# Heterogeneous Surface Crystallization Observed in Undercooled Water

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We report laboratory observations of higher freezing temperatures when an ice-forming nucleus is near the surface of an undercooled water drop than when the nucleus is immersed in the drop. The nucleation rate at the water surface is a factor of $10^{10}$ greater than in bulk water, thereby complementing and providing evidence for homogeneous surface crystallization, which has been hypothesized recently. Interpretation of the data via classical nucleation theory shows that the free energy of formation of a critical ice germ is decreased by a factor of approximately 2 when the substrate is near the air−water interface. Furthermore, the analysis suggests that the jump frequency of molecules from the liquid to the solid may be greatly enhanced at the interface.

## Introduction

Early in the 18th century Daniel Gabriel Fahrenheit demonstrated that liquid water can be undercooled, that is, remain unfrozen even below the melting temperature of ice. Nearly three centuries after Fahrenheit's pioneering studies, the nature of undercooled water and its transformation to ice remains the subject of intensive research.[1−7] Yet undercooling of water is more than a curiosity; for example, it is now known that much of the water in atmospheric clouds is undercooled and understanding how ice forms in these clouds is a major challenge in the atmospheric sciences with implications for precipitation formation and global radiative transfer.[2,6,8,9]

Nucleation of ice from liquid water is a notoriously difficult topic, and the presence of a foreign substrate, or ice-forming nucleus, as occurs in heterogeneous nucleation, adds greater complexity to the problem.[4] For example, it is has been observed that the same ice-forming nucleus tends to trigger freezing of an undercooled water droplet at a higher temperature in contact mode (dry particle contacting water drop) than in immersion mode (particle immersed in water drop).[6,9] The reason for this enhancement is unknown, but it provides a hint that the water surface could be of special interest in ice nucleation. In fact, it has been recently suggested that homogeneous ice nucleation is thermodynamically more favorable when occurring at the liquid surface.[3,7] The phenomenon may be quite general, as nucleation has been observed to occur preferentially at the surface of liquid clusters in molecular dynamics studies of several liquids.[10,11] Here we present experimental evidence that ice nucleation rates are enhanced near the air−water interface and therefore support the surface crystallization hypothesis.[3,7] Furthermore, the observations suggest that contact nucleation is simply a manifestation of the enhanced surface nucleation rate.[12]

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## Experimental Approach

The observed statistical nature of the nucleation process provides insight into the physical mechanisms responsible for ice formation. Specifically, in an experiment, we observe the number of frozen drops $N_f$ at a given time. Based on the assumption that freezing events are random and uncorrelated for a given nucleation rate, we can consider the random number of freezing events to be given by the inhomogeneous Poisson process:[5,13]

$$p(N) = \frac{\left(\int_0^t J \, dt\right)^N \exp\left(-\int_0^t J \, dt\right)}{N!} \qquad (1)$$

Then the number of "surviving" drops after time $t$ is $p(N = 0) = 1 - N_f/N_0$, such that via ergodicity the probability of freezing is

$$P \equiv \frac{N_f}{N_0} = 1 - \exp\left(-\int_0^t J \, dt\right) \qquad (2)$$

where $J$ is the total nucleation rate for the system (number of nucleation events per unit time) and $N_0$ is the number of drops in the ensemble. Using this ideal model of perfect randomness as motivation, we have designed an experiment to observe large numbers of freezing events for a single ice-forming nucleus. By avoiding variations in nucleus composition, size, morphology, etc., the resulting data approximate a statistical ensemble, the random variable being freezing temperature.[14] The observed probability of freezing is compared to the phenomenological Poisson process model with the temperature dependence taken from classical nucleation theory.

