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Discussions

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

**Anonymous Referee #3**

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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.

Major points :

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.

Indeed, most ACP readers will be interested in the derived nucleation rate for immersion nucleation. Thus, I would start the theoretical section with the general expression for the nucleation rate, i.e. the product of the concentration of critical clusters $c_g = C_0 \exp(-\Delta G/k_B T)$, corrected by the Zeldovich factor times the flux of water molecules towards those clusters $F_w$:

$J_{het} = Z c_g F_w$

Thermodynamic effects of the particle on vicinal water affect $c_g$ and $Z$ (through $\Delta G$, the nucleation barrier for critical germ size) while kinetic effects affect $F_w$ (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.

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 $J_{het}$ would be useful. I would suggest to add a dedicated section on that point in the discussion (and remove section 2.2).

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:

- 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 cluster), it should be positive: $g^E = +A_w\zeta(1-\zeta)$ with $A_w = 2k_BT_c/N$. 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), ...). In Eq. (17) $\Lambda_E$ 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).
- page 7, Eq. (17): I have: $a_w = (a_{w,eff})^{\frac{1}{1+\zeta}}(a_{w,eq})^{\frac{\zeta}{1+\zeta}}\exp(\Lambda_E\zeta\frac{1-\zeta}{1+\zeta})$ instead of the formula of the author. This formula is used in many instances, for example in Eqs. (19), (20), (21), (22), and (45)

**Specific comments:**

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)
2. p 4, Eq (1) differs from the common expression in Prupaccher and Klett, which also includes $N_c\Omega$, the number of water molecules in contact with the cluster
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
4. p 10, Eq (24): I am not convinced that with that definition, $\Delta\mu_i$ should be referred to as supersaturation
5. p 10, line 9: unit of $s$ should be $molec^{\frac{1}{3}}$ so that the units match in Eqs (23) and (25)
6. p 10, Eq 27: should be $n^{-\frac{4}{3}}$ rather than $n^{-\frac{1}{3}}$
7. p 11, line 2: specify here again the condition for mechanical equilibrium

8. p 12, Eq (22) & 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 $C_0 = a_0^{-1}$ where $a_0$ is the cross-sectional area of a water molecule. This should already be written line 25. The numerical value of $a_0$ (or a formula) should be mentioned.

   Furthermore, it is surprising that the author takes $C_0 = a_0^{-1}$. 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.

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:

   $$Z = \left[ -\frac{\frac{\partial^2 \Delta G}{\partial n^2}|_{n=n^*}}{2\pi k_B T} \right]^{\frac{1}{2}} = \left[ \frac{\Delta G_{het}}{3\pi k_B T n^* (n^* + 2)} \right]^{\frac{1}{2}} \tag{1}$$

   with $n^* = [n^*_{hom}]_{a_{w,eff}}$. The derivation should be briefly explained.

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)

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 $T_{f,eq}$ can be referred to as an equilibrium temperature. In the legend and ylabel of Fig. 4, please add the symbol $T_{f,eq}$.

12. p 21 l 22: "regular solution" -> mixture ?

13. 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 $a_0$ 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 "$molec$"

## References

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, The Journal of Chemical Physics, 138, 174 501, doi:10.1063/1.4802992, https://doi.org/10.1063/1.4802992, 2013.

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