

Review of

## On the Thermodynamic and Dynamic Aspects of Immersion Ice Nucleation

by D. Barahona

### General comment:

In this manuscript the role of different ordered structures of water close and far from an immersed particle is investigated. A theory of immersion freezing based on these different states is derived. The theoretical investigations are compared to real measurements of heterogeneous nucleation rates in different experiments. Since ice nucleation in general, and especially heterogeneous nucleation is not well understood and the theoretical investigations are not convincing at the moment, a theory based on thermodynamics of water is a very interesting step for improving our knowledge of heterogeneous ice nucleation. Thus, in general this is a valid contribution for Atmospheric Chemistry and Physics.

However, before the manuscript can be accepted, some issues has to be clarified. Therefore I recommend major revisions of the manuscript. In the following I will explain my concerns in details:

### Major points

1. Representation of the theory:

The topic of ice nucleation is quite complicated and usually only classical nucleation theory or some additional topics are well known in the ice cloud community, whereas the more detailed thermodynamic basis is usually hidden in many discussions. In this study, the author has to present details for the development of the theory but also has to make sure that the reader can follow his line of arguments. It would be very helpful if the author would present a kind of roadmap at the very beginning to describe what he wants to derive finally and which steps will be necessary in order to do so. Otherwise the reader is really lost in details, which stem either from standard thermodynamic arguments or are of phenomenological type.

2. Derivation of equation (17)

I could not reproduce the central equation (17) in the form the author did, I ended with the expression

$$a_w = a_{w,eff} \left( \frac{a_{w,eq}}{a_{w,eff}} \right)^{\frac{\zeta}{1+\zeta}} \exp \left( \Lambda_E \zeta \frac{1-\zeta}{1+\zeta} \right) \quad (1)$$

This is crucial, since the equation is often used in the following derivation. For instance, I have several reservations about equation (19), since the limit  $\zeta \rightarrow 1$  is not well defined. The author has to check his derivation of equation (17) and, if necessary also the derivation of the subsequent theory. In section 2.3.3 the model is extended to the spinodal limit and the limit  $\zeta \rightarrow 1$  is investigated, which is unbounded in the current representation, but probably not for the derivation I have found. Thus, it is not clear to me if the discussion in this section still holds.

### Minor points:

1. Could you explain the sign of the excess energy  $g^E = -A_w \zeta (1 - \zeta)$ ? What is the thermodynamic reason for this choice?
2. What are the thermodynamic conditions for the derivation of the critical temperature, i.e. where do the conditions  $\frac{\partial^2 \mu_{vc}}{\partial \zeta^2} = 0$  and  $\frac{\partial^3 \mu_{vc}}{\partial \zeta^3} = 0$  come from? Please explain this shortly in the text.
3. In section 2.3.2 the water activity shift for heterogeneous nucleation is derived from the theory. Could you compare this results also numerically with the use of a constant shift in actual parameterisations and comment this? How large is  $\zeta$  for the usual parameterisations?
4. In figure 4 different curves of water activity are shown. As far as I understand, the colors (dark red to yellow) indicate different versions of the new theory ( $a_{w,hct}$ ). Thus, the label  $a_{w,hct}$  as red in the diagram is misleading.