The experimental approach is in the spirit of several previous studies of the statistics of ice nucleation.[15−18] In our experiments, a single drop ($\sim$30 $\mu$L) of ultrapure water (filtered, distilled, deionized, and UV irradiated) is placed directly over a platinum resistance thermometer (PRT). We first carried out experiments with the drop surrounded by naphthenic petroleum oil ("Gunk"
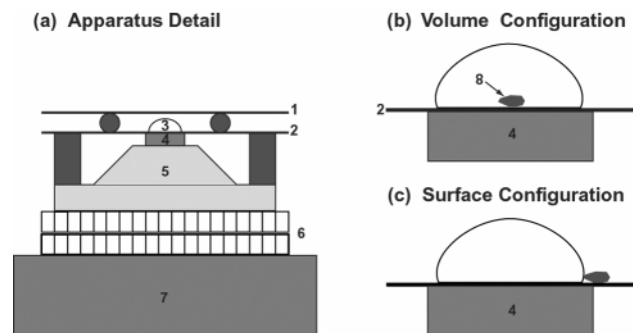
**Figure 1.** Apparatus used in experiments carried out in the air medium; (a) Detail of the sample stage. The water drop [3] is positioned on a silanized microscope coverslip [2] that covers the PRT [4] (width ~4 mm), which in turn contacts an isothermal copper stage [5]. The drop is covered [1] to minimize evaporation. Temperature is controlled by a thermoelectric (Peltier) cooler/heater arrangement [6] mounted on a liquid-cooled heat sink at the base [7]. The sample stage is housed in an insulated chamber purged with filtered dry air. A binocular microscope equipped with digital camera is used for drop preparation and observing freezing events; (b) Schematic showing the ice-forming nucleus [8] fully immersed within the drop volume. When the particle is fully immersed, gravity causes it to settle to the base of the drop. Visual observations of the particle moving around inside the drop (in response to slight vibrations from the cooling unit) suggest that it remains fully within the interior of the drop over the course of the experiments, without ever contacting the substrate; (c) Schematic showing the ice-forming nucleus positioned at the surface of the drop.

Power Steering Fluid M2713) and later developed the apparatus to run the experiment in air (filtered air with frost point less than 208 K). In both approaches, we used silicate-glass-rich trachyandesitic volcanic ash particles as ice-forming nuclei with diameter between ~100–300 $\mu$m. Figure 1 shows a schematic of the stage developed for the experiments carried out in air. Using the very fine point of a hypodermic syringe needle and a steady hand (and aided by a binocular microscope), an ice-forming nucleus of interest is placed either at the surface of the drop, or within it; drop surface tension tends to hold the ice-forming nucleus in either one of these locations. In the case of the oil apparatus, this is done prior to immersing the drop in the oil medium. In the case of the air apparatus, the position of the ice-forming nucleus can be manipulated at any time after the drop is positioned over the PRT. A number of cooling and heating cycles are then initiated, in which the liquid drop is cooled until it freezes, then heated until it fully melts. During the cooling stage, the temperature is decreased linearly with time (with active control to within 0.1 K) and when the water drop freezes, we detect the enthalpy of freezing directly using the PRT. The system is fully automated so that we can measure hundreds of freezing events on a single ice-forming nucleus.

## Observations and Analysis

We have made several simple tests to confirm the robustness of the experimental technique, and the results agree with expectations from the classical nucleation theory. A remarkable, unexpected observation, however, is the tendency for the freezing temperature of an ice-forming nucleus to vary between two "modes". When the ice-forming nucleus is immersed in the liquid drop, the mean freezing temperature is lower than when the ice-forming nucleus is at the drop surface. Examples of freezing temperatures and the resulting probability distributions for an ice-forming nucleus at the surface (red and green curves) and then immersed in the bulk (magenta curve) are shown in Figures 2 and 3. The temperature difference between the two modes is typically 4–5 K, which is much larger than
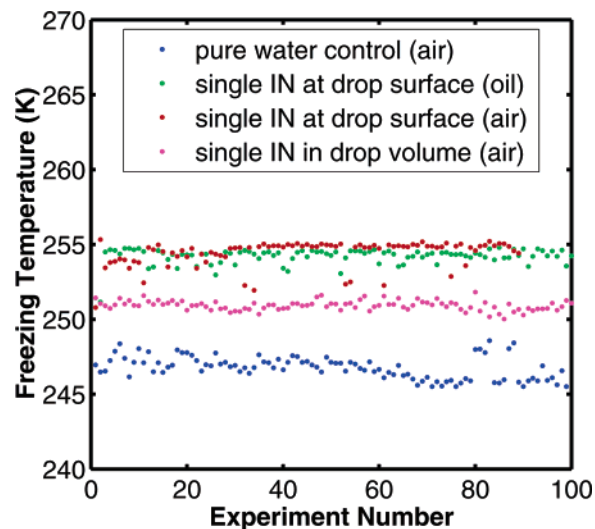


