Homogeneous freezing of evaporating cloud droplets

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Abstract. Freezing of evaporating cloud droplets by homogeneous nucleation is an important mechanism for ice formation in the atmosphere, but it has been studied very little. Extension of the standard theory of homogeneous freezing to evaporating conditions results in an analytical expression for the freezing probability. A dimensionless freezing number $F_h$ characterizes the process and is found to be proportional to the fifth power of the initial drop radius. For any finite value of $F_h$, the derived expression predicts that only a fraction of any uniform drop population will freeze, regardless of the time available. New laboratory measurements of individual droplets levitated electro dynamically confirm the essential features of the expression and yield nucleation rates that are consistent with those determined by others.

1. Introduction

Homogeneous freezing nucleation is an important mechanism by which ice is produced in the atmosphere, particularly in the upper troposphere and lower stratosphere. For example, the altitude, size, lifetime, and radiative properties of cirrus clouds are thought to be highly sensitive to freezing rates [Sassen and Dodd, 1988; Heymsfield and Miloshevich, 1993; Jensen and Toon, 1994]. Other phenomena related to homogeneous freezing are the formation of polar stratospheric clouds and their relevance to the problem of stratospheric ozone depletion [Jensen et al., 1991; Tabazadeh et al., 1997], as well as the formation of ice fogs commonly found in the arctic [Benson, 1970]. Although McDonald [1953] brought homogeneous freezing to the forefront of cloud physics research well over 40 years ago, this topic is still an area of active scientific investigation. During the last decade, in fact, there has been a resurgence of interest, driven partially by new measurement techniques [Sassen and Dodd, 1988; DeMott and Rogers, 1990; Huang and Bartell, 1995; Krämer et al., 1996] and new theoretical developments [Pruppacher, 1995; Jeffery and Austin, 1997]. Despite the wide variety of techniques used in the study of homogeneous freezing, relatively few consider the freezing of evaporating water droplets. Two exceptions are the studies of Kuhns and Mason [1968] and Krämer et al. [1996]. In these studies simple approximations were used to account for droplet evaporation. Here, we present an expression derived from the standard theory of homogeneous nucleation that accounts for the evaporation of cloud droplets. We also present new laboratory measurements that confirm the expression and yield an independent measure of the homogeneous freezing rate.

2. Freezing Probability for Evaporating Droplets

Atmospheric cloud droplets do not freeze at 0 °C, the melting point of pure ice, because the formation of an ice-liquid interface is energetically expensive. Even though bulk ice is more stable than bulk liquid water at temperatures below the melting point, a small ice embryo has a large surface-to-volume ratio and, therefore, its surface energy dominates its total free energy. Beyond some critical radius, the total free energy of an ice embryo decreases with increasing radius, thus allowing for further growth. The homogeneous freezing rate, $J_{fs} \left[ m^{-3}s^{-1} \right]$, is the product of the number of critical embryos and the rate at which additional molecules are incorporated into an existing critical embryo. For a droplet of volume $V$, the probability of freezing is obtained by integrating the product of $J_{fs}$ and $V$ over time. The resulting expression for the freezing probability $P(t)$ is [Hobbs, 1974, p. 464]

$$\ln (1 - P) = - \int_{0}^{t} V(t') J_{fs}(T) \, dt',$$  \hspace{1cm} (1)

where we have emphasized the time dependence of volume and the temperature dependence of the nucleation rate.

Because convective clouds contain regions of active mixing with relatively cold, dry environmental air, we expect that at any given time there are large numbers of evaporating cloud droplets in a cloud. For the specific case of evaporating water droplets, we make several assumptions that allow for an analytical solution to Eq. 1. This solution may be applied to both real clouds and laboratory experiments in which water droplets experience subsaturated environments.

