

## ***Interactive comment on “Comment on evidence for surface-initiated homogenous nucleation” by J. E. Kay et al.***

**J. E. Kay et al.**

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We thank AR #1 for reading our comment and providing her/his constructive review. Below we respond to several specific issues AR #1 raised:

### **1) Attack frequencies**

We have amended the paragraph discussing attack frequencies to clarify questions from AR #1. It now reads:

*We distinguish between a two-dimensional surface nucleation and a near-surface formation of a three-dimensional embryo.*

*The former is a genuinely two-dimensional process associated with the formation of a monolayer-thick film at the surface of a droplet. For this scenario, calculation of the free-energy barrier is complicated. The pre-exponential factor, which is proportional to the*

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surface density of water molecules, also includes the rate of growth of the monolayer-thick critical embryo. At this point, it is impossible to predict nucleation rates for this truly two-dimensional process. Therefore, we do not discuss this possibility.

The latter, considered in the theoretical discussions of Tabazadeh et al. (2002a,b), is simply three-dimensional nucleation occurring in a near-surface shell. In general, the probability of embryo formation is proportional to the volume of the liquid where nucleation takes place. Thus, for the near-surface nucleation scenario, the pre-exponential factor is proportional to the volume of the shell. If  $R_c$  is a typical size of the critical embryo and  $R_d$  is the droplet radius, the ratio of the attack frequencies for near-surface and volume nucleation is  $R_c/R_d$ , or less than  $10^{-3}$  for a micron-size droplet. This small ratio indicates that the rate of a near-surface nucleation process is only comparable with that of classical volume nucleation if the energy of a critical embryo at the surface of a droplet is significantly lower than the energy of a similar embryo formed in the bulk. We are unaware of any convincing evidence for such a large free energy difference.

## 2) Direct evaluation of the imperfect wetting criterion

We agree that it is logically inconsistent to use measurements that are based on volume nucleation to discriminate between volume and surface nucleation. We thank AR #1 for pointing this out. We have amended the text as follows:

*Direct evaluation of the imperfect wetting criterion at  $-40^\circ\text{C}$  is inconclusive. In general, reported values for surficial energies are found by fitting observed nucleation rates to the classical expression for volume-based nucleation. If we ignore this logical inconsistency, direct evaluation using experimental values suggests the imperfect wetting criterion may be met, but the evidence is not compelling.*

## 3) Partial wetting and Elbaum

The text is confusing and we have attempted to make it clearer. We cite Elbaum and Schick (1991) because their work suggests that thermodynamic advantage that led to

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partial wetting in a vacuum at 0 °C (Elbaum et al., 1993) was probably very small.

#### 4) **Typographic errors and inconsistencies**

We have corrected the figures to reflect the difference between nucleation rates and freezing rates. We have made the subscripts for surficial energies consistent. We have fixed the noted spelling and typographic errors.

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Interactive comment on Atmos. Chem. Phys. Discuss., 3, 3361, 2003.

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