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Interactive Comment

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

Anonymous Referee #2

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General comments

In this paper, D. Barahona provides a new formulation of the energy of activation for (homogeneous) ice nucleation. Different from previous expressions, the new formulation does not require fitting to homogeneous freezing rates. It is given as a sum over two contributions to the energy barrier: one from the breaking of hydrogen bonds in the liquid phase and one from molecular rearrangement. The resulting expression gives values in the order of magnitude o f previous formulations, and when applied in a CNT formulation for the homogeneous freezing rate, the latter agrees well observations down to very low temperatures.

The paper is interesting, but not easy to digest. I actually don't think it is a good fit for ACP, as the considerations are rather basic physics and physical chemistry than athmospheric physics. The paper emphasizes the advantages of the new model for temperatures down to 190K, but this is hardly of relevance for homogeneous freezing of water in the atmosphere. Of the listed references, only three cited papers have been published in ACP, and two of them are by the author himself. In my opinion this paper would have found a more suitable readership if it had been submitted e.g. to JPC or PCCP. If it remains in ACP, it should be revised such that it becomes more accessible for this audience, including experimentalists working on laboratory measurements of homogeneous freezing or modellers interested in the parameterization of these processes for models of the atmosphere.

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 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).

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 $T/(T - 118K)$. This similarity is certainly no coincidence and should be discussed further. Furthermore, this means that the new expression contains the same empirical fit parameters (E, T_0) which are criticized in the Zobrist formulation.

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Specific comments

- Please give units for the variables in Table 1.
- 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 $f(T, a_w) = P(W)$?
- 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 $T < 200K$. 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 figures displays an unfair comparison.
- It should be mentioned that the B14 formulation of surface tension is also a fit to observations.
- I disagree with the use of the word 'correlation' for all sorts of mathematical expressions and fits throughout the manuscript (e.g. page 18164, lines 2, 3 and 5).
- Please add more details to the caption of Fig. 1 (e.g. what are the bright and dark blue spheres? what are states 1 und 2? Why is $G_{ice,eq}$ higher than $G_{ice,1}$ and $G_{ice,2}$?).
- Why is the temperature dependence of the data shown in Fig. 4b very different from the predicted temperature dependence? This should be discussed.

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Technical corrections

- page 18152, line 14: temperature → temperatures
- 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’.

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

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