (51)

Equation (??) represents the effect of the immersed particle on the rate of growth of the ice germ. For $\zeta = 0$, ~~$D = D_\infty$, i.e.,~~ the particle does not affect the flux of water molecules to the nascent ice germ. However when $\zeta \to 1$, ~~$D \propto \exp(-1/\sigma_E)$; since $\sigma_E \sim 0.01$~~ $D_\infty(\zeta) \propto \exp\left(-\frac{1}{1-\zeta\sigma_E}\right)$; since $\sigma_E \to 1$, interface transfer becomes severely limited. This effect is much stronger than the reduction in the dissipated work from an increased ζ (Section ??) and dominates D.

~~Finally, collecting terms and replacing Eqs.~~ Introducing Eqs. (??) and (??), (??) and (??) into Eq. (??) ~~, we obtain for the heterogeneous nucleation rate~~ ??) and rearranging we obtain,

$$f_{het}^* = \frac{D_\infty\Omega}{v_w d_0}\left(\frac{D_\infty}{D_0}\right)^{\frac{\zeta\sigma_E}{1-\zeta\sigma_E}}\left[1+\left(\frac{a_w}{a_{w,eq}}\right)^{n_t(1-\zeta)}\right]^{-1},$$ (52)

where $\Delta\mu_s = -k_B T \ln\left(\frac{a_w}{a_{w,eq}}\right)$ was used.

2.6 Nucleation Rate

The results of Sections ?? to ?? provide the basis to write an expression for the ice nucleation rate of droplets by immersion freezing. Before completing such a description we need to provide an expression of Z. Application of Eq. (??) typically leads to the known expression (?),

$$1+\frac{a_w}{a_{w,eq}}^{n_t}\exp\left(-\frac{\Delta G_{het}}{k_B T}\right) = J_0\exp\left(-\frac{\Delta G_{het}}{k_B T}\right), \left[\frac{\Delta G_{het}}{3\pi k_B T (n^*)^2}\right]^{1/2}.$$

$$(\tag{53}$$

where J_0 is the preexponential factor and ΔG_{het} is given by On the other hand using Eq. (**??**) . In writing into Eq. (**??**) it has been assumed that $C_0 = a_0^{-1}$ being a_0 the average cross-sectional area of a water molecule . This indicates that **??**) we obtain,

$$Z_{\text{d}} = \left[\frac{\Delta G_{\text{het}}(n^* - 2)^{1/3}}{3\pi k_{\text{B}} T (n^*)^{7/3}} \right]^{1/2} \tag{54}$$

where the subscript "d" indicates that energy dissipation is taken into account and $n^* = n^*_{\text{hom}} + 2$. For $n^* > 3$ it is easily verifiable that $Z_{\text{d}} \approx Z$. Indeed the discrepancy between Z_{d} and Z is only 30% at $n^* = 3$ and much smaller for larger ice germs. However for $n^* = 2$, $Z_{\text{d}} = 0$. This issue is rather fundamental and may represent the breaking of the assumption that each germ grows by addition of a single molecule at a time involved in the general framework presented in Section **??**. Unfortunately solving this issue is beyond the scope of this work. Hence Eq. (**??**) will be used keeping in mind that for very small ice germs it represents only an approximation.

With the above considerations it is now possible to substitute Eqs. (**??**), (**??**) and (**??**) into Eq. (**??**) to obtain the heterogeneous ice nucleation rate,

$$J_{\text{het}} = \frac{2 Z D_\infty \Omega}{3 v_w^2} \left(\frac{D_\infty}{D_0} \right)^{\frac{\zeta \sigma_{\text{E}}}{1 - \zeta \sigma_{\text{E}}}} \left[1 + \left(\frac{a_w}{a_{\text{w,eq}}} \right)^{n_t(1-\zeta)} \right]^{-1} \exp \left(- \frac{[\Delta \mu_i (n^*_{\text{hom}} + 2)]_{a_{\text{w, eff}}}}{2 k_B T} \right), \tag{55}$$

where $d_0 = (6 v_w/\pi)^{1/3}$ and $a_0 = \pi d_0^2/4$ were used, and, $\Omega = \Gamma_{\text{w}} s(n^*)^{2/3} a_0$, is the surface area of the particle has a well-defined surface area and that most of the molecules incorporated into the ice germreside near the liquid-particle interface. ice germ. Other symbols and values used are listed in Table **??**.

2.7 The role of active sites

In some materials There is evidence that in dust and other INP ice is formed preferentially in the vicinity of surface patches that provide some advantage to ice nucleation, commonly referred as active sites. The existence of active sites have been established experimentally for deposition ice nucleation (i.e., ice nucleation directly from the vapor phase) (**?**), and there is also evidence that they may be also important for immersion freezing (e.g., **?**). In the classical view active sites have the property of locally reducing n^* and decrease ΔG_{het} , increasing J_{het}. In the so-called singular hypothesis $J_{\text{het}} \to \infty$ at each active site . In the modern interpretation each active site has an associated characteristic temperature at which it nucleates ice.

Current interpretation assigns $J_{het} \to \infty$ at each active site, with some variability due to "statistical fluctuations" in the germ size (**?**). Some CNT-based approaches to describe immersion freezing account for the existence of active sites by assuming distributions of contact ~~angles~~ angle for each particle. Hence each active site is assigned a characteristic contact angle instead of a characteristic temperature ~~(e.g., ?)~~(e.g., **??**).

The view of the role of active sites as capable of locally decreasing ΔG_{het} relies heavily on an interpretation of immersion freezing that mimics ice nucleation from the vapor phase (Fig. **??**a). ~~However it may be too simple~~ Such a description is however too limited for ice formation within the liquid phase. For example, it is implicitly assumed that the active site brings molecules together, similar to an adsorption site. However a particle immersed within a liquid is already surrounded by water molecules (Fig. **??**b). In fact, nascent ice structures are associated with low density regions within the liquid (**?**). Thus ~~the~~ in the classical view the active site should be able to permanently "pull molecules apart" instead of bringing them together. This creates a conceptual problem. To locally reduce ΔG_{het} active sites should be able to ~~maintain~~ permanently create empty spaces within the liquid, maintaining adjacent water molecules in a different thermodynamic state than the rest of the liquid. In other words, they would have the unusual property of creating a thermodynamic barrier maintaining their surrounding water in a non-equilibrium state. Such situation is unlikely in immersion freezing.

The concept of local nucleation rate also presents some difficulties. In the strict sense J_{het} is the velocity with which the size distribution of molecular clusters in an equilibrium population crosses the critical size ~~(?). The~~ (**??**). In immersion freezing the domain of such a distribution is the whole volume of the ~~liquid. It then becomes apparent that~~ droplet. Thus only a single value of J_{het} can be defined for a continuous liquid phase, independently of where the actual nucleation process is occurring, since no permanent spatial gradients of T or concentration exist within equilibrium systems. Having otherwise implies that parts of the system would need to be maintained in a non-equilibrium state, having their own cluster size distribution. This requires the presence of non-permeable barriers within the liquid, a condition not encountered in immersion freezing. Similarly, the characteristic temperature of an active site is an unmeasurable quantity since a system in equilibrium has the same temperature everywhere. Hence it would be impossible to distinguish whether the particle as a whole or only the active site must reach certain temperature before nucleation takes place.

