

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

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Received and published: 29 July 2003

Although we have discussed most of the issues raised in this commentary in 4 published papers (Tabazadeh et al., 2002a, b; Djikaev et al., 2002, 2003), I will try to briefly say a few words about thermodynamics of surface nucleation, which is incorrectly described in this commentary. More details on thermodynamics of surface-induced nucleation can be found in two theoretical papers that we have written on this subject (Djikaev et al., 2002, 2003), which were not cited or discussed in this commentary.

Comment on section 2.1: Please note that when the nucleus forms at the surface of the liquid one facet of the crystal replaces the preexisting liquid-vapor interface. This option is not available when the crystal nucleates in the bulk. The reason that the surface mode is thermodynamically favored is NOT related to the free energy of the

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final crystal state. What the authors are comparing here is the free energy of the crystal at the final state. They correctly point out that the free energy of the crystal in the final state must be similar for both modes of nucleation, but the final state is not what should be compared here. The free energy barrier to nucleation is the CHANGE between the final and initial states. What separates the two processes here is the large difference in the initial state of the system and NOT the final state. In fact what causes the nucleation to occur at the surface, at least from a thermodynamic point-of-view, is related to the fact that the work of formation for creation of a surface nucleus is less than that of the bulk nucleus. This occurs because an area, equivalent to a crystal facet, gets destroyed in the process of creating a surface nucleus. According to basic thermodynamics, creation of surfaces and/or interfaces requires work and destruction of surfaces and/or interfaces is a gain in free energy. Please see Djikaev et al. articles for more details.

Comment on section 2.2: Please note that condensation of water on a heterogeneous surface and nucleation of ice in supercooled water are NOT similar processes and CANNOT be compared in the simple manner described in this commentary. Also, we have not made a claim that critical point and wetting are related, as this commentary seems to imply. We simply stated what Cahn noted in his article. One also needs to be careful to state that since a liquid layer appears to be thick to a naked-eye, then the surface is fully wetted. Optical instruments are needed to measure the contact angle to make such a claim. I doubt that liquid water wets all surfaces that it condenses on. Regarding the Elbaum et al. study, one cannot just look at wetting of ice by one crystal facet. An ice crystal has many facets with different packing densities. While one facet may be fully wettable others may not. All that is needed for a crystal to form at the surface is just one facet that is not fully wettable. When the crystal is created (or nucleated) in supercooled water, the crystal will nucleate in such a way that the nonwettable facet will be placed against the air, while the wettable facets will immerse in the bulk. I again note that it is the difference in the free energy that drives nucleation (not the final state as the authors of this commentary claim), and to take this path the

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system will choose the path of lowest free energy change. Thus if one facet of the crystal, placed against the air, can provide such a path, then the nucleation will occur at the surface. Please see Djikaev et al. articles for more details.

Comment on Section 3: I believe the authors have missed the most important conclusion of our PNAS paper, that is, if the nucleation occurs in the volume, then the rates of freezing in oil and air ambients must be the same. Since bulk properties of water don't vary as one immerses the droplets in different ambient phases, the fact that the measured (and reported) nucleation rates varied by orders of magnitude, when the ambient phases were changed, was used in our paper to provide support for nucleation occurring at the ambient-water interface. Thus, I disagree with the authors stating that the oil experiments provide irrelevant information for atmospheric studies. The point we have made in the PNAS paper is that if the nucleation in air was volume-based, then the rate of nucleation in air and oil should be equivalent, and current laboratory data indicates that they are not. Please see our PNAS paper for more details.

Finally it seems that it is perhaps more proper to submit this commentary to PNAS because the bulk of this commentary criticizes a paper that we published in PNAS in 2002 on freezing of supercooled water droplets and not the commentary that I published in ACP in 2003 on freezing of nitric acid droplets. The focus of the ACP commentary was on possible effects of contamination on measured laboratory nucleation rates of nitric acid droplets, an issue that is not the focus of this commentary.

The word "homogeneous" is misspelled in the title and throughout the text.

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

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