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Discussions

Interactive comment on "On the Thermodynamic and Dynamic Aspects of Immersion Ice Nucleation" *by* Donifan Barahona

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1 Response to 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 nearby 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 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, particularly as many authors may not regularly consult more fundamental journals like JCP. Most of the concepts discussed in this work are basic thermodynamics and 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(−∆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 ∆G, 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 the reviewer suggests with a broad definition of J_{het} then followed by Eq. (32). The distinction paragraphs of sections of 2.3.3, 2.4 have now been moved to a new broad introduction before Section 2.1. It must be noted however that the distinction between “kinetic” and “thermodynamic” effects is not clear cut in the proposed model since the flux of water molecules to the nascent ice germ is controlled by the thermodynamic driving force (Barahona, 2015). This is also clarified.

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 nucleation 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 hypotheses 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 reorganization of the paper. Since now a broad formulation of J_{het} is introduced earlier in the work it is easier to distinguish how each theory defines the relevant terms (nucleation work, molecular flux). The suggested table may be confusing since the equations involved are quite long. It is worth mentioning that the theory presented here builds upon previous work (**?**Barahona, 2015) and therefore does not only differs from CNT 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 revised work. The comparison against CNT was partially addressed in Figure 7.

Following the reviewer’s suggestion a new, separate section has been introduced to clarify this.

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 conclusions of the study. The corrected derivation of the involved equations 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:* $a_w = a_{\mathit{w,\ eff}}^{\frac{1}{1+\zeta}} a_{w,eq}^{\frac{\zeta}{1+\zeta}} \exp\left(\Lambda_E \frac{1-\zeta}{1+\zeta}\right)$ *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: The wrong expression for $\Delta\mu_{\mathrm{S}}$ was written in the text. $\Delta\mu_{\mathrm{S}}$ must actually be calculated at $a_{\mathrm{w,\ eff}}$, hence Eq. (14) of 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. Equation (14) was also used to simplify Eq. (40); this has been corrected as well. The derivation of Eq. (1) is shown at the end of this document (Eq. 12).

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* $A_w = \frac{2k_BT_C}{N}$*. In the current formulation the first part of Eq. (9), i.e.* $\frac{\partial^2\mu_{VC}}{\partial\zeta^2} = 0$ *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).*

Fig. 1. Comparison between using the original(dashed lines) and the corrected (solid lines) expressions for $a_{\mathrm{w,\ eff}}$.

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 $a_{\mathrm{w,\ eff}}$, i.e.,

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

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

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

In the corrected version (Eq. 20 of this document):

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

The mixing term is only significant when $\zeta \sim 0.5$, since the energy of mixing vanishes for pure components. In Figure 1 (see supplement file) the effective water activity, the work of nucleation and the nucleation rate are drawn for $a_w = 1$ at different temperatures and values of ζ, and for the original (dashed) and corrected (solid) expressions for $a_{\mathsf{w,eff}}$. 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}. Although these are significant differences, $a_{\text{w,eff}}$, 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" 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. The derivation is also found in several textbooks (e.g., Prausnitz et al., 1998)). This limits the number of definitions introduced in the text.

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 susceptible to grow into ice germs (i.e., the monomer concentration). Defining it as $1/a_0$ early in the text would unnecessarily limit the scope of the equation. For calculations we use $a_0 = \pi d_0^2$ with $d_0 = \left(\frac{6*v_w}{pi}\right)^{1/3}$ being v_w the molecular volume of water. This has been added to Table 1.

To address the reviewer's concern the following line was also added to the Section: "C_0 could be defined either per-area or per-volume basis".

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 appropriate to write C_0 as proportional to the volume of the vicinal layer. Unfortunately this would bring confusion since historically heterogeneous nucleation rates are normalized to the particle surface area. $C_0 = 1/a_0$ is thus consistent with current literature and avoids a formal definition of the volume of the vicinal layer which could be quite challenging.

However I disagree that this means that only the molecules in direct contact with the particle are considered vicinal water. The only assumption involved is that the density of 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 the Zeldovich factor without dissipation holds in the new theory. This is exact for the germ forming regime, but it is 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 reorganized following the reviewer's suggestion.

