Atmos. Chem. Phys. Discuss., 3, 3361–3372, 2003
www.atmos-chem-phys.org/acpd/3/3361/

Atmospheric Chemistry and Physics Discussions

Comment on evidence for surface-initiated homogenous nucleation

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Received: 11 March 2003 – Accepted: 12 June 2003 – Published: 1 July 2003

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Abstract

We investigate theoretical, laboratory, and atmospheric evidence for a recently proposed hypothesis: homogenous ice nucleation occurs at the surface, not in the volume, of supercooled water drops. Using existing thermodynamic arguments, laboratory experiments, and atmospheric data, we conclude that ice embryo formation at the surface cannot be confirmed or disregarded. Ice nucleation rates measured as a function of drop size in an air ambient could help distinguish between volume and surface nucleation rates.

1 Introduction

In a recent commentary, Tabazadeh (2003) suggests volume nucleation rates for large droplets cannot be extrapolated to predict nucleation rates for sub-micron stratospheric aerosols. Here, we comment on the basis for this argument, namely the referenced articles (Tabazadeh et al., 2002a,b) which provide "both experimental and theoretical support for the formation of the nucleus on the surface of the supercooled droplets" and lead to the conclusion that "freezing in particles most likely initiates at the surface layer".

The mechanisms and processes which control phase transitions from liquid water to ice affect many atmospheric processes including radiative transfer and chemical reaction rates. Homogenous nucleation rates have traditionally been based on nucleation initiated in the volume of supercooled water drops (Pruppacher and Klett, 1997). If homogeneous nucleation initiates at the surface, as proposed by Tabazadeh et al. (2002a,b), nucleation rates have different drop size and temperature dependences, and therefore, predict different distributions of ice in the atmosphere (Fig. 1).

Theoretical and thermodynamic justification, re-interpretation of laboratory data, and comparisons to atmospheric observations have been used to support the hypothesis that freezing initiates on the surface of supercooled water (Tabazadeh et al., 2002a) and concentrated aqueous nitric acid solution droplets (Tabazadeh et al., 2002b). These analyses bring forth new and interesting ideas on where freezing initiates in supercooled drops. However, we propose the importance of surface-initiated nucleation in the atmosphere remains unknown for three main reasons: 1) Evaluation of thermodynamic criteria for water-ice phase changes does not demonstrate a preference for surface nucleation in supercooled water. 2) Though laboratory data analysis suggest a role for surface nucleation, nucleation rate measurements to directly test this hypothesis in an air ambient are not available. 3) Surface (Tabazadeh et al., 2002a) and volume nucleation rates (Pruppacher, 1995) cannot be distinguished with atmospheric observations of deeply super-cooled water (Sassen and Dodd, 1988; Heymsfield and Miloshevich, 1993, 1995; Rosenfeld and Woodley, 2000; Field et al., 2001).

2 Theoretical and thermodynamic justification

2.1 Theoretical basis

There are two main differences between models of volume and surface-initiated nucleation rates: 1) the pre-exponential factor ("attack" frequency) 2) the free energy barrier for embryo formation. Though the meanings of these terms are clear for the volume nucleation rates, they are less clear for surface-initiated nucleation. The dimensionality of a surface nucleation process will strongly affect both the thermodynamics and kinetics of the freezing process. Therefore, 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. In this case, the attack frequency is proportional to the surface molecular density and the free energy barrier reflects the creation of a two-dimensional ice embryo at the surface. The latter, considered in the theoretical discussions of Tabazadeh et al. (2002a,b), is a variation of a three-dimensional nucleation occurring in a near-surface shell whose thickness is on the order of the size of a

critical embryo.

For a near-surface nucleation rate, the attack frequency is proportional to the volume of the near-surface shell. If R_c is a typical size of the critical embryo and R_d is the droplet radius), R_c/R_d is approximately 10^{-3} for a micron-size droplet. This small value indicates that the rate of a near-surface nucleation is comparable with a classical volume nucleation only 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.

