Atmospheric
Chemistry
and Physics
Discussions

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

D. Barahona

donifan.o.barahona@nasa.gov

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1   Response to 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. Specifically, the calculation of the nucleation rate is now the central theme of the theoretical derivation. Additional explanation has also been included contrasting the classical approach and the proposed theory. The derivation of the equation of state of vicinal water was reworked to make it clearer and correct errors/typos. Finally, the Section on kinetics has been reorganized introducing general concepts earlier in the text. 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

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

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

Response: The wrong expression for $\Delta\mu_{\text{S}}$ was written in the text. $\Delta\mu_{\text{S}}$ must actually be calculated at $a_{\text{w, eff}}$, hence Eq. (14) of should read:

$$\Delta\mu_{\text{S}} = -k_{\text{B}} T \ln\left(\frac{a_{\text{w, eff}}}{a_{\text{w, eq}}}\right), \tag{2}$$

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. (2) is shown at the end of this document (Eq. 10).

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.(18),

$$a_{\text{w}} = a_{\text{w, eff}} \left(\frac{a_{\text{w, eq}}}{a_{\text{w, eff}}}\right)^{\zeta} \exp(\Lambda_{\text{mix}}) \tag{3}$$

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and from Eq.(19)

$$a_{\text{w, eff}} = \left(\frac{a_{\text{w}}}{a_{\text{w, eq}}^{\zeta}}\right)^{\frac{1}{1-\zeta}} \exp\left(-\frac{\Lambda_{\text{mix}}}{\zeta - 1}\right). \tag{4}$$

Since $\Lambda_{\text{mix}} = 0$ for $\zeta = 1$, then Eq.(3) implies that $a_{\text{w}} = a_{\text{w, eq}}$ for $\zeta = 1$. Hence from Eq.(4) $a_{\text{w}} = a_{\text{w, eq}} = a_{\text{w, eff}} = 1$, indicating that $\zeta = 1$ corresponds to 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. Motivated by this I have re-worked the derivation correcting errors and making it more readable. Since the excess term plays a minor role, the correction only resulted in up to two orders of magnitude difference in J_{het}, but following essentially the same behavior. 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 locally 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

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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; $\frac{\partial^2 \mu_{vc}}{\partial \zeta^2} = 0$ thus limits the metastable region. The last condition, $\frac{\partial^3 \mu_{vc}}{\partial \zeta^3} = 0$, indicates that the metastable region reduces to a single point and that 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, $\zeta \approx 1 - \frac{\Delta a_{w,\,het}}{\Delta a_{w,\,hom}}$, hence $0 < \zeta < \sim$ 1 (the upper limit is somewhere around $.96$ due to mixing effects). This relationship is true only in the germ-forming regime where J_{het} is mainly dictated by thermodynamics. Kärcher and Lohmann (2003) suggested the approximation $J_{het} \approx J_{hom}[f(\Delta a_{w,\,het})]$. 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 that Knopf and Alpert (2013) also parameterized J_{het} as a function of $\Delta a_{w,\,het}$. However their expressions are material-specific and 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.

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

$$\mu_{vc} = (1 - \zeta)\hat{\mu}_{LL} + \zeta\hat{\mu}_{IL}, \tag{5}$$

where $\hat{\mu}_{LL}$ and $\hat{\mu}_{LL}$ 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 (5) 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,

$$\mu_{vc} = (1 - \zeta)\mu_{LL} + \zeta\mu_{IL} + \Delta G_{mix} \tag{6}$$

where $\Delta G_{mix} = (\hat{\mu}_{IL} - \mu_{IL})\zeta + (1 - \zeta)(\hat{\mu}_{LL} - \mu_{LL})$ is the Gibbs energy of mixing. For a mechanical mixture of pure LL and IL species, $\Delta G_{mix} = 0$, whereas for an ideal solution ΔG_{mix} is determined by the ideal entropy of mixing (Prausnitz et al., 1998). Reorganizing Eq. (6) we obtain,

$$\mu_{vc} = \mu_{LL} + \zeta\Delta\mu_{il} + \Delta G_{mix} \tag{7}$$

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

$$\mu_{IL} = \mu_{eq} + k_B T \ln(a_{IL}), \tag{8}$$

and

$$\mu_{\text{LL}} = \mu_{\text{eq}} + k_{\text{B}}T\ln\left(\frac{a_{\text{w, eff}}}{a_{\text{w, eq}}}\right), \tag{9}$$