These difficulties can be reconciled if instead of promoting nucleation through a thermodynamic mechanism, active sites provide a kinetic advantage to ice nucleation. A way in which this can be visualized is shown in Fig. **??**b. The vicinal water is in equilibrium with the particle, and exhibits a larger degree of ordering near the interface. Since in immersion freezing the formation of ice in the liquid depends on molecular rearrangement~~rather than clustering~~, the active site should produce a transient structural transformation that allows the propagation of ice. These sites would be characterized by defects where templating is not efficient allowing greater molecular movement hence facilitating restructuring. Their presence is guaranteed since particles are never uniform at the molecular scale. In this view active sites create ice by promoting fluctuation instead of by locking water molecules in ~~a strict configuration~~strict configurations. It implies that for uniform systems (e.g., a single droplet with a single particle) ΔG_{het} depends on the equilibrium between the particle and the vicinal water and active sites enhance fluctuation around specific locations. This obviates the need for the hypothesis of a well-defined characteristic temperature for

each active site. It however does not mean that active sites are transient. They are permanent features of the particle and should have a reproducible behavior, inducing ice nucleation around the same place in repeated experiments (e.g., **?**).

Within the framework presented above, there can only be one J_{het} defined in the droplet volume. The presence of active sites introduces variability in J_0 instead of ΔG_{het}. The latter is determined by the thermodynamic equilibrium between the particle and its vicinal water. Although the theory presented here does not account for internal gradients in the droplet-particle system, in practice it is likely that the that the observed J_{het} corresponds to the most active site in the particle. Variability in J_{het} would be introduced by fluctuation in the cluster size distribution in the liquid and from multiplicity of active sites in the particle population. In this sense the proposed view is purely stochastic.

3 Discussion

3.1 ~~Thermodynamic freezing~~ Relationship betwen water activity and temperature

~~To~~ If a droplet is in equilibrium then a_{w} is a function of the environment relative humidity. Thus the relationship between a_{w} and the freezing temperature, T_{f}, conveys important information about the potential of a particle to catalyze the formation of ice, and can be used to generate parameterizations of immersion ice nucleation for cloud models (**???**). Using the the results of Section **??** it is possible to analyze the effect of the immersed particle on ~~the thermodynamics of ice nucleation the concept of "Thermodynamic Freezing Temperature", $T_{\text{f,eq}}$, is introduced, defined as the equilibrium temperature between the ice germ and the droplet. It differs from the experimentally measured freezing temperature, T_{f}, in that the latter~~ ice formation from a thermodynamic point of view, separated from kinetic effects. This is because for a given T, Eq. (**??**) represents a thermodynamic relationship between $a_{\text{w, het}}$ and $a_{\text{w, hom}}$, and because homogeneous ice nucleation is almost entirely driven by thermodynamics (**??**). Still, $a_{\text{w, hom}}$ is defined at some ~~value of J_{het}. When $\frac{\mathrm{d}J_{\text{het}}}{\mathrm{d}T}$ is large, as for example in homogeneous ice nucleation, T_{f} approximates $T_{\text{f,eq}}$. This concept is useful since the thermodynamics on ice nucleation can be analyzed in terms of $T_{\text{f,eq}}$, independently of any prescribed~~ J_{hom} threshold, implying that $a_{\text{w, hom}}$ is not completely free from kinetic effects. However the threshold J_{hom} is high enough, typically around $\sim 10^{16}\,\mathrm{m}^{-3}\mathrm{s}^{-1}$, that they must be negligible. A high J_{hom} threshold is also consistent with attempts to define $a_{\text{w, hom}}$ on a pure thermodynamic basis using either a high value of C^* (**?**), or the maximum compresiblity of water (**?**). The freezing temperature found in this way will be called "Thermodynamic freezing temperature", T_{ft}, to indicate that kinetic limitations to ice germ growth are almost absent. It must be emphasized that T_{ft} only establishes the potential of an INP to induce freezing, regardless of whether a high value of J_{het} ~~threshold~~can be experimentally realised.

~~An example of this is the water activity criterion,~~ Figure **??** shows the $T_{\text{ft}} - a_{\text{w, het}}$ relationship defined by Eq. (**??**)~~. Since it results from an equilibirum relation, it represents a constraint between $T_{\text{f,eq}}$ (instead of T_{f}) and a_{w}. This is shown in Fig. **??**. For $\zeta = 0$, $T_{\text{f,eq}}$ coincides by design with the homogeneous freezing line and it is calculated setting~~ calculated using $\Delta a_{\text{w, hom}} = 0.304$ ~~(**?**). Curves~~ (**??**). The figure resembles experimental results found by several authors (e.g., **?????**) where curves for $\zeta > 0$ align with constant water activity shifts to $a_{\text{w, eq}}$~~, as exemplified by the two lines~~. To make this evident, lines were drawn using constant values of ~~$\Delta a_{\text{w, het}} = 0.05$~~ $\Delta a_{\text{w, het}} = 0.05, 0.15$, and ~~$\Delta a_{\text{w, het}} = 0.20$. As $\zeta \to 1$, $T_{\text{f,eq}}$~~ lies closer to the

675   ~~thermodynamic equilibrium. Constant $\Delta a_{w,\,het}$ has been reported in several studies (e.g., ????).Thus the~~ 0.20 which coincide with lines corresponding to $\zeta = 0.2, 0.3$ and 0.7, respectively. This shows that Eq. (**??**) is a good approximation to Eq. (**??**), and constitutes a theroetical derivation of the water activity criterion. The fact that such behavior can be ~~reproduce~~ reproduced by Eq. (**??**) validates the regular solution approximation ~~of Eq. (??). It also~~ used in Section **??** and supports the idea that the effect of the immersed particle on ~~$T_{f,eq}$~~ ice nucleation can be explained as relative increase in the "ice-like" character of the

680   vicinal water.

3.2   Ice nucleation regimes

A consequence of the linkage between the properties of vicinal water and ΔG_{het} is the existence of distinct nucleation regimes. This was mentioned in Section **??** and here it is explored in detail. Recall from Fig. **??**, that for a given T ΔG_{het} passes by a minimum ~~at ζ_c~~ defined by the condition ~~$\frac{\partial^2 \Delta G_{ne}}{\partial n^2} = 0$~~ $\left(\frac{\partial^2 \Delta G}{\partial n^3}\right)_{n=n^*} = 0$. Figure **??** ~~,~~(right panel) ~~shows~~ depicts a similar

685   behavior but maintaining ζ constant instead of T. It shows that there is a temperature, T_s, at which ΔG_{het} is minimum. For $T > T_s$ ΔG_{het} increases with increasing T because n^* increases ~~, as shown in~~ (Fig. **??**, ~~(~~left panels). This is the typical behavior predicted by ~~CNT~~ the classical model (e.g., **?**) hence such regime will be termed "germ-forming" since ΔG_{het} is determined by the formation of the ice-liquid interface.

   ~~On the other hand,~~ A different behavior is found for $T < T_s$, where ΔG_{het} decreases with increasing T. In this regime n^*

690   remains almost constant at very low values, ΔG_{het} is small and results mostly from the dissipation of work. Ice nucleation ~~does not proceed~~ is not limited by the formation of ~~an ice germ~~ the ice-liquid interface but rather by the propagation of small fluctuations in the vicinity of pre-formed ice-like regions. Therefore it is controlled by diffusion of water molecules to such regions rather than by ΔG_{het}. This is akin to a spinodal decomposition process (**?**) and will be termed "spinodal ice nucleation". It is however not truly spinodal decomposition since it requires a finite, albeit small, amount of work to occur.