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 pseudoequilibrium temperature between liquid and ice, for a given a_w. Qualitatively it must be the temperature at which freezing would be observed if no kinetic limitations existed, so that freezing is only dictated by thermodynamics (hence it must be the 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 $a_{\mathrm{w,hom}}$ (Holten and Anisimov, 2012) 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 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

$$\mu_{\mathrm{VC}} = (1-\zeta)\hat{\mu}_{\mathrm{LL}} + \zeta\hat{\mu}_{\mathrm{IL}}, \tag{7}$$

where $\hat{\mu}_{\mathrm{LL}}$ and $\hat{\mu}_{\mathrm{LL}}$ 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 (7) 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,

$$\mu_{\mathrm{vc}} = (1-\zeta)\mu_{\mathrm{LL}} + \zeta\mu_{\mathrm{IL}} + \Delta G_{\mathsf{mix}} \tag{8}$$

where $\Delta G_{\mathsf{mix}} = (\hat{\mu}_{\mathrm{IL}} - \mu_{\mathrm{IL}})\zeta + (1-\zeta)(\hat{\mu}_{\mathrm{LL}} - \mu_{\mathrm{LL}})$ is the Gibbs energy of mixing. For a mechanical mixture of pure LL and IL species, $\Delta G_{\mathsf{mix}} = 0$, whereas for an ideal solution ΔG_{mix} is determined by the ideal entropy of mixing (Prausnitz et al., 1998). Reorganizing Eq. (8) we obtain,

$$\mu_{\mathrm{vc}} = \mu_{\mathrm{LL}} + \zeta\Delta\mu_{\mathrm{il}} + \Delta G_{\mathsf{mix}} \tag{9}$$

where $\Delta\mu_{\mathrm{il}} = \mu_{\mathrm{IL}} - \mu_{\mathrm{LL}}$. $\Delta\mu_{\mathrm{il}}$ can be approximated by using the equilibrium between bulk liquid and ice as reference state so that (Kashchiev, 2000),

$$\mu_{\mathrm{IL}} = \mu_{\mathrm{eq}} + k_{\mathrm{B}}T\ln(a_{\mathrm{IL}}), \tag{10}$$

and

$$\mu_{\mathrm{LL}} = \mu_{\mathrm{eq}} + k_{\mathrm{B}}T\ln\left(\frac{a_{\mathrm{w,\,eff}}}{a_{\mathrm{w,\,eq}}}\right), \tag{11}$$

where $a_{\mathrm{w,\,eff}}$ is termed the "effective water activity" and it is the value of a_{w} associated with the LL regions in the vicinal water, and a_{IL} is the water activity in the IL regions. Assuming that similarly to bulk ice the solute does not significantly partition to the IL phase, then $a_{\mathrm{IL}} \approx 1$. With this, and combining Eqs.(10) and (11), and rearranging we obtain,

$$\Delta\mu_{\mathrm{il}} = -k_{\mathrm{B}}T\ln\left(\frac{a_{\mathrm{w,\,eff}}}{a_{\mathrm{w,\,eq}}}\right), \tag{12}$$

The central assumption behind Eq. (12) is that $a_{\mathrm{w,\,eq}}$ corresponds to the equilibrium water activity between liquid and ice, or in other words that near equilibrium $\Delta\mu_{\mathrm{il}} \approx \Delta\mu_{\mathrm{s}}$, being $\Delta\mu_{\mathrm{s}}$ the excess free energy of solidification of water.

In reality $\Delta\mu_{\mathrm{s}}$ 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 semi-empirical 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 $\Delta\mu_{\mathrm{s}}$ and $\Delta\mu_{\mathrm{il}}$. Holten et al. (2013) have shown that a regular solution can reasonably approximate the chemical potential of supercooled water. Moreover, the authors also showed that taking into account clustering of water molecules upon mixing leads to better agreement with MD simulations and experimental results.