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. Assuming that similarly to bulk ice the solute does not significantly partition to the IL phase, then $a_{\text{IL}} \approx 1$. With this, and combining Eqs.(8) and (9), and rearranging we obtain,

$$\Delta\mu_{\text{il}} = -k_{\text{B}}T\ln\left(\frac{a_{\text{w, eff}}}{a_{\text{w, eq}}}\right), \tag{10}$$

The central assumption behind Eq. (10) 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 free 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. 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 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),

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$$\Delta G_{\text{mix}} = \frac{k_{\text{B}}T}{N}\left[\zeta\ln(\zeta) + (1-\zeta)\ln(1-\zeta)\right] + A_w\zeta(1-\zeta) \tag{11}$$

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. (11) 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 $\Delta\mu_{\text{il}} \approx \Delta\mu_{\text{s}}$.

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,

$$\frac{\partial^2\Delta G_{\text{mix}}}{\partial\zeta^2} = 0 \,, \frac{\partial^3\Delta G_{\text{mix}}}{\partial\zeta^3} = 0. \tag{12}$$

Using Eq. (11) into Eq. (12) and solving for A_w gives for $T = T_c$,

$$A_w = \frac{2k_{\text{B}}T_c}{N}. \tag{13}$$

Physically, T_c represents the stability limit of the vicinal water, at which it spontaneously separates into IL and LL regions. Equation (13) 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. (10), (11), and (13), into Eq. (7) we obtain,

$$\mu_{\mathrm{vc}} = \mu_{\mathrm{LL}} - \zeta k_{\mathrm{B}} T \ln\left(\frac{a_{\mathrm{w,\,eff}}}{a_{\mathrm{w,\,eq}}}\right) + \frac{k_{\mathrm{B}} T}{N}\left[\zeta \ln(\zeta) + (1-\zeta)\ln(1-\zeta)\right] + \frac{2k_{\mathrm{B}} T_{\mathrm{c}}}{N}\zeta(1-\zeta). \tag{14}$$

Making,

$$\Lambda_{\mathrm{mix}} = \frac{1}{N}\left[\zeta \ln(\zeta) + (1-\zeta)\ln(1-\zeta)\right] + \frac{2}{N}\frac{T_{\mathrm{c}}}{T}\zeta(1-\zeta), \tag{15}$$

Equation (14) can be written in the form,

$$\mu_{\mathrm{vc}} = \mu_{\mathrm{LL}} - \zeta k_{\mathrm{B}} T \ln\left(\frac{a_{\mathrm{w,\,eff}}}{a_{\mathrm{w,\,eq}}}\right) + k_{\mathrm{B}} T \Lambda_{\mathrm{mix}} \tag{16}$$

Equation (16) 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. (16) 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. (16) this implies,

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$$\mu_{\mathrm{w}} = \mu_{\mathrm{LL}} - \zeta k_{\mathrm{B}} T \ln\left(\frac{a_{\mathrm{w,\,eff}}}{a_{\mathrm{w,\,eq}}}\right) + k_{\mathrm{B}} T \Lambda_{\mathrm{mix}}. \tag{17}$$

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. (8), Eq. (17) can be written in terms of the water activity in the form,

$$a_{\mathrm{w}} = a_{\mathrm{w,\,eff}}\left(\frac{a_{\mathrm{w,\,eq}}}{a_{\mathrm{w,\,eff}}}\right)^{\zeta} \exp(\Lambda_{\mathrm{mix}}). \tag{18}$$

From Eq. (18) $a_{\mathrm{w,\,eff}}$ can be readily obtained in the form,

$$a_{\mathrm{w,\,eff}} = \left(\frac{a_{\mathrm{w}}}{a_{\mathrm{w,\,eq}}^{\zeta}}\right)^{\frac{1}{1-\zeta}} \exp\left(-\frac{\Lambda_{\mathrm{mix}}}{\zeta - 1}\right). \tag{19}$$

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