695   ~~In principle~~ Since for each value of ζ there is a minimum in ΔG_{het} (Fig. **??**), then theoretically all INPs are capable of nucleating ice in both regimes. However~~depending on ζ, one of them may lie outside~~, in practice spinodal ice nucleation would only occur if T_s lies within the 233 K $< T <$ 273 K range where immersion freezing occurs. For example, for $\zeta = 0.1$, Fig. **??**, right panel, suggests that the minimum in ΔG_{het} occurs at $T_s < 220$ K. Since homogeneous ice nucleation should occur above this temperature, ~~the spinodal regime cannot be observed for an~~ INP characterized by $\zeta = 0.1$ will not exhibit

700   spinodal ice nucleation. Thus these particles would always nucleate ice in the classical germ-forming regime ($T > T_s$). Since in this regime ΔG_{het} increases very rapidly with T (and J_0 is large, Section **??**), the observed freezing temperature would be close to ~~$T_{f,eq}$~~T_{ft}. The situation is however different for $\zeta = 0.9$, since $T_s \approx 270$ K. ~~For these INP ice formation likely occurs in the spinodal regime~~ These INP are capable of nucleating ice in both the spinodal ($T < T_s$) ~~. In this case~~ and the ($T > T_s$) germ-forming regimes. However as shown in Section **??** spinodal nucleation is favored since kinetic limitations are

705   stronger near thermodynamic equilibrium ($T \sim 273$ K). For the spinodal regime ΔG_{het} is very low and decreases slighly with increasing T, indicating that the thermodynamic barrier to nucleation is virtually removed. Ice formation is therefore almost entirely controlled by kinetics and it is likely that ~~T_f differs from $T_{f,eq}$~~the observed freezing temperature, T_f, differs from T_{ft}.

The existence of the spinodal nucleation regime signals the possibility of an interesting behavior in freezing experiments, where the same ΔG_{het} may correspond to two very different INP. To show this the values of ΔG_{het} and n^* corresponding to $J_{\text{het}} = 10^6$ m^{-2} s^{-1} are shown in Fig. ??, black lines. These lines form semi-closed curves when plotted against temperature indicating that the same ΔG_{het} may correspond to two different values of ζ. The upper branch (with high ΔG_{het}) corresponds to the germ-forming regime and the lower branch to the spinodal regime. This picture is further convoluted by the fact that high ζ also implies strong kinetic limitations during ice nucleation and is further discussed in Section ??.

3.3 Preexponential Factor

Kinetics effects on ice nucleation are typically analyzed in terms of the preexponential factor, which is proportional to f_{het}^* in the form,

$$J_0 = \frac{Z f_{\text{het}}^*}{a_0}. \tag{56}$$

J_0 expresses the normalized flux of water molecules to the ice germ, corrected by Z. Figure ??, shows J_0 calculated using Eqs. (??) and (??). Results from CNT (Eq. ??) are also shown. In general J_0 varies with T and ζ. The sensitivity of J_0 to T is determined by D_∞ (?) with J_0 increasing with T, since water molecules increase their mobility. Also at higher T less work is dissipated during interface transfer. These effects dominate the variation in J_0.

For $\zeta < 0.5$, J_0 follows essentially the same behavior as for $\zeta = 0$, suggesting that the particle has a limited effect on the mobility of vicinal water. The kinetics of ice nucleation around these particles would be reasonably well described by assuming a negligible effect of the particle on J_0, as done in CNT.

However as ζ increases the presence of the particle tends to significantly decrease J_0. This is evidenced by the CNT-derived values for $\theta = 10°$ and $\theta = 90°$, which represents particles with high and low particle-ice affinity, respectively, and correspond to the range of expected variability in CNT. The $\theta = 90°$ and $\zeta \sim 0$ lines in Fig. ?? are within an order of magnitude of each other, in agreement with homogeneous nucleation results (?). The $\theta = 10°$ line is also close to the $\zeta \sim 0.5$ curve. In both cases J_0 increases by about two orders of magnitude between 220 K and 273

K and decreases by about two orders of magnitude from $\zeta = 0.0$ to $\zeta = 0.5$, or from $\theta = 90°$ to $\theta = 10°$ in CNT. The latter reflects the effect of variation in Z on J_0.

The behavior of J_0 for $\zeta > 0.5$ dramatically differs from CNT. For $\zeta > 0.5$, and particularly for $\zeta > 0.8$, J_0 decreases strongly with increasing T. This is because for $\zeta = 1$ and $T = 273$ K ice -liquid interfacial transport is not possible, since its driving force is the separation of μ_{vc} from thermodynamic equilibrium. As the system moves near these conditions D becomes very small. This is the result of the high IL fraction of the vicinal water limiting the number of configurations available to form cooperative regions, and that are required to induce water mobility (Section **??**). This behavior cannot be reproduced by CNT since no explicit dependency of D on the properties of the vicinal layer is accounted for. For $\zeta > 0.99$ J_0 decreases by more than 30 orders of magnitude from 220 K to 273~~K, i.e.,~~; molecular transport nearly stops. Ice nucleation may not be possible at such extreme, despite the fact that these particles very efficiently reduce ΔG_{het} (Fig. **??**); water may remain in the liquid state at very low temperature. Such an effect has been experimentally observed in some biological systems (**?**).

3.4 Nucleation Rate

The ~~discussion above indicates that~~ interplay between kinetics and thermodynamics reveals the complex behavior of J_{het} ~~is determined by two competing effects~~ in immersion ice nucleation. Particles highly efficient at decreasing ΔG_{het} also decrease the rate of interfacial diffusion to the point where they may effectively prevent ice nucleation. On the other hand, INP with low ζ do not significantly affect J_0 however they also have a limited effect on ΔG_{het}. This is confounded with the presence of two thermodynamic nucleation regimes, where ΔG_{het} may be large and increases with T ("germ-forming"), and another one where ΔG_{het} is very small and decreases as T increases ("spinodal nucleation").

This picture can be simplified since within the range 233 K $< T <$ 273 K, where immersion freezing ~~occurs~~ is relevant for atmospheric conditions, INP with $\zeta > 0.7$ are at the same time more likely to nucleate ice in the spinodal regime and to exhibit strong kinetic limitations. Similarly for $\zeta < 0.6$ the transition to spinodal nucleation occurs below 233 K (Fig. **??**). These INP tend to nucleate ice in the germ-forming regime and without significantly affecting J_0. Thus the thermodynamic regimes introduced in Section **??** loosely correspond to ~~dynamical~~ kinetic regimes. Roughly, ice nucleation in the spinodal regime is controlled by ~~dynamics~~ kinetics and in the germ-forming regime it is controlled by thermodynamics. This is a useful approximation but it should be used with caution. Even in the germ-forming regime the particle affects the ~~dynamics of~~ kinetics of ice-liquid interfacial transfer to some extent. Similarly, in the spinodal regime ΔG_{het} is small, but finite.

Figure **??** shows the behavior of J_{het} as T increases for different values of ζ. J_{het} in the germ-forming regime resembles ~~closely~~ the behavior predicted by CNT~~since~~. J_{het} increases steeply at some T, and increases with ζ. Similarly for CNT, J_{het} becomes higher for lower T and for lower θ. This is characteristic of the thermodyamic control on J_{het} where ΔG_{het} and $\frac{d\Delta G_{het}}{dT}$ are large (Fig. **??**), and J_0 is relatively unaffected by the particle. ~~Thus for $\zeta < 0.6$~~ In this regime it is always possible to find a contact angle (typically between ~~40°~~ 10° and 100°) that results in ~~overlap between~~ close agreement of J_{het} ~~and $J_{het, CNT}$~~ between CNT and NNF predictions (Fig. **??**), particularly for $J_{het} < 10^{12} \text{cm}^{-2}\text{s}^{-1}$ which covers most values of atmospheric interest. This is also true for $a_w = 0.9$ (Fig. **??**, right panel) although the approximation to the equilibrium temperature signals a steeper ~~$J_{het, CNT}$ than J_{het}, with the former~~ behavior in CNT peaking at higher values than NNF. Since $\frac{dJ_{het}}{dT}$ is large, J_{het} ~~shows~~ may

28

show threshold behavior. This is characteristic of freezing mediated by some dust species like Chlorite and Montmorrillonite (???).

