

ACPD Manuscript: "Thermodynamic derivation of the energy of activation for ice nucleation"

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Reviewer Comments

Summary/Overall Quality: Barahona extends his previous NNF thermodynamic homogeneous ice nucleation phenomenological model to include variations in the interfacial molecular transfer diffusion coefficient with water activity and temperature (considered as the energy required to break hydrogen bonds in the liquid) combined with the non-equilibrium work required for the collective transient arrangement during interfacial molecular transfer. Interestingly, these two aspects are one and the same in that the activation energy arises from breaking hydrogen bonds and it is this energy that is dissipated as liquid water molecules turns into ice molecules. This new phenomenology provides an improved prediction of homogeneous ice nucleation rates compared to the previous NNF model and experiment (Bartell2003, Manka2012, and Koop2000) over the temperature range of 180-240K at a water activity of unity.

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 (D_{mu}), DG , and W .

The free energies Figure: Please change energy units in Figure to kcal/mol or kJ/mol and discuss how difficult it is, from a fundamental point of view, to get the nucleation free energetics of these processes correct.

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

The author expresses the significance in the NNF compared to CNT, in that the former is 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. 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.

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

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.

I recommend publication once the above comments have been addressed and the text and figures modified accordingly.

Typos, etc.: N/A