2.2 The imperfect wetting criterion

One basic thermodynamic criterion for evaluating where nucleation initiates is the "wetting criterion". For surface nucleation to dominate, wetting should not occur or be imperfect. In other words, the surface tension of a solid-vapor interface (σ_{iv}) minus the surface tension of a replaced liquid-vapor interface (σ_{wv}) must be less than the surface tension of a solid-liquid interface (σ_{iw}), $\sigma_{iw} + \sigma_{wv} - \sigma_{iv} > 0$. Several well-known results have been brought in to support surface nucleation via the imperfect wetting criterion Tabazadeh et al. (2002a,b). However, we believe that this literature has been misrepresented.

First, Tabazadeh et al. (2002a,b) use Cahn's results (Cahn, 1977) to imply that perfect wetting below the critical point should not usually occur. In other words, Tabazadeh et al. (2002a,b) suggest imperfect wetting below the critical point (647 K for water) is expected and as a result, surface nucleation should be favored. In fact, Cahn argues that perfect wetting should be observed at a critical point and that a phase transition from perfect to imperfect wetting should take place at some temperature below the critical temperature. Cahn's argument does not imply that perfect wetting is improbable away from the critical point. Wetting transitions have nothing to do with critical points (Dietrich, 1988; de Gennes, 1985; Schick, 1990). Moreover, our everyday experience shows that saturated water vapor may condense on various substrates both in the form of droplets (no wetting) and as a thick liquid film (perfect wetting) at temperatures well below the critical temperature of 647 K.

Second, Tabazadeh et al. (2002a,b) use optical studies (Elbaum et al., 1993) to suggest that water only partially wets an ice surface at 0˚C. Indeed, Elbaum's experiments completed in a vacuum reveal water forming a film of limited thickness on an ice surface at 0˚C (i.e. partial wetting). However, the difference of surface energies (σ_{iw} + σ_{wv} - σ_{iv}) at the triple point in a vacuum was predicted to be three orders of magnitude smaller than any of the individual surface energies (Elbaum and Schick, 1991). More importantly, when these same experiments were completed in air, the water-ice interfaces exhibited complete wetting at 0˚C. In addition, as surface energies are strong functions of temperature, Elbaum et al. (1993)'s experiments completed at 0˚C cannot be used to evaluate the partial wetting criterion at −40˚C.

Direct evaluation of the imperfect wetting criterion at −40˚C is inconclusive. When experimental value extrapolations (and uncertainties) are evaluated at −40˚C (Pruppacher and Klett, 1997), the interface energy between ice and air (σ_{iv}) varies from 102–111 mJ m^{-2} depending on the crystallographic orientation, the surface tension of water (σ_{wv}) is approximately 87 mJ m^{-2}, and the interface energy between ice and water (σ_{iw}) varies experimentally from 15–25 mJ m^{-2}. Thus, the imperfect wetting criterion may be met, but the evidence is not compelling.

In addition, interfacial free energies only equal their asymptotic values (σ_{iw}, σ_{wv}, σ_{iv}) when all three phases have macroscopic dimensions. For near-surface nucleation, the ice embryo and the thickness of a liquid layer separating ice embryo facets from the vapor phase are microscopic. Therefore, surface tensions associated with a wet ice-vapor interface depend on the microscopic thickness of the liquid layer separating the embryo and the vapor phase. In this case, the free energy can only be computed by taking into account long-range van der Waals intermolecular forces. These forces are known, for example, to determine the interfacial energies in the case of surface melting (Dash et al., 1995). For a small embryo, even computing the free energy of a dry facet requires consideration of the long-range potential of surrounding water.