There is however no value of θ that would lead to overlap between CNT and NNF for $\zeta > 0.7$. These conditions corresponds largely to spinodal ice nucleation. J_het is kinetically controlled since ΔG_het is small and J_0 varies widely with T (Fig. ??). As in the germ-forming regime J_het also reaches significant values, but increases more slowly with decreasing T (Fig. ??). Higher ζ leads to J_het becoming significant at higher T. But unlike in the germ-forming case, curves with higher ζ tend to plateau at progressively lower values of J_het since they become kinetically limited by their approximation to thermodynamic equilibrium. For $\zeta \sim 0.7$ some of the curves of Fig. ?? also display germ-forming behavior at high T, and are characterized by sudden decrease in $-\frac{dJ_\text{het}}{dT}$ as T decreases. The sudden change of slope corresponds to the region around the minimum ΔG_het (Fig. ??) and signals the transition from germ-forming to spinodal ice nucleation. Such behavior has been observed in some INP of bacterial origin (?).

Figure ?? also indicates that nucleation regimes cannot be assigned based on the values of J_het or T_f. In both regimes, J_het may reach substantial values, hence T_f may cover the entire range 233 K $< T <$ 273 K. What is even more striking is that J_het curves with $\zeta > 0.7$ tend to cross those with $\zeta < 0.7$. This means that two INP characterized by very different ζ can have the same freezing temperature. This result thus challenges the common notion that INP with higher freezing temperatures are intrinsically more active at nucleating ice, or in other words, that by measuring T_f alone it is possible to characterize the freezing properties of a given material. In reality to discern whether the observed T_f corresponds to a good (in the thermodynamic sense) INP acting in the spinodal regime or a less active INP acting in the germ-forming regime it is necessary to measure $\frac{dJ_\text{het}}{dT}$ along with T_f.

3.5 Application to the water activity-based nucleation rate

$\Delta a_\text{w, het}$ has been determined in several studies and used to predict and parameterize J_het in atmospheric models (e.g., ??). Thus it is useful to analyze under what conditions ζ can be estimated using measured $\Delta a_\text{w, het}$ values. Rearranging Eq. (??) we obtain,

$$\Delta a_\text{w, het} + \Delta a_\text{w, hom}\left(1 - \zeta - \frac{\Delta a_\text{w, hom} - \Delta a_\text{w, het}}{\Lambda_\text{E}}\right) + \Lambda_\text{mix} = 0. \tag{57}$$

If $\Delta a_\text{w, hom}$ and $\Delta a_\text{w, het}$ are known, ζ can be estimated iteratively solving Eq. (??). Note that Λ_mix is temperature dependent (Eq. ??) implying a slight dependency of ζ on T when $\Delta a_\text{w, het}$ is constant. However since Λ_mix is also typically small ζ is almost proportional to $1 - \frac{\Delta a_\text{w, het}}{\Delta a_\text{w, hom}}$.

805   To test Eq. (**??**) the data for Leonardite (LEO) and Pawokee Peat (PP) particles (humic-like substances) obtained by **?** are used. The authors reported $\Delta a_{w,\,het} = 0.2703$ for LEO and $\Delta a_{w,\,het} = 0.2466$ for PP. These values are assumed to be independent of a_w and T with an experimental error in $\Delta a_{w,\,het}$ of 0.025. J_{het} for both materials is depicted in Fig. **??**. Since J_{het} was obtained from two different samples and from repeated freezing and melting experiments these results represent actual nucleation rates. Application of Eq. (**??**) over the $T = 210\,\text{K}-250\,\text{K}$ range ~~results in $\zeta = 0.053 - 0.058$~~ and using $\Delta a_{w,\,hom} = 0.304$

810 results in $\zeta = 0.049 - 0.058$ for LEO and ~~$\zeta = 0.092 - 0.101$~~ $\zeta = 0.096 - 0.121$ for PP. Within this temperature range these values correspond to the germ-forming regime, hence J_{het} is thermodynamically-controlled. Comparison against the experimentally determined J_{het} for three different values of a_w is shown in Fig. **??**. Within the margin of error there is a reasonable agreement between the modeled and the experimental J_{het}.

    Figure **??**, top panels, however reveals that even if J_{het} becomes significant around the values predicted by Eq. (**??**), $-\frac{d\ln J_{het}}{dT}$

815 is overestimated, particularly for PP. This ~~raises the possibility that these INP may~~ may indicate that that these INP nucleate ice in the spinodal regime. To test this, J_{het} was fitted to the reported measurements by varying ζ within the range where spinodal nucleation would be ~~active~~dominant. To avoid agreement by design a single ζ was used for all experiments for each species resulting in ~~$\zeta = 0.951$~~ $\zeta = 0.949$ for PP and ~~$\zeta = 0.955$~~ $\zeta = 0.952$ for LEO (Fig. **??**, bottom panels). For PP J_{het} and $-\frac{d\ln J_{het}}{dT}$ agree better with the experimental values, whereas for LEO the agreement improves at high T but worsens at low

820 T. ~~For both species~~ In this regime J_{het} seems to be slightly overestimated by the theory at the lowest a_w tested. This may be due to small uncertainties in a_w that play a large role in J_{het} (as for example the assumption of a T-independent a_w(**?**), **?**). There is the possibility that the humic acid present in PP may slightly dissolve during the experiments (D. Knopf, personal communication), which would impact not only a_w but also may modify the composition of the particles, hence ζ.

    The exercise above suggests that ice nucleation in PP may follow a spinodal mechanism. Using a single value of $\Delta a_{w,\,het}$ to

825 predict ζ, as expressed mathematically by Eq. (**??**), seems to work for LEO. Since Eq. (**??**) represents a thermodynamic relation between $\Delta a_{w,\,hom}$ and $\Delta a_{w,\,het}$, it is expected to work well ~~for nucleation in~~ when nucleation is thermodynamically-controlled, i.e. the germ-forming regime~~(low ζ)~~. However it ~~fails~~ may fail for spinodal ice nucleation since it does not consider the effect of the particle on J_0. ~~Note that~~ $\Delta a_{w,\,het}$ however carries important information about J_{het} (**?**) but for spinodal ice nucleation the relationship between $\Delta a_{w,\,het}$ and ζ must be more complex than predicted by Eq. (**??**) since kinetic limitations play a

830 significant role. Figure **??** also shows that similar T_f can be obtained by either high or low ζ. The particular regime in which an INP nucleates ice ~~affects mainly~~ determines $-\frac{d\ln J_{het}}{dT}$, hence ~~its sensitivity to size and~~ the sensitivity of the droplet freezing rate to the particle size and to the cooling rate.

3.6   Limitations

It is important to analyze the effect of several assumptions introduced in Section **??** on the analysis presented here. One of the

835 limitations of the approach used in deriving Eq. (**??**) is that it employs macroscale thermodynamics in the formulation of the work of nucleation. The effect of this assumption is however minimized in several ways. First, unlike frameworks based on the interfacial tension, NNF is much more robust to changes in ice germ size since the product $\Gamma_w s \Delta h_f$ remains constant (Section **??**). Second, in the spinodal regime ΔG_{het} is independent of n^* and only for $T > 268\,\text{K}$ and in the germ-forming regime, the

approach presented here may lead to uncertainty (Section **??**). Thus Eq. (**??**) remains valid for most atmospheric conditions, although caution must be taken when $T_\mathrm{f} > 268$ K. Alternatively the framework presented here could be extended to account explicitly for the effect of size on Δh_f and Γ_w (e.g., **?**).