For droplets sufficiently large that the continuum theories of heat and mass transfer are valid, evaporating droplets have a constant temperature (the wetbulb temperature), in which case $J_{fs}(T)$ in Eq. 1 is constant. The integration time in Eq. 1 begins at zero, which is taken to be the time at which the droplet is suddenly cooled to a temperature low enough that $J_{fs}(T)$ is not infinitesimally small. To solve for the volume of an evaporating water droplet as a function of time requires the simultaneous solution of the equations for water vapor diffusion away from the surface of the droplet and heat transfer into the droplet. The two equations are coupled by the (Clusius-Clapeyron) equation for the equilibrium vapor pressure of liquid water as a function of temperature. In essence, as a droplet cools due to evaporation the equilibrium vapor pressure of the droplet is reduced, thereby reducing the rate of evaporation. When thermal diffusion inside of the droplet can be ignored and the droplet temperature is assumed to be close to that of the environment, an approximation for the rate of change...
of the droplet radius is \( \frac{dr}{dt} = \frac{\xi}{r} \) [Rogers and Yau, 1989, chap. 7]. If environmental variables such as temperature, pressure, and water vapor pressure are assumed to be constant, the growth parameter \( \xi \) is constant. Here we have ignored ventilation effects, which are negligible for droplet sizes less than about 100 \( \mu \)m [Pruppacher and Klett, 1997, p. 541]. Integrating this equation yields a parabolic droplet growth and evaporation law, which may be written in terms of volume for substitution into Eq. 1.

Two time scales naturally arise in this problem: an evaporation time scale, \( \tau_{\text{evap}} \equiv -\tau^2/2\xi \), where \( \tau \) is the initial droplet radius, and a droplet freezing time scale, \( \tau_{\text{freeze}} \equiv (J_s V_0)^{-1} \), where \( V_0 \) is the initial droplet volume. Using these time scales and the droplet evaporation law allows Eq. 1 to be integrated. The resulting expression for the droplet freezing probability is

\[
\ln(1 - P) = \frac{2}{5} \frac{\tau_{\text{evap}}}{\tau_{\text{freeze}}} \left[ \left(1 - \frac{t}{\tau_{\text{evap}}} \right)^{5/2} - 1 \right].
\]

(2)

For \( t \ll \tau_{\text{evap}} \) we may expand Eq. 2 as a binomial series and retain first-order terms, leaving \( \ln(1 - P) \approx -t/\tau_{\text{evap}} \), or \( P \approx 1 - \exp\left( -J_s V_0 t \right) \), which is the standard result derived for constant-volume droplets [Pruppacher and Klett, 1997, p. 211].

Equation 2 may be generalized by defining a dimensionless time, \( \tilde{t} \equiv t/\tau_{\text{evap}} \), and a homogeneous freezing number, \( F_h \equiv \tau_{\text{evap}}/\tau_{\text{freeze}} \). We note that \( F_h \) has a strong dependence on initial droplet size, namely \( F_h \propto r_0^5 \). When the freezing number is much greater than one (\( F_h >> 1 \)) a freezing event is highly probable, whereas when the freezing number is much less than one (\( F_h << 1 \)), a freezing event will not occur by the time the droplet has evaporated. The behavior of freezing probability is shown in Fig. 1, a plot of \( P \) versus \( \tilde{t} \) for \( F_h = 0.1, 1, \) and 10. Within the droplet evaporation time, droplets with \( F_h = 0.1 \) have essentially no chance of freezing, while droplets with \( F_h = 10 \) are almost assured of freezing. Qualitatively, droplets with \( F_h \approx 1 \) tend to evaporate, thereby reducing the number of freezing events expected per unit time, \( J_s V_0 \), before any freezing is able to occur. The result is that if many droplets with \( F_h \approx 1 \) are allowed to evaporate, roughly 30% of them will freeze.

### 3. Laboratory Measurements of Evaporation Freezing

We conducted a laboratory investigation of the homogeneous freezing of evaporating water droplets at low temperatures (\( \sim -35^\circ \)C). The experiment consisted of injecting individual water droplets into a known, subsaturated environment and observing the initial size and the time of freezing. When repeated for a large number of droplets, the measurements may be compared to Eq. 2. In addition, by comparing measurements and theory we are able to determine the homogeneous freezing rate for the specific temperature and pressure corresponding to the experiment.

The data presented here were collected with a laboratory system specifically designed for studying individual cloud particles under upper-tropospheric conditions [Shaw, 1998]. The system consists of an electrodynamic levitation cell for suspending individual particles, housed within an environmental control chamber where variables such as temperature, pressure, and relative humidity are controlled and monitored. Data on the size and phase of trapped particles are obtained from light-scattering measurements. For example, the radius of a liquid droplet is obtained by comparing measured scattered light with Mie scattering theory [Bohren and Huffman, 1983, chaps. 4 & 13]. The transition of a liquid droplet to the solid phase is easily identified by an abrupt change from regular interference fringes to a distorted, irregular pattern. The two key variables measured are the radius as a function of time and the elapsed time before a freezing event occurs or for complete evaporation.

