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

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This work concerns some important aspects of modeling crystal nucleation in water within the framework of classical nucleation theory (CNT). The author proposes a new approach to the “activation energy” ΔG_{act} , important constituents of the expression for the rate of crystal nucleation in liquid water. The approach is certainly interesting, but it seems to rely on some assumptions whereof the applicability is either not clear or even questionable.

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[Interactive Discussion](#)

[Discussion Paper](#)

Comment 1:

The paper emphasizes a very important point for significantly improving the CNT-based crystal nucleation model. Until recently, CNT considered the formation and growth of an ice crystal to occur due to "...spontaneous density fluctuations within the liquid phase forming an initial stable ice germ, which then grows by incorporation of water molecules from an equilibrium cluster population..." (p.18154) via the diffusion of water molecules across the liquid-ice interface similar to the molecular diffusion in the bulk liquid. Besides pointing out (a more or less well established fact) that the liquid properties near solid nucleus may differ from bulk liquid properties. the author makes a very important statement that, in a more adequate phenomenological picture of crystal nucleation and growth, the formation and growth of an ice crystal "...requires the collective rearrangement of several water molecules.... This view does not imply that water is incorporated in clusters to the ice, but rather that the rearrangement of the molecules facilitates the incorporation of each molecule into the preexisting ice lattice... Such lattice is assumed to be the exposing surface of a metastable ice germ...."

Clearly, this is much more adequate qualitative picture of ice nucleation in liquid water. However, the new approach to evaluating ΔG_{act} , proposed by the author, is still based on some elements of the "older" CNT model. Namely, the author's approach apparently still considers the "collective rearrangement of several water molecules ... that ... facilitates" their "incorporation into the preexisting ice lattice ... " as occurring by the "...direct interface transfer" via diffusion of water molecules from the vicinal liquid to the ice crystal.

This still seems to be an over-simplification of the general picture of ice nucleation and growth. In a more realistic model the incorporation of water molecules into the ice lattice is likely to occur via both translational and orientational fluctuations in the immediate vicinity of the ice crystal. The formation of "frozen" hydrogen bonds is initially thermodynamically unfavorable, but it does occur due to collective "translational

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Interactive Discussion

Discussion Paper



and orientational" fluctuations of vicinal water molecules (just like in "vapor-to-liquid" nucleation the initial steps of the formation of "liquid" clusters are thermodynamically unfavorable but do occur due to fluctuations). Note, that the translational fluctuation may involve a water molecule moving not only in the liquid-to-lattice" direction, but also in the "lattice-to-liquid" direction.

Comment 2:

Author's approach to the derivation of a thermodynamic expression for ΔG_{act} (subsection 2.1) is largely based on the application of the macroscopic classical thermodynamics to microscopic sub-systems (consisting of a few molecules). First of all, this must be substantiated and all the assumptions must be explicitly stated. Secondly, the statements about the violation of the Second Law of the thermodynamics do not seem to be correct. The Second Law of Thermodynamics (as all thermodynamics) is strictly speaking applicable only to physical system in the thermodynamic limit (with the number of molecules $N \rightarrow \infty$ and volume $V \rightarrow \infty$ so that N/V remains finite). It does not apply to microscopic systems (a few molecules) and it does not forbid the decrease in the entropy in a non-isolated microscopic sub-system of a macroscopic system.

Comment 3:

In section 2, outlining the theoretical basis of the proposed model, it is assumed (as often done in CNT), that the ice crystal is formed away from the air-liquid interface so that it is not affected by surface tension effects. However, most of the experimental work on crystal nucleation in water is performed by observing the freezing of droplets.^{1–3}

Therefore, the conventional "semi-empirical" (page 18154) application of CNT to ice nucleation is based on empirical values of theoretical parameters (such as σ_{iw} and ΔG_{act}) extracted by fitting the experimental results for the crystal nucleation rate **in**

droplets with a CNT expression (1) for J_{hom} valid **only in the bulk**. Such empirical values of fitting parameters are therefore very likely to be inaccurate. Therefore, if they are used in the CNT expression (1) for J_{hom} under conditions, different from where they were obtained, the predictions can be expected to be in disagreement (probably "stark") with experimental data on the nucleation rate for these (new) conditions.

Typical sizes of experimental (as well as atmospherically relevant) droplets allow one to assume that the formation of a single crystal nucleus in a droplet immediately leads to the crystallization of the latter, i.e., the time of growth of a crystal nucleus to the size of the whole droplet is negligible compared to the time t_1 necessary for the first nucleation event in the droplet to occur.³ Consequently, $t_1 = 1/I$, where I is the per-particle (pp) nucleation rate, i.e., the total number of crystal nuclei appearing in the whole volume of the liquid droplet per unit time.

Most atmospheric models consider homogeneous crystal nucleation in droplets to be exclusively volume-based, with $I = J_{hom}V_1$, where V_1 is the volume of a single droplet. This is not correct when the crystallizing liquid is in a dispersed state, as in the case of freezing atmospheric droplets^{1,2} and many experiments.³.

As shown in ref.4, the total per-particle nucleation rate (which is determined in experiments via eq.(1)), must have the form $I = J_v^s V_1^s + J_{hom}(V_1 - V_1^s)$, where J_v^s is the number of crystal nuclei forming *homogeneously* in a surface-stimulated mode^{5–8} per unit time in unit volume of the subsurface nucleation layer whereof the total volume is V_1^s . As shown in ref.4, homogeneous crystal nucleation in water droplets of radii smaller than $R \approx 0.2 \mu\text{m}$ occurs predominantly in the surface-stimulated mode; the first term on the RHS of eq.(3) dominates if freezing occurs in droplets $R < 0.2 \mu\text{m}$. The volume-based mode prevails in droplets with radii greater than $R \approx 2 \mu\text{m}$. Both modes provide contributions of the same order of magnitude to the total per-particle rate of crystal nucleation in droplets with radii approximately from $0.2 \mu\text{m}$ to $2 \mu\text{m}$.

Therefore, while extracting σ^{iw} and ΔG_{act} by matching experimental crystal nucleation

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rates with the predictions of CNT, the CNT expression for the per particle nucleation rate must be taken in the form of eq.(3) rather than eq.(2). Likewise, it is eq.(3) that must be used for predicting crystal nucleation rates in droplets smaller than $2 \mu\text{m}$, not eq.(2).

Minor remark:

The goal of the author is to derive a thermodynamic expression for the activation energy ΔG_{act} in order to avoid considering it as an adjustable parameter in the CNT. However, the final equation (14) for ΔG_{act} contains parameters E and T_0 which are themselves adjustable parameters in the Vogel-Fulcher-Tammann equation, eq.(12). The question arises if the goal has been achieved to the full extent or not...

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