Further improvement could be achieved by implementing a more sophisticated equation of state for the vicinal water. Here a two-state assumption has been used, such that μ_vc is a linear combination of ice-like and liquid-like fractions. Such approximation has been used with success before (**??**). However it is known that the structure of supercooled water represents an average of several distinct configurations (**?**). These are in principle accounted for in the proposed approach since ζ represents a relative, not an absolute increase in the IL fraction. However there is no guarantee that such increase can be linearly mapped in the way described in Section **??**. Fortunately this would only mean in practice that the ~~observed~~ value of ζ for a given material is linked to the particular form of the equation of state used to describe the vicinal water.

Equation (**??**) is also blind to the surface properties of the immersed particle. The implicit assumption is that the effect of surface composition, charge, hydrophilicity and roughness on J_het can be parameterized as a function of ζ. The example shown in Section **??** suggests this is indeed the case. Making such relations explicit must however lie at the center of future development of the proposed approach. Similarly a heuristic approach was used to study the effect of irreversibility on the nucleation work. This can be improved substantially by making use of a generalized Gibbs approach (**?**), which unfortunately may also increase the number of free parameters in the model. None of these limitations is expected to change the conclusions of this study, however they may affect the values of ζ fitted when analyzing experimental data. The approach proposed here however has the advantage of being a simple, one parameter approximation that can be easily implemented in cloud models.

4   Summary and Conclusions

~~Current immersion freezing theory relies~~ Immersion freezing is a fundamental cloud process and its correct representation is critical for accurate climate and weather predictions. Current theories rely on a view that mimics ice formation from the vapor, neglecting several interactions unique to the liquid. This work develops for the first time a comprehensive approach to account for such interactions. The ice nucleation activity of immersed particles is linked to their effect on the vicinal water. It is shown that the same mechanism that lowers the thermodynamic barrier for ice nucleation also tends to decrease the mobility of water molecules, hence the interfacial transfer coefficient. The role of the ~~particle~~ immersed particle in ice nucleation can be understood as increasing order in the adjacent water facilitating the formation of ice-like structures. Thus, instead of being purely driven by thermodynamics, heterogeneous ice nucleation in the liquid phase is a process determined by the competition between thermodynamic and kinetic constraints to the formation and propagation of ice.

~~To distinguish between thermodynamic and dynamic effects on ice nucleation the concept of thermodynamic freezing temperature was introduced. The~~ In the new approach the properties of vicinal water ~~were approximated assuming~~ are approximated using a regular solution between high and low density regions, with composition defined by an aerosol specific parameter, ζ, which acts as a "templating factor" for ice nucleation. This ~~assumption~~ model leads directly to the derivation of the so-called water activity criterion for heterogeneous ice nucleation. It also results on an identity between the homogeneous and hetero-

geneous work of nucleation (Eq. **??**) implying that by knowing an expression for ΔG_{hom}, ΔG_{het} can be readily written. This is advantageous as homogeneous ice nucleation is far better understood than immersion ice nucleation, and, because it avoids a mechanistic description of the complex interaction between the particle, the ice and the liquid. To describe ΔG_{hom} the NNF framework (**?**) ~~which does not use the capillarity assumption of typical CNT expressions~~ was employed. This approach was extended to include non-equilibrium dissipation effects.

A model to describe the effect of the immersed particle on the mobility of water molecules, <u>hence on the kinetics of immersion freezing,</u> was also developed. ~~The model is built~~ <u>This model builds</u> upon an expression for the interfacial diffusion flux that accounts for the work required for water molecules to accommodate in an ice-like manner during interface transfer. Here this expression is extended to account for the reduction in the ~~configurational entropy of water caused by the presence of the immersed particle, leading to increased viscosity and decreased mobility of water molecules near the particle surface. As a result, the preexponential factor tends to decrease significantly for $\zeta > 0.7$~~<u>molecular flux to the ice germ (expressed as an strong decrease in J_0) as the system moves towards thermodynamic equilibrium.</u>

Accounting for the effect ~~on the particle of~~ <u>of the particle on</u> the vicinal water suggests the existence of a spinodal regime in ice nucleation where a pair of molecules with orientation similar to that of bulk ice may be enough to trigger ~~the propagation of the ice-lattice (e.g., ?). However ice nucleation in this regime~~ <u>freezing (e.g., **?**). Ice nucleation in the spinodal regime requires a highly efficient templating effect by the particle, however</u> also tends to be strongly limited by the kinetics of <u>ice-liquid</u> interfacial transfer. ~~Ice nucleation in the spinodal regime requires a highly efficient templating effect by the particle.~~ Compared to the classical germ-forming regime, nucleation by ~~an~~ <u>a</u> spinodal mechanism is much more limited by diffusion and exhibits a more moderate increase in J_{het} as temperature decreases. The existence of two nucleation regimes and the strong kinetic limitations occurring in efficient INP imply that the freezing temperature ~~may be~~ <u>is</u> an ambiguous measure of ice nucleation activity. This is because for a given T two INP characterized by different ζ may have the same J_{het}, although with very different sensitivity to surface area and cooling rate.

The relationship between the measured shift in water activity $\Delta a_{\text{w, het}}$ and ζ was analyzed and tested using data for humic-like substances. It was found that assuming a fixed water activity shift to predict J_{het} could be appropriate for low ζ (the germ-forming regime) however may lead to overprediction of $-\frac{d\ln J_{\text{het}}}{dT}$ for high ζ. ~~Thus~~ <u>This is because</u> the so-called water activity criterion represents ~~an exact~~ <u>a</u> thermodynamic relation between a_{w} and $~~T_{\text{f,eq}}, \text{instead of}~~ T_{\text{f}}$ <u>but does not account for kinetic limitations.</u>

Immersion freezing research has seen a resurgence during the last decade (**?**). A wealth of data is now available to test theories and new approaches to describe ice formation <u>in atmospheric models.</u> To effectively doing so it is necessary to develop models that realistically capture the complexities of the liquid phase. Further development of the approach presented here will look to better describe the non-reversible aspects of nucleation as well as to establish a more complete description of the properties of the vicinal water. Application to the freezing of atmospheric aerosol requires the definition of the ice nucleation spectrum, which will be pursued in a future work. Nevertheless, the present study constitutes for first the time an approximation to the modeling of ice nucleation that links the ~~dynamics and the kinetics~~ <u>modifications of the properties</u> of vicinal water ~~with the~~ <u>by immersed particles with their</u> ice nucleation ability~~of immersed particles~~. The approach presented here may help expanding

our understanding of immersion ice nucleation and facilitate the interpretation of experimental data in situations where current models fall short. Application of these ideas in cloud models will allow elucidating under what conditions different nucleation regimes ~~may~~ occur in the atmosphere.