**Figure 2.** Random freezing temperatures observed for one ice-forming nucleus in three different physical conditions. When the ice-forming nucleus is immersed in the undercooled water droplet (magenta), the mean freezing temperature is approximately 251 K. When the ice-forming nucleus is placed at the surface of the droplet the mean freezing temperature is higher, both when the undercooled droplet is surrounded by oil (green) and by air (red). A control experiment with a pure water droplet (blue) confirms that nucleation by the substrate is negligible when an ice-forming nucleus is present. Note that sudden jumps in nucleation temperature in the control experiment (e.g., at numbers 80–85) likely are due to variations in substrate properties encountered as the droplet migrates slightly throughout the set of experiments.
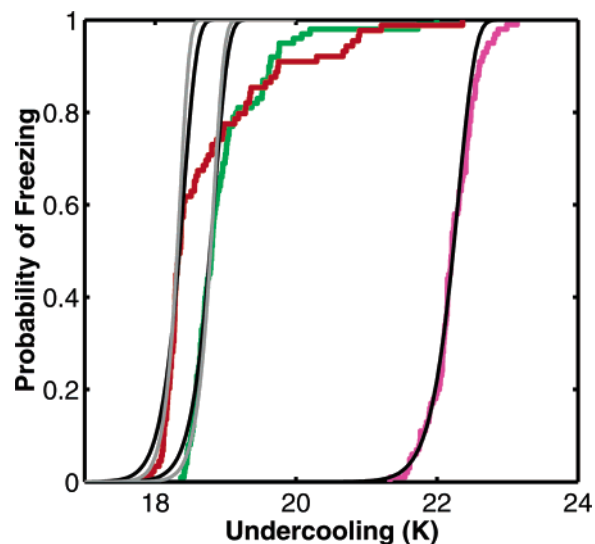


**Figure 3.** Probability distributions for the ice-forming nucleus in three different physical conditions: colors as in Figure 2. The thin black curves correspond to the classical nucleation theory fit using the thermodynamic wetting parameter. The thin gray curves correspond to the classical nucleation theory allowing for changes in the kinetic growth rate in addition to the thermodynamics. See text for details and interpretation. Note also that the long tails in the red and green curves at large undercoolings are due to occasional movement of the ice-forming nucleus away from the droplet surface.

the temperature variance of either mode alone. The result is surprisingly robust and is observed for all particle compositions we have investigated regardless of whether the water drop is surrounded by oil, as shown by the green curve, or air, as shown by the red curve. Furthermore, the result is largely independent of the history of the ice-forming nucleus: whether it is placed at the drop surface to begin with or is moved there after being immersed in the bulk is immaterial. The exact location relative

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to the surface (e.g., mostly inside versus mostly outside the drop) is not of primary importance, but there is some evidence that the fraction of the ice-forming nucleus surface in contact with the water surface influences the freezing temperature. This is observed in the sporadic low temperatures in the red and green points in Figure 2 and the corresponding long tails of the two surface-mode probability distributions in Figure 3: the particle position can change slightly between freezing events, reflected by lower freezing temperatures when it moves away from the surface. For this reason, we expect that these large-undercooling tails are not representative of a statistical ensemble of the surface nucleation mode but rather are outliers due to statistical nonstationarity.