According to the regular solution model, modified by clustering (Holten et al., 2013, c.f. Eq. 16),

$$\Delta G_{\mathsf{mix}} = \frac{k_{\mathrm{B}}T}{N}\left[\zeta\ln(\zeta) + (1-\zeta)\ln(1-\zeta)\right] + A_w\zeta(1-\zeta) \tag{13}$$

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. $N = 6$ corresponds to clustering in hexamers and is near the optimum fit between MD simulations and the solution model (Holten et al., 2013). 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 appropriate in this case. For $N = 6$ the difference between the two models is negligible (Holten et al., 2013).

The second term on the right hand side of Eq. (13) is an empirical functional form used to approximate the enthalpy of mixing selected so that $\Delta G_{\text{mix}} = 0$ 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 also implicitly corrects the approximation $\Delta\mu_{\mathrm{il}} \approx \Delta\mu_{\mathrm{s}}$.

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

$$\frac{\partial^2 \Delta G_{\text{mix}}}{\partial \zeta^2} = 0\,,\ \frac{\partial^3 \Delta G_{\text{mix}}}{\partial \zeta^3} = 0. \tag{14}$$

Using Eq. (13) into Eq. (14) and solving for A_w gives for $T = T_{\mathrm{c}}$,

$$A_w = \frac{2 k_{\mathrm{B}} T_{\mathrm{c}}}{N}. \tag{15}$$

Physically, T_c represents the stability limit of the vicinal water, at which it spontaneously separates into IL and LL regions. Equation (15) thus provides 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.

Combining Eqs. (12), (13), and (15), into Eq. (9) we obtain,

$$\mu_{\mathrm{vc}} = \mu_{\mathrm{LL}} - \zeta k_{\mathrm{B}} T \ln\left(\frac{a_{\text{w, eff}}}{a_{\text{w, eq}}}\right) + \frac{k_{\mathrm{B}} T}{N}\left[\zeta \ln(\zeta) + (1-\zeta)\ln(1-\zeta)\right] + \frac{2 k_{\mathrm{B}} T_{\mathrm{c}}}{N}\zeta(1-\zeta). \tag{16}$$

Making,

$$\Lambda_{\mathrm{mix}} = \frac{1}{N}\left[\zeta \ln(\zeta) + (1-\zeta)\ln(1-\zeta)\right] + \frac{2}{N}\frac{T_{\mathrm{c}}}{T}\zeta(1-\zeta), \tag{17}$$

Equation (16) can be written in the form,

$$\mu_{\mathrm{vc}} = \mu_{\mathrm{LL}} - \zeta k_{\mathrm{B}} T \ln\left(\frac{a_{\text{w, eff}}}{a_{\text{w, eq}}}\right) + k_{\mathrm{B}} T \Lambda_{\mathrm{mix}} \tag{18}$$

Equation (18) 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. (18) and it is calculated in 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, $\mu_{\mathrm{vc}} = \mu_{\mathrm{w}}$, where μ_{w} is the chemical potential of water in the bulk of the liquid, i.e., away from the particle. Using Eq. (18) this implies,

$$\mu_{\mathrm{w}} = \mu_{\mathrm{LL}} - \zeta k_{\mathrm{B}} T \ln\left(\frac{a_{\text{w, eff}}}{a_{\text{w, eq}}}\right) + k_{\mathrm{B}} T \Lambda_{\mathrm{mix}}. \tag{19}$$

Using again the equilibrium between bulk liquid and ice as reference state, so that

$\mu_\mathrm{W} = \mu_\mathrm{eq} + k_\mathrm{B} T \ln(a_\mathrm{W})$, and using Eq. (10), Eq. (19) can be written in terms of the water activity in the form,

$$a_\mathrm{W} = a_\mathrm{w,\,eff}\left(\frac{a_\mathrm{w,\,eq}}{a_\mathrm{w,\,eff}}\right)^{\zeta}\exp(\Lambda_\mathrm{mix}). \tag{20}$$

From Eq. (20) $a_\mathrm{w,\,eff}$ can be readily obtained in the form,

$$a_\mathrm{w,\,eff} = \left(\frac{a_\mathrm{W}}{a^{\zeta}_\mathrm{w,\,eq}}\right)^{\frac{1}{1-\zeta}}\exp\left(-\frac{\Lambda_\mathrm{mix}}{\zeta - 1}\right). \tag{21}$$

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