Table 1. List of symbols.

|	
a_0	Cross-sectional area of a water molecule, $\pi d_0^2/4$, m^2
A_w	Phenomenological interaction parameter
a_w	Activity of water
$a_\text{w, eff}$	Effective water activity
$a_\text{w,eq}$	Equilibrium a_w between bulk liquid and ice (**?**)
~~$a_\text{w, v}$ Activity of water near the immersed particle~~$a_\text{w, het}$	Thermodynamic freezing threshold for heterogeneous ic
$a_\text{w, hom}$	Thermodynamic freezing threshold for homogeneous ice
C_0	Monomer concentration, m^{-2}
E, T_0	Parameters of the VFT equation defining D_∞, 892 and
D	Diffusion coefficient for interface transfer, m^2 s^{-1}
D_∞	Self-diffusion coefficient of bulk water (**?**), m^2 s^{-1}
D_0	Fitting parameter, 3.06×10^{-9} m^2 s^{-1} (**?**)
d_0	Molecular diameter of water, $(6v_w/\pi)^{1/3}$, m
~~f_f Freezing fraction~~f_het^*	Impingement factor for heterogeneous ice nucleation, s$^-$
f_hom^*	Impingement factor for homogeneous ice nucleation, s$^-$
~~g^E Excess Gibbs free energy,~~ G	Gibbs free energy, J
~~$G_\text{liq}, G_\text{ice}$ Gibbs free energy of liquid and ice, respectively, h_vc Enthalpy of vicinal water,~~ h	Planck's constant, Js
J_0	Preexponential factor m^{-2} s^{-1}
J_het	Heterogeneous nucleation rate, m^{-2} s^{-1}
~~$J_\text{het, CNT}$ Heterogeneous nucleation rate from CNT,~~ k_B	Boltzmann constant, J K^{-1}
N	Number of ~~molecules in a cluster involving ice-liquid bo~~
~~N_c Number of atoms in contact with the ice germ, 5.85×10^{18} (**?**)~~ n	Number of molecules in a ice cluster
n^*	Critical germ size
n_hom^*	Critical germ size for homogeneous ice nucleation
n_t	Number of formation paths of the transient state, 16 (**?**)
$p_\text{s,w}, p_\text{s,i}$	Liquid water and ice saturation vapor pressure, respectiv
~~Continued.~~ s	Geometric constant of the ice lattice, 1.105 ~~(?)~~molec$^{1/3}$
S_i	Saturation ratio with respect to ice
$S_\text{c,0}$	Configuration entropy of water*
S_c	Configuration entropy of vicinal water
T	Temperature, K
T_c	Critical separation temperature, ~~219.802~~ 211.473 K

Table 1. Continued.

v_{w}	Molecular volume of water in ice (**?**), m^{-3}
$v_{\text{w,0}}$	Molecular volume of water at 273.15 K
~~$\bar{W}, \bar{W}_{\text{vc}}$~~ $\bar{W}$	~~Transition probability in the bulk liquid and in the vicinal water, respectively~~ Average transition probability
~~W_{d}~~ W_{diss}	Work dissipated during cluster formation, J
W_{d}	Work dissipated during interface transfer, J
Z	Zeldovich factor
$\Delta a_{\text{w, het}}$	$a_{\text{w, het}} - a_{\text{w,eq}}$
$\Delta a_{\text{w, hom}}$	$a_{\text{w, hom}} - a_{\text{w,eq}}$, 0.304 (**??**)
ΔG	Work of cluster formation, J
ΔG_{act}	Activation energy for ice nucleation, J
ΔG_{hom}	Nucleation work for homogeneous ice nucleation, J
ΔG_{het}	Nucleation work for heterogeneous ice nucleation, J
~~ΔG_{CNT} Nucleation work from CNT,~~ Δh_{f}	Heat of solidification of water, J mol^{-1} (**??**)
~~$\Delta \mu_{\text{r}}$~~ $\Delta \mu_{\text{s}}$	Excess free energy of solidification of water, J
$\Delta \mu_{\text{i}}$	~~Supersaturation~~Driving force for ice nucleation, J
~~A_{E}~~ Λ_{mix}	Dimensionless ~~interaction parameter,~~ $-\frac{2}{N}\frac{T_c}{T}$ mixing parameter, defined in Eq. (**??**)
Φ	Energy of formation of the ice-liquid interface, molec$^{1/3}$ J
Γ_{w}	Molecular surface excess of at the interface, 1.46 (**??**)
~~γ_{c} Cooling rate,~~ $-\frac{\text{d}T}{\text{d}t}$ $\mu_{\text{w}}, \mu_{\text{s}}, \mu_{\text{vc}}$	Chemical potential of water, ice and vicinal water, respectively J
$\rho_{\text{w}}, \rho_{\text{i}}$	Bulk density of liquid water and ice, respectively, Kg m^{-3} (**?**)
σ_{E}	Dimensionless residual entropy
σ_{iw}	Ice–liquid interfacial energy J m^{-2} (**?**)
θ	Contact angle
ζ	Templating factor
Ω_{g}	Ice germ surface area, m^{-2}