In order to validate the theory of evaporation freezing and to measure the homogeneous freezing rate, \( J_{\text{obs}} \), we injected...
Figure 3. Probability of freezing (or fraction of droplets frozen) as a function of droplet radius. Laboratory data are shown as diamonds with only one error bar shown to reduce clutter. The three lines are from Eq. 2; the thick solid line corresponds to $J_{ts} = 8 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$, the top thin line to $J_1 = 1.2 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$, and the bottom thin line to $J_{ts} = 4 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$.

The freezing data collected in our system confirm the description of the freezing of evaporating cloud droplets given in Sec. 2. For example, Fig. 2 shows an example where about 60% of the number of droplets launched actually froze. The data are fitted using Eq. 2, as shown by the thick line, with $J_{ts}$ being the only free parameter. Of the other variables, time is measured directly, and radius is measured using Mie scattering theory, and the evaporation constant $\xi$ is evaluated from the time and radius measurements. Specifically, if the square of the radius is plotted as a function of time, the droplet evaporation law predicts a straight line with slope $2\xi$. The thin line shown in Fig. 2 is based on the assumption of constant volume. Chi squared tests confirm that, while the disagreement between the data and the constant-volume curve is significant, the evaporation-freezing curve is a satisfactory description of the data.

Our droplet-launching technique produces drops of radius ranging from roughly 10 to 50 $\mu \text{m}$. The data are displayed on a single curve (rather than as a family of curves as in Fig. 1) by dividing the data into radius bins and plotting the fraction of droplets that froze within some specified time interval as a function of initial radius. Figure 3 shows freezing data at $-35.3 \pm 0.2 ^\circ \text{C}$ and three curves from Eq. 2, with a time interval of 50 s. The homogeneous freezing rate determined by these measurements ($J_{ts} = 8 \times 10^5 \pm 4 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$) agrees with measurements made at $-35 ^\circ \text{C}$ using independent techniques [Pruppacher, 1995, fig. 3], although there is considerable scatter in the rates reported in the literature.

4. Conclusions

The expression for freezing probability of evaporating water droplets has been shown to be useful for analyzing laboratory data. It may be applied to the atmosphere as well, as long as the approximations made in the derivation are not violated. When a population of cloud droplets begins to evaporate, there is a freezing number associated with each droplet, which allows for an estimate of the freezing probability of each droplet. Of course, in the atmosphere it is unlikely that droplets will come into contact with completely dry air as in the laboratory, and cloud droplets will not be pure water but will contain other chemical species. These issues must be considered if detailed information on droplet freezing rates is required.

We have presented an extension of the standard theory of homogeneous nucleation for the condition of evaporating cloud droplets. Approximations that often are valid in the atmosphere and laboratory allow for an analytical expression for the probability of freezing. The derived expression depends on a dimensionless freezing number which is proportional to the fifth power of the initial droplet radius. The expression also predicts that only a fraction of a population of cloud droplets will freeze before the droplets completely evaporate. Laboratory measurements of freezing rates for evaporating cloud droplets have been compared to the standard, constant-volume equation for droplet freezing probability as well as the equation derived here for evaporating droplets. The data support the conclusions that under certain conditions only a fraction of droplets will freeze before evaporating and that the freezing probability is strongly size dependent. When compared to the expression for evaporation freezing, the measurements yield nucleation rates that are consistent with previous measurements.

A focus of future studies will be to obtain larger data sets to improve statistics and reduce error bars. In addition, future work will concentrate on the applicability of these studies to heterogeneous nucleation and on the possible effects of chemical species on homogeneous freezing rates. Finally, we note that no enhancement in the nucleation rate due to kinetically-induced droplet cooling [Cooper, 1995] was observed in these experiments. Similar measurements at lower pressures are more likely to isolate kinetic effects [Shaw and Lamb, 1998] and results from such experiments will be published in a future article.

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