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Discussions

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 his/her assessment.

Comment by the Reviewer: The manuscript is well written throughout, except in the Activation energy section 2.1. The reviewer found this section confusing to follow and thus recommends a clearer discussion and mathematical development in the text with corresponding clarifications reflected in Figure 1. In particular, identifying and labeling the connection between the specific activation energy for interface transfer (Dmu), DG, and W.The free energies Figure: Please change energy units in Figure to kcal/mol or kJ/mol...

Response: Section 2.1 has been rewritten to clarify several points raised during this discussion. Figure 1 has been simplified to make it clearer, explicitly showing the relation between W and ΔG.

Comment by the Reviewer: ... discuss how difficult it is, from a fundamental point of view, to get the nucleation free energetics of these processes correct.

Response: This was discussed in Section 4. It is acknowledged that the specification of water properties at very low temperature is very difficult and in general all studies use some form of thermodynamic continuation to define $a_{w,eq}$ and Δh_f for $T < 235$ K. This point has been emphasized in the revisited paper.

Comment by the Reviewer: It would be nice to see the differences in the critical germ sizes predicted between the models as well as those deduced from experiment.

Response: The activation energy does not affect the critical germ size. The requested comparison is shown in Barahona (2014, Figure 5). The activation energy does affect the measured freezing temperature, which may translate into a different critical size estimated at the point of freezing. However this is highly dependent on the nucleation threshold chosen to calculate the freezing temperature and therefore may be misleading.

Comment by the Reviewer: Furthermore, the author can make a correspondence between the CNT interfacial free energy and the NNF formalism and plot the effective surface tension of both for comparison.

Response: This is shown in Figure 2 of Barahona (2014). The interfacial tension in NNF is not modified by the activation energy since it is obtained without fitting nucleation rates. Thus the requested figure would remain unchanged from B14.

Comment by the Reviewer: The author expresses the significance in the NNF com-

pared to CNT, in that the former if free from the bias induced by uncertainties in the parameterization of the interfacial free energy between water and ice. However, the NNF model has expanded the number of variables (i.e., degrees of freedom) compared to CNT, and hence it isn't too surprising that better agreement over a broad temperature range is found between prediction and experiment.

Response: The number of degrees of freedom is not increased. None of the parameters of the model presented is obtained by fitting nucleation rates and therefore are not degrees of freedom in the same sense as in CNT. Certainly the physical properties of water are not degrees of freedom either since they are determined independently. It was shown in B14 that the parameters Γ_w and s used in the definition of the interfacial energy must be restricted to narrow ranges to be physically valid. They are not found by fitting nucleation rates but instead from physical arguments. Varying them over a wider range than discussed in Section 3.5 of B14 would invalidate the theory.

Comment by the Reviewer:

The reviewer suggests the author consider a sensitivity analysis, similar to previous work by the author, of his new NNF model on the relevant variables. This will help to better constrain the parameters as well as determine which variables have the most profound influence on the homogeneous nucleation rate.

Response: The sensitivity analysis regarding the effect of uncertainty in the interfacial energy on J_{hom} was carried out in Barahona (2014). As shown in Figure 8 of B14 the uncertainty in J_{hom} from variation in Γ_w and s is about two orders off magnitude and decreases with decreasing T since the nucleation rate becomes more dependent on ΔG_{act} and less dependent on the interfacial energy (this is emphasized in the revisited paper). Regarding the uncertainty in the activation energy, it is mostly a function of $a_{w,eq}$ and n_t. It is acknowledged that $a_{w,eq}$ may be uncertain at low T. The approximation used in this work is supported by experimental results (e.g., Koop et al . (2000)). Regarding n_t it is estimated that the preexponential factor would increase by about two

orders of magnitude by a change in n_t from 16 to 15. However a plausible range of variability for n_t is hard to estimate since the characteristics of the transient state are not known. Essentially a value of n_t less than 16 would indicate that some of the rearrangement routes to form four-coordinated water are prohibited. More research is needed to elucidate this point. Another assumption that may impact the model is that of microscopic reversibility which becomes weaker at low T since water dynamics becomes slower and it cannot be always assumed that the water molecules are in equilibrium within the bulk liquid. Unfortunately giving a plausible range of variability is challenging since deviations from equilibrium are difficult to quantify, even with molecular dynamics methods. This analysis has been included in Section 3 of the revisited paper.

Comment by the Reviewer: As a minor issue, the data points represented in Figure 4 are difficult to discern. Perhaps some arrows might help?

Response: This has been corrected.

Comment by the Reviewer:

Finally, the author should provide some comments on the connection between the phenomenological thermodynamics in the new NNF and a more rigorous statistical mechanics formulation in terms of configurational partition functions of nucleating clusters from the liquid. This can aid in the identification of relevant reaction coordinates, interaction energies, fields, etc. so as to bridge the continuum and molecular scales.

Response:

Section 2.1 has been thoroughly expanded to give a better representation of the processes involved in interface transfer. However a rigorous non-equilibrium statistical mechanics formulation of the partition function is non trivial and still matter of research. Such approach would be addressed in future studies.