* From the data of **?** the following fit was obtained: $S_{\text{c,0}} = k_{\text{B}} v_{\text{w}}/v_{\text{w,0}}(-7.7481 \times 10^{-5}T^2 + 5.5160 \times 10^{-2}T - 6.6716)$ (J K^{-1}) for T between 180 K and 273 K.
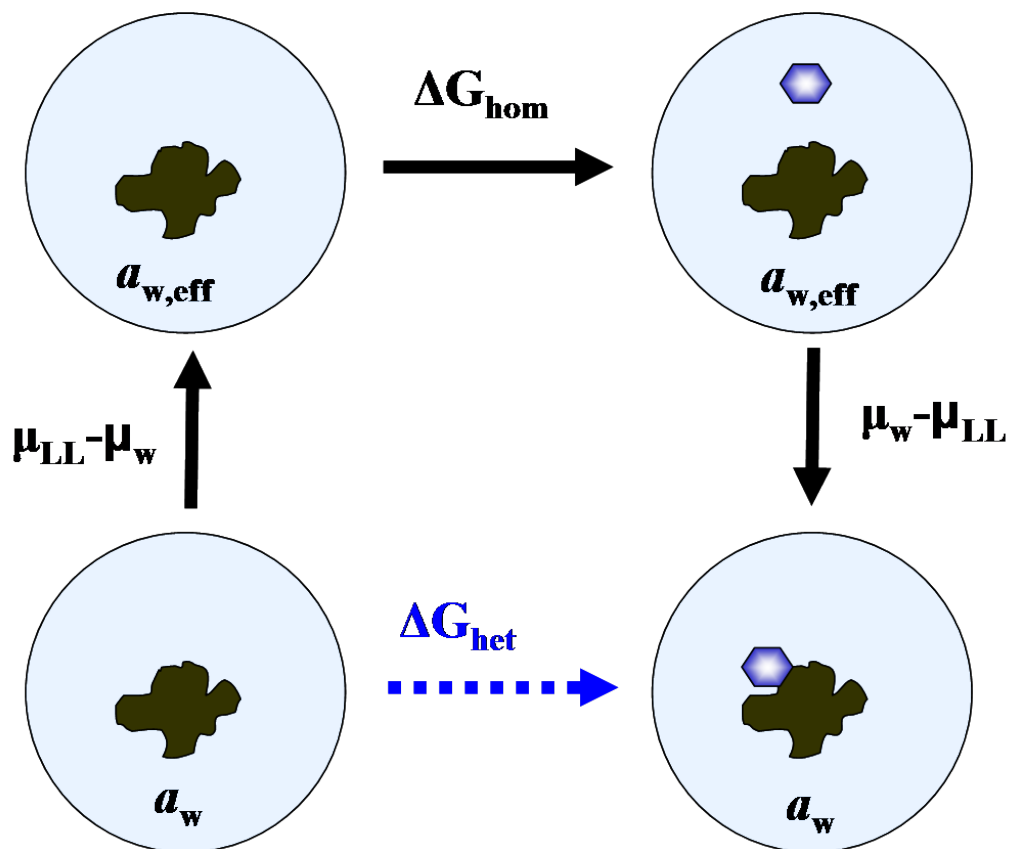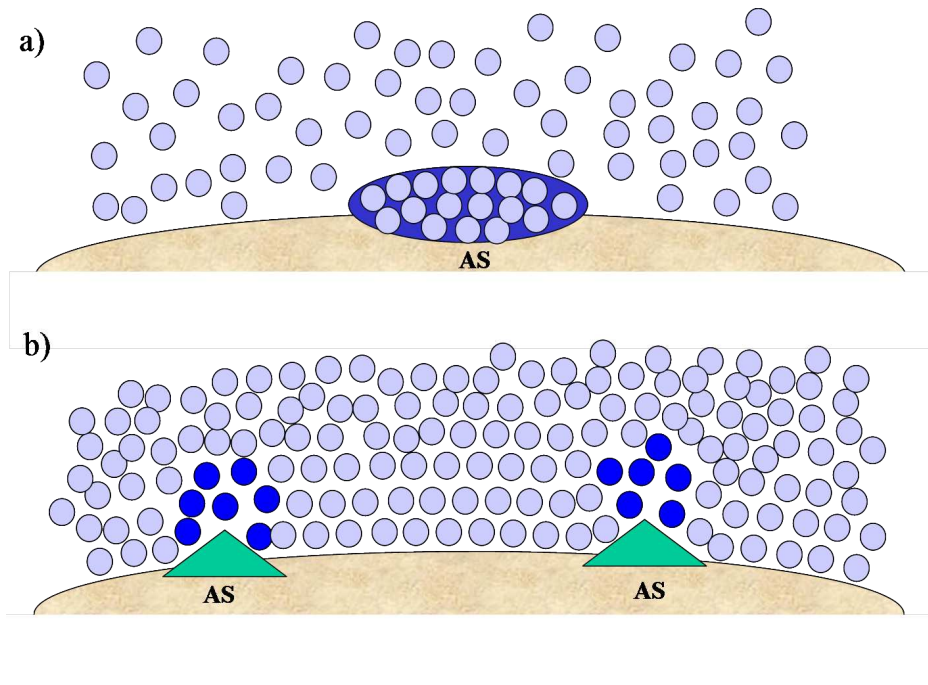
Figure 1. Diagram representing a thermodynamic path including homogeneous ice nucleation with the same work as heterogeneous freezing.
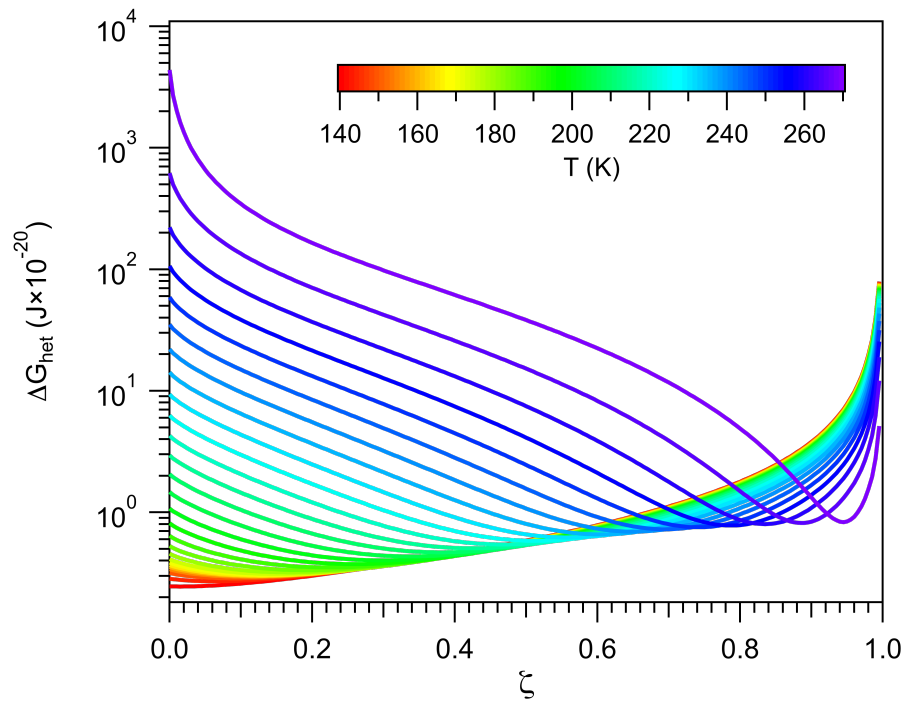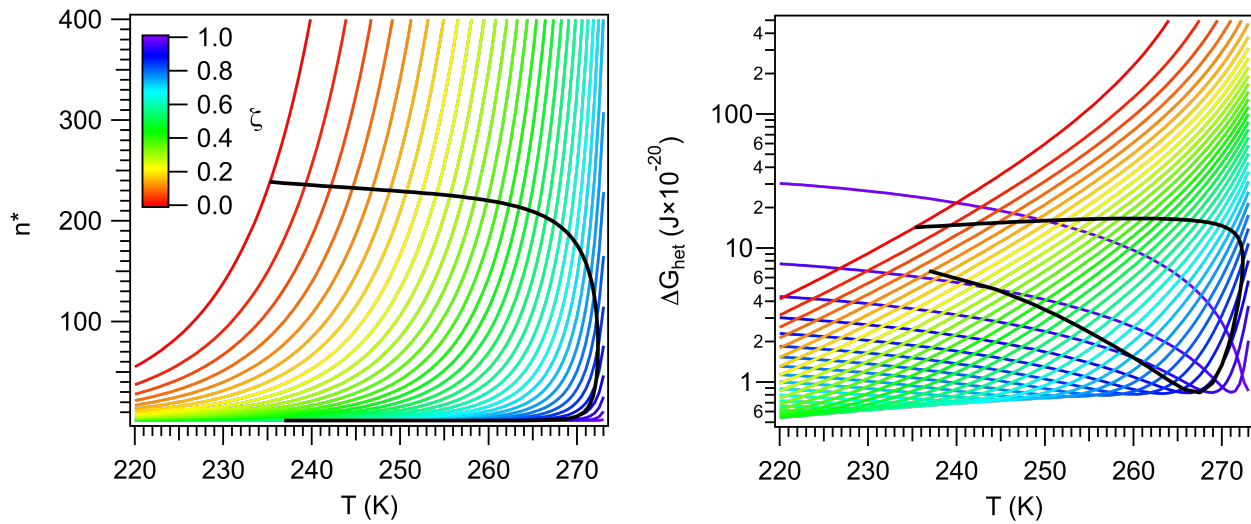
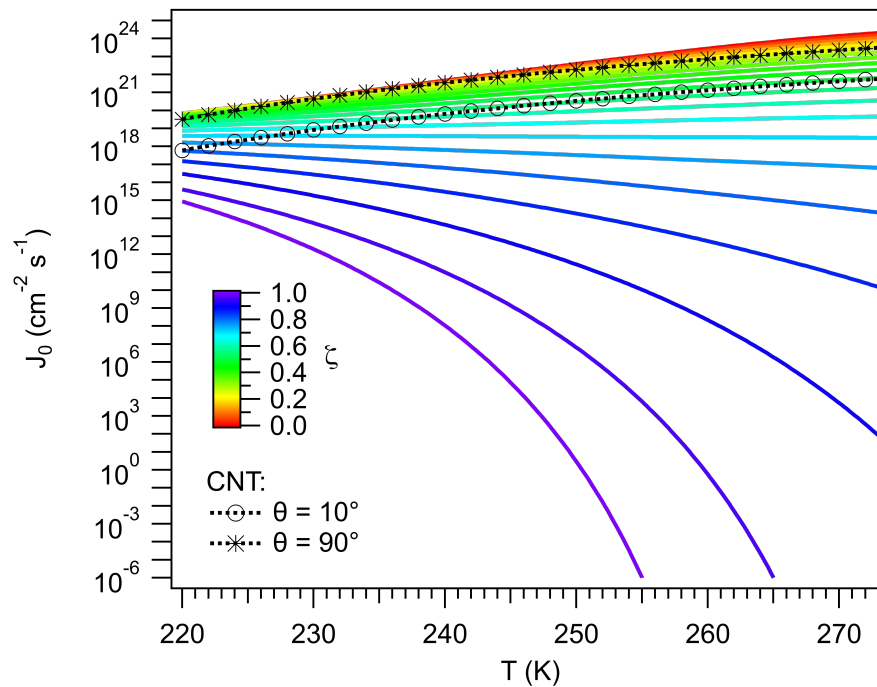**Figure 2.** Work of heterogeneous ice nucleation. Color indicates different temperatures.