3 Re-analysis of laboratory data

Re-analysis of laboratory data by Tabazadeh et al. (2002a,b) suggests both surface and volume nucleation may occur in laboratory experiments. Though volume ice nucleation rates from nitric acid solutions differ by four orders of magnitude, these experimental data collapse to within one order of magnitude when expressed as a surface rate. In addition, two of the data sets, which show the thermodynamically perplexing result of decreasing nucleation rates at lower temperatures, have flatter nucleation rates when plotted as surface rates. Compiled nucleation rates also indicate that freezing can initiate on the surface or in the volume of supercooled water drops. Volume-initiated nucleation is indicated by similar nucleation rates/nucleation rate slopes despite a large range in droplet radii. When volume-initiated rates are replotted as surface-initiated rates, they exhibit more scatter (e.g. measurements made in heptane grease + sorbitan tristearate for drop sizes ranging from 3–300 µm, Taborek, 1985). On the other hand, surface-initiated nucleation is indicated by measurements that exhibit variability in nucleation rates/nucleation rate slopes with different droplet sizes and ambients. When one reported volume nucleation rate (measurements made in heptane grease + sorbitan trioleate for drop sizes ranging from 3–65 µm, Taborek, 1985) is plotted as a surface-initiated rate, it falls on a straighter line. Indeed, these interesting observations imply surface nucleation may be a freezing mechanism in laboratory experiments.

Unfortunately, many of the quoted laboratory measurements have been made with an oil/surfactant ambient (e.g. Taborek, 1985), not an air ambient. As plotted in Tabazadeh et al. (2002a), nucleation rate measurements in an air ambient (Demott and Rogers, 1990) for a single drop size (radius 5 µm) do not exhibit scatter in either the volume or the surface domain. Nucleation rate measurements made as a function of drop size in an air ambient could help determine if freezing rates are a function of available volume or surface area. These measurements could reveal the importance of surface nucleation in the atmosphere.

4 Atmospheric relevance

At present, the most atmospherically relevant comparison is between Pruppacher (1995) volume nucleation rates and Tabazadeh et al. (2002a) surface nucleation rates. In this comparison, the pre-exponential term of the nucleation rates represent differing molecular densities (volume nucleation proportional to drop volume vs. 2D surface nucleation proportional to drop surface area). In addition, both free energy terms are based on nucleation rate measurements made in air (Demott and Rogers, 1990). Above 0.2 µm, volume nucleation rates predict higher freezing temperatures than surface nucleation rates (Fig. 1).

According to our calculations, it is not possible to distinguish between surface and volume nucleation on the basis of atmospheric measurements (Table 1, Fig. 2). Both volume nucleation theory (Pruppacher, 1995) and surface nucleation rates (Tabazadeh et al., 2002a) predict higher freezing temperatures than atmospheric observations of 17 µm-sized water droplets at −37.5°C (Rosenfeld and Woodley, 2000). On the other hand, both volume nucleation theory (Pruppacher, 1995) and surface nucleation rates (Tabazadeh et al., 2002a) predict lower freezing temperatures than observations of 5 to 7 µm-sized droplets freezing at temperatures ranging from −35.6 to −36°C (Sassen and Dodd, 1988; Heymsfield and Miloshevich, 1993, 1995; Field et al., 2001). Deep supercooling (−40.7°C) of unactivated haze droplets have been suggested (Heymsfield and Miloshevich, 1993), but these observations are limited by the water detection capabilities of a Rosemount icing probe (detection threshold 0.002 g m^{-3}, Heymsfield and Sabin, 1989). Atmospheric dynamics (e.g. updraft velocities) and the challenges of constraining droplet composition, temperature and humidity, make comparisons of atmospheric observations with laboratory-parameterized nucleation rates difficult.

5 Conclusions

For the past 50 years, homogenous nucleation rates have been based on ice embryo formation in the volume of supercooled drops. However, the potential for ice embryo formation at the surface of atmospheric drops cannot be proven or eliminated using existing experimental, thermodynamic, or atmospheric data. We support Tabazadeh (2003)'s plea for more measurements of nucleation rates. In particular, nucleation rate measurements for a range of particle sizes in an air ambient would help clarify an active research question: where does freezing initiate in supercooled water droplets?

Acknowledgements. JEK thanks the University of Washington's Department of Earth and Space Sciences Peter Misch Fellowship for funding; and T. Koop, T. Peter, A. Gillespie, and D. Hegg for discussions that helped shape this comment.

