

Interactive comment on “Thermodynamic derivation of the energy of activation for ice nucleation” by D. Barahona

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

Comment by the Reviewer: My second major remark refer to the designation of the new formulation for the activation energy as a “phenomenological model”. In my understanding, “phenomenological” means being based on observations. However, the author stresses that there is no empirism entering this expression (which I’m not too sure about, see below). Wikipedia gives the following definition: “A phenomenological model (sometimes referred to as a statistical model) is a mathematical expression that

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relates several different empirical observations of phenomena to each other, in a way which is consistent with fundamental theory, but is not directly derived from theory. In other words, a phenomenological model is not derived from first principles.” - I don’t think this is what describes the approach of the author, and the wording should be changed (or justified).

Response: The proposed model is phenomenological in the sense that it is derived from ascribing certain characteristics to the process of interface transfer (e.g., collective behavior, work dissipation, and a defined interface) as heuristics to reach a thermodynamic view of the ice germ growth. A true mechanistic description of the interface transfer process requires an molecular dynamics approach. The definition given by the reviewer is somehow too strict, and may stem from an older view where molecular dynamics simulations were not available and approximations to the behavior of microscopic systems were considered full mechanistic theories. To address the reviewer’s concern the model is referred simply as “theoretical” in the revisited work.

Comment by the Reviewer: Thirdly, the derived expression oddly is very similar to the Zobrist et al (2007) formulation (compare equations 14 and 18). When eq. 14 is evaluated at $a_w = a_{w,eq}$, the two expressions differ only by the factor $T=(T \dots 118K)$. This similarity is certainly no coincidence and should be discussed further.

Response: The two expressions are fundamentally different. Equation 14 is never evaluated at $a_w = a_{w,eq}$, since it implies equilibrium conditions for which nucleation is not possible. Secondly, the apparent similarity originates because the bulk diffusion coefficient is expressed by the same relation, that is the VFT equation. However in the case of expressions like the one derived by Zobrist et al. (2007) the relation between D_∞ and ΔG_{act} is hypothesized a priori while in this work it results from the explicit consideration of the thermodynamics of interface transfer. This has been addressed in the revisited work.

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Comment by the Reviewer: Furthermore, this means that the new expression contains the same empirical fit parameters (E , T_0) which are criticized in the Zobrist formulation.

Response:

The criticism raised on expressions like the one formulated by Zobrist et al (2007) refers to the a priori assumption that the activation energy for interface transfer must have the same form as that of the bulk, neglecting the dynamics of the interface, not on the usage of the diffusion coefficient. The parameters E and T_0 describe the bulk diffusion coefficient, a physical property of water. They are not degrees of freedom of CNT and are not found by matching nucleation rate measurements. Other physical properties like the equilibrium water activity, the water density and the enthalpy of fusion also have fitted parameters. It is not a claim of this work that besides the activation energy all other physical properties of water can also be obtained from the proposed model.

Comments by the Reviewer:

- page 18158, line 15: ‘the probability of such collective arrangement is given by $f(T, a_w)$.’ This is a fundamental point for the further derivations, but it is not well explained why this probability should be exactly the same as the factor in the diffusion coefficient (eq. 5).
- page 18160, line 6: Again, why is $f(T, a_w) = P(W)$

Response: The function $f(T, a_w)$ is introduced to distinguish between the bulk diffusion coefficient D_∞ and the diffusion coefficient across the interface, D . The latter must be taken as an “effective diffusivity”, since it parameterizes processes that are not necessarily diffusive in nature (e.g., molecular rearrangement). In the view proposed in this work the breaking of hydrogen bonds is a necessary but not sufficient condition for the incorporation of water molecules into the ice germ. Molecular rear-

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angement is required for interface transfer and requires surpassing an energy barrier. The molecules in the liquid fluctuate in different ways, some of which lead to spontaneous organization. The probability of a spontaneous process occurring in a given direction is determined by the work required for such fluctuation, W . Since interface transfer requires the spontaneous organization of water molecules into ice-like structures with probability described by $f(T, a_w)$, it follows that if W describes the work required for collective rearrangement, the probability of fluctuation $P(W)$ must be equal to $f(T, a_w)$. This explanation has been added to Section 2.1.

Comments by the Reviewer: page 18163, line 24ff: As discussed here, it was shown by Ickes et al (2015) that the combination of the Z07 activation energy and the Reinhardt and Doye (2013) surface tension gives the best agreement to observations of the freezing rate, including observations at $T < 200\text{K}$. So if this combination was used instead of Z07 together with the B14 surface tension, this would agree much better to observations than what is shown in Fig. 4. This figure displays an unfair comparison.

Response: The surface tension from B14 was used in all expressions to highlight differences due solely to the activation energy. The comparison is not unfair. Using the expression of Reinhardt and Doye (2013) leads to lower nucleation rates than when using the expression from B14. At 220 K and $a_w = 1$, Fig 17 of Ickes et. al 2015 gives J_{hom} around $10^{23} \text{ m}^{-3}\text{s}^{-1}$, whereas the value shown in Fig 4 is about $10^{27} \text{ m}^{-3}\text{s}^{-1}$ (after units conversion). The latter is closer to the experimental results. To address the reviewer’s concern J_{hom} calculated using the expression of Reinhardt and Doye (2013) has been added to Fig 4.

Comments by the Reviewer: Please add more details to the caption of Fig. 1 (e.g. what are the bright and dark blue spheres? what are states 1 and 2? Why is $G_{\text{ice},2}$ higher than $G_{\text{ice},1}$ and $G_{\text{ice},2}$?).

Response: Figure 1 represents an idealization of the process described in this work.

However I agree that the cartoon adds little to the discussion and may instead lead to confusion. It has been removed from the plot and Fig. 1 replaced with a simpler Figure.

Comments by the Reviewer: Why is the temperature dependence of the data shown in Fig. 4b very different from the predicted temperature dependence?

Response: This is already discussed in Section 3. The theoretical reasons are unclear. However another possibility may be a slight drift in a_w during the experimental measurements. The data shown in Fig. 4b was obtained with similar techniques in which the initial a_w is set but is not controlled during the experiment (in fact in both cases the initial a_w is reported, instead of a_w at the point of freezing). It is shown in Fig. 4b and discussed in Section 3 that a decrease in a_w of 0.02 during the experiments would introduce a spurious temperature dependency and be enough to explain the discrepancy between the theory and the measurements.

However I agree that the discrepancy is troubling. Additional experimental results from Larson and Swanson, (2006) for the homogeneous freezing of ammonium sulfate were added to the Figure. They show a stronger dependency on T than the data of Alpert et al. (2011), although still lower than the predicted by the model. However the uncertainty in the temperature in the Larson and Swanson, (2006) data is too large to establish a statistically significant difference. It is acknowledged that further research is required to elucidate this point.

Comments by the Reviewer:

- Please give units for the variables in Table 1.
- It should be mentioned that the B14 formulation of surface tension is also a fit to observations.
- page 18152, line 14: temperature → temperatures
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- page 18155, line 16: into → on?
- page 18164, line 10: insert 'of' before 'Jeffery and Austin'
- page 18179, Fig. 4: Please use a distinct line style and line color instead of the minuscule crosses for 'CNT, this work'.

Response: All technical comments have been addressed in the revisited work.

References

Larson, B. H. and Swanson, B. D.: Experimental investigation of the homogeneous freezing of aqueous ammonium sulfate droplets, *J. Phys. Chem. A*, 110, 1907–1916, 2006.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 15, 18151, 2015.