If we assume that experimental conditions are identical between measurements, the measured probability distributions can be interpreted in the context of the inhomogeneous Poisson model with the temperature dependence given by classical nucleation theory. This theory specifies a nucleation rate $J(T)$ that depends on the thermodynamics of cluster formation and the kinetics of cluster growth: $J(T) = K(T) \exp(-\Delta G^*/k_B T)$. The thermodynamics of the process are embodied in the Boltzmann factor for formation of a critical cluster, where $\Delta G^* = 16\pi\sigma^3 f/3\Delta\mathscr{G}^2$ is the free energy of formation for a critical cluster, $\sigma$ is the water−ice interfacial free energy, and $\Delta\mathscr{G}$ is the change in free energy per unit volume resulting from a water−ice phase change. The factor $f$ accounts for the catalytic role of an ice-forming nucleus, and presumably depends on water, ice, and substrate interfacial free energies. The kinetics of nucleation are quantified by a rate constant $K(T)$ related to the frequency at which water molecules can be added to an ice germ.

More specifically, the kinetic rate constant is $K(T) = n_w k^+ A$, where $n_w$ is the surface density of water molecules in the undercooled water, $k^+$ is the rate at which water molecules are added to a critical cluster, and $A$ is the surface area of the ice-forming nucleus. The rate can be expressed as $k^+ = (k_B T/h) \exp(-\Delta g/k_B T)$ using the absolute reaction rate theory, with $\Delta g$ being the activation energy for self-diffusion.[19] Note that the Zeldovich factor and two other factors have a product of the order of 1 and therefore are ignored here.[9] An approximate form for the Gibbs free energy is obtained by integrating the Clausius−Clapeyron equation under the assumption that the enthalpies of vaporization and sublimation are constant,[20,21] such that $\Delta\mathscr{G} = -n_i k_B T \ln(p_w/p_i) \approx n_i l_f \Delta T/T_0$, where $p_w$ and $p_i$ are the vapor pressures of liquid water and ice, respectively, $n_i$ is the number of molecules per unit volume in ice, $l_f$ is the latent heat of fusion,[20] $T_0$ is the melting point, and $\Delta T \equiv T_0 - T$ is the undercooling. The temperature-dependent classical nucleation rate is therefore

$$J(T) = n_w \frac{k_B T}{h} A \exp\left(-\frac{\Delta g}{k_B T}\right) \exp\left(-\frac{16\pi\sigma^3 T_0^2 f}{3 k_B T (n_i l_f)^2 \Delta T^2}\right) \quad (3)$$

In the analysis here, we use the best estimates[9] of the temperature dependencies of $\Delta g$, $\sigma$, $n_i$, $n_w$, and $l_f$, although the qualitative conclusions and interpretation are not sensitive to plausible uncertainties in these quantities. It is likely, in fact, that the uncertainty in temperature-dependent quantities used in our analysis is small compared to possible deficiencies in the classical nucleation theory itself. The theory serves here primarily as a phenomenological model of the temperature dependence of nucleation rate and for the purpose of identifying the relative roles of kinetics and thermodynamics in our experiments.

The measured nucleation rates are compared to the classical nucleation theory via eq 2, with $\alpha = dT/dt$ such that

$$P = 1 - \exp\left(-\alpha^{-1} \int_{T_0}^{T} J(T) \, dT\right) \quad (4)$$

The theory is fit to the measured nucleation rates in two ways: First, with $f$ as a single free parameter and second with both $f$ and a factor $f_k$ multiplying the rate constant as free parameters. The latter allows not only the mean freezing temperature to be varied, but also the variance of freezing temperature.

The thin lines in Figure 3 correspond to the classical nucleation theory as fit to the experiments. With only one free parameter, which assumes that the kinetics of freezing are identical in the bulk and at the water surface, the data constrain the wetting parameter to be $f = 0.281 \pm 0.001$ (ice-forming nucleus at air−water interface), $f = 0.296 \pm 0.001$ (ice-forming nucleus at oil−water interface), and $f = 0.430 \pm 0.001$ (ice-forming nucleus immersed in water). