Atmospheric
Chemistry
and Physics
Discussions
Open Access

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

D. Barahona

donifan.o.barahona@nasa.gov

Received and published: 27 October 2015

I thank Dr. Djikaev for the comments on the manuscript. They are adressed in detail below.

Comment by the Reviewer:

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.

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 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.

Response: The picture suggested by the reviewer is consistent with the proposed model. There are some limitations in using the framework of classical nucleation theory. One of them is, as the reviewer states, that the flux of water molecules is parameterized in a diffusion-like manner. However in the proposed model not only the random jump of water molecules is accounted for, but also the probability that ice-like structures are formed during those jumps. Thus although parameterized in the form of a diffusion coefficient, the proposed model contains the essential elements of the physics behind the formation of the interface, namely the fluctuation character of the vicinal molecules and the formation of "frozen" hydrogen bonds. Section 2.1 has been rewritten to emphasize this.

Comment by the Reviewer: 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.

Response: The derivation of the activation energy is based on the fluctuation theorem

(FT) which is a result non-reversible statistical thermodynamics instead of "classical macroscopic thermodynamics" as the reviewer suggests. FT relates the macropcospic response of a thermodynamic system to its microscopic dynamics under the assumption that the latter is stochastic and Markovian. These are typically valid assumptions at conditions away from the glass transition temperature. A further assumption is that of microscopic reversibility, which requires that thermodynamic potentials can be locally defined within the liquid. This assumption was also used to write the work dissipated during interface transfer. This is guaranteed near equilibrium, however in non-equilibrium conditions only holds for systems starting at equilibrium. Thus the application of FT for interface transfer is valid only if each molecule can be considered in equilibrium with its local environment within the liquid, which is again valid away from the glass transition temperature. Finally, a heuristic approach was used to write an expression for the dissipated work, which basically involves counting the minimum number of different ways in which four-coordinated water can be built. This is a simple geometric argument (akin for example to bond-counting), and is based on the result of Adam and Gibbs (1965) who showed that the transition probability within liquids is determined by the size of the smallest cooperative region. To address the reviewer's concern section 2.1 has been rewritten putting additional emphasis on the model's approximations.

Comment by the Reviewer: 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 → ∞ and volume V → ∞ 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.

Response: The picture of an "apparent" violation of the second law was used as resource to describe the spontaneous organization of molecules into ice-like structures,

which in a macroscopic system would be impossible (what the reviewer refers to as "thermodynamically unfavorable"), but that are possible in small systems. As mentioned above it is possible to write thermodynamic potentials for microscopic systems near the equilibrium where microscopic reversibility holds. The statements have been modified to clarify these points.

Comment by the Reviewer: 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...

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... 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 ...

Response: A significant surface-to-volume ratio in small droplets does not guarantee a predominance of surface based nucleation. The reviewer has made several arguments in favor of a significant role of surface stimulated nucleation (SSN) in ice formation, however there are experimental results both supporting and challenging this view (Sigurbjörnsson and Signorell, 2008; Kay et al. 2003). SSN requires a germ growing in a particular orientation so that at least one its "facets" is aligned with the droplet-vapor interface. The reviewer has calculated the probability of such rare process and showed that SSN would still be thermodynamically favored over volume-based nucleation. However this result requires several assumptions that have not been shown unequivocally to hold. For example it is assumed that the exposing interface aligned with

the droplet-vapor interface has a well-defined interfacial tension with a value similar to that of the bulk. Also the flux of water molecules to the nascent germ in volume and surface based processes is assumed to be the same. However this is not guaranteed as one can imagine that the water molecules between the growing ice and the droplet-vapor interface would be subject to a confinement effect reducing their mobility. Finally, as it is shown in this work, at very low temperature the nucleation rate is increasingly less controlled by thermodynamics and more dependent on the preexponential factor (e.g., the activation energy), which would limit the effect of SSN on ice formation.

It is certainly out of the scope of this work to settle the debate on the role of SSN in ice formation. To address the reviewer's concern it has been emphasized in the revisited work that all expressions are applicable to cases where ice nucleation is predominantly volume-based, and that only experimental results where nucleation rates were interpreted as volume-based are used. It is however acknowledged in the revisited work that more research is needed on this topic.

Comment by the Reviewer: The goal of the author is to derive a thermodynamic expression for the activation energy ΔGact 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...

Response: It has, to its full extent. E and T_0 are not part of CNT, but define the bulk diffusion coefficient. They can be measured and determined independently of CNT. They are akin to constants used other correlations for physical properties like viscosity, heat of fusion, density and the like. E and To are not adjustable parameters; their values cannot be adjusted to match measured nucleation rates without losing their theoretical meaning. Moreover, E and To are related to the configuration entropy of water, and in principle also admit a thermodynamic derivation.

C8593

References

Kay, J., Tsemekhman, V., Larson, B., Baker, M., and Swanson, B.: Comment on evidence for surface-initiated homogeneous nucleation, Atm. Chem. Phys., 3, 1439–1443, 2003.
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.
Sigurbjörnsson, Ó. F. and Signorell, R.: Volume versus surface nucleation in freezing aerosols, Physical Review E, 77, 051 601, 2008.