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Table 1. Aircraft observations of freezing

Observation reference	Drop radius µm	Drops per cm^{-3} air	Temperature ˚C
1. Rosenfeld and Woodley (2000)	8.5	700	−37.5
2. Heymsfield and Miloshevich (1995)	3	70	−37
3. Heymsfield and Miloshevich (1993)	2.5	25	−35.7
4. Sassen and Dodd (1988)	2.5	100	−35.6

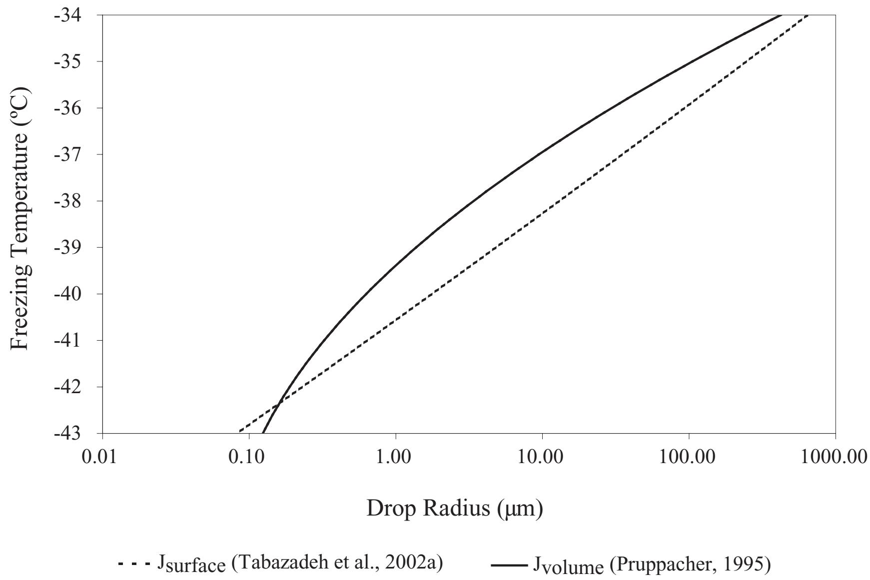

Fig. 1. Estimated freezing temperature (J=1 s^{-1}) as a function of drop radius for surface [Js (Tabazadeh et al., 2002a)] and volume [Jv (Pruppacher, 1995)] nucleation rates.

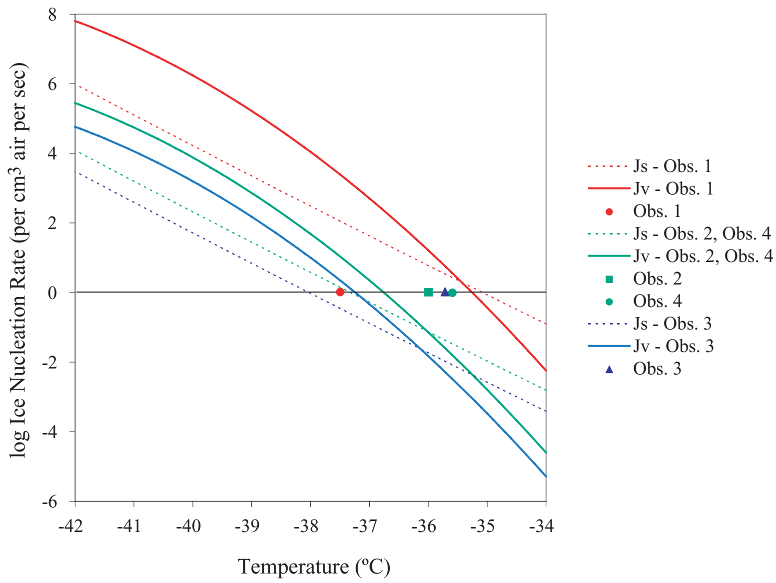

Fig. 2. Atmospheric observations (Table 1) and freezing temperature predictions (i.e. solid line at J=1 s^{-1}) based on parameterizations of surface [Js (Tabazadeh et al., 2002a)] and volume [Jv (Pruppacher, 1995)] nucleation rates. It is not possible to distinguish between surface and volume nucleation on the basis of these atmospheric measurements. We used a monodisperse size distribution in these calculations.