Figure 3. Different representations of immersion freezing. (a) An ice germ (dark blue) forming on an active site (AS) by random collision of water molecules (light blue). (b) Low density regions (dark blue) forming in the vicinity of active sites within a dense liquid phase (light blue).
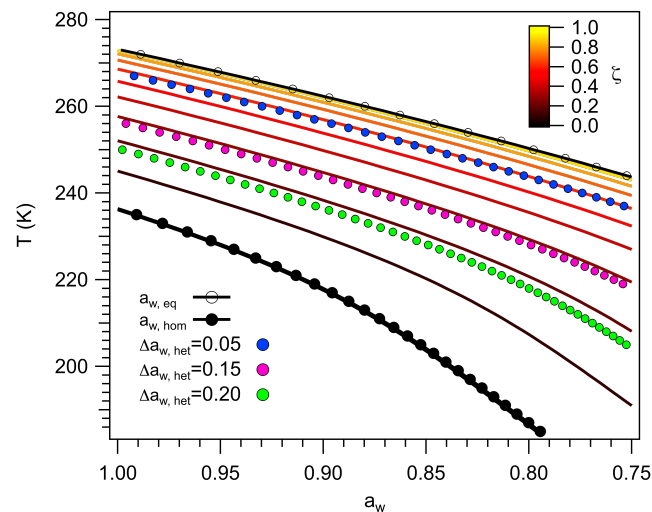

Figure 4. ~~Thermodynamic freezing~~ Freezing temperature as a function of water activity. ~~Color~~ Colored lines correspond to $a_{w,\,het}$ ~~(Eq. ??)~~ for different values of ζ. Also shown are ~~a_w~~ the water activities at equilibrium and at the homogeneous freezing threshold, $a_{w,\,eq}$ and $a_{w,\,hom}$, respectively, and lines drawn applying constant water ativity shifts, $\Delta a_{w,\,het}$, of 0.05, 0.15 and 0.20.

Figure 5. Critical germ size (left panel) and work of heterogeneous ice nucleation (right panels) for different values of ζ (color). Black lines correspond to constant ~~$J_{het} = 10^{12}$~~ $J_{het} = 10^6$ m^{-2} s^{-1}.

Figure 6. Preexponential factor. ~~Color~~ Colored lines indicates different values of ζ. Black lines correspond to results calculated using CNT for different values of the contact angle, θ.
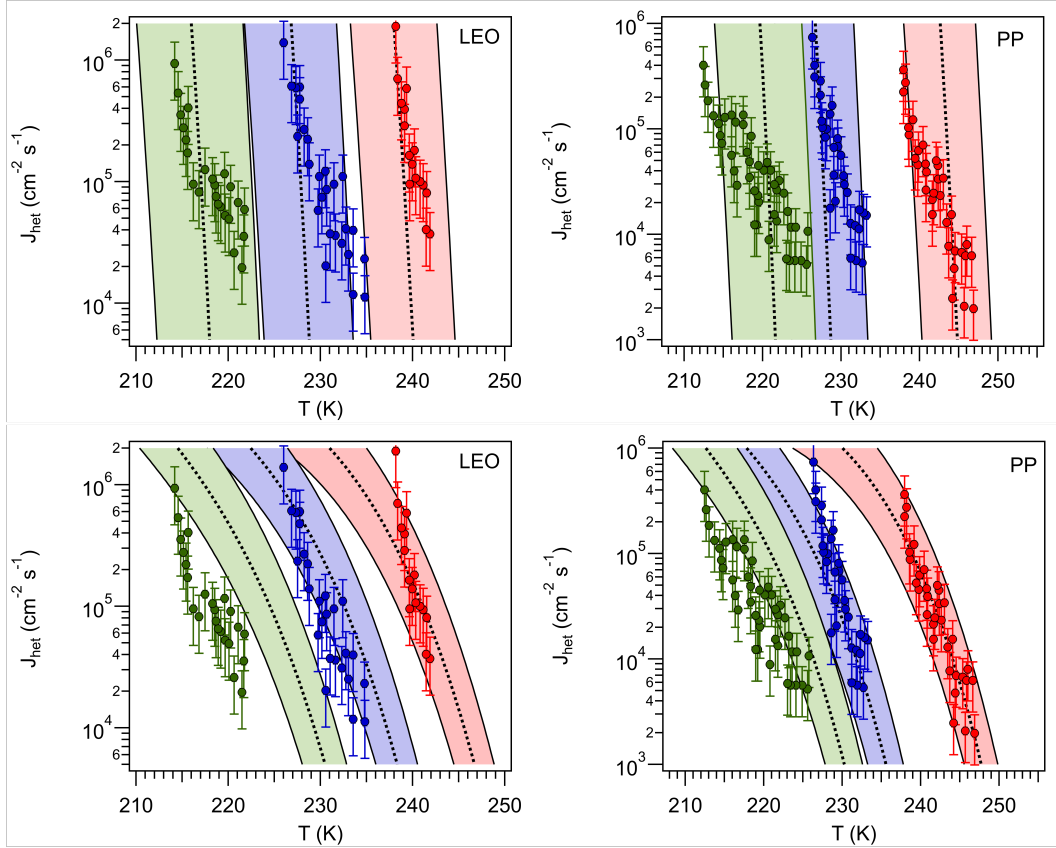
Figure 8. Top panels: Heterogeneous ice nucleation rate calculated using a constant shift in a_{w} (black, dotted, lines) for Leonardite (LEO $\Delta a_{\text{w, het}} = 0.2703$) and Pawokee Peat (PP, $\Delta a_{\text{w, het}} = 0.2466$) (top panels). Red, blue and green colors correspond to a_{w} equal to 1.0, 0.931 and 0.872, respectively, for LEO and 1.0, 0.901 and 0.862 for PP. Shaded area corresponds to $\Delta a_{\text{w, het}} \pm 0.025$. Markers correspond to experimental measurements reported by **?**; error bars represent an order of magnitude deviation from the reported value. Bottom panels: J_{het} calculated for constant $\zeta = 0.955$ $\zeta = 0.949$ for LEO and $\zeta = 0.951$ $\zeta = 0.952$ for PP. The shaded area corresponds to $a_{\text{w}} \pm 0.01$ and $\zeta \pm 0.001$ $\zeta \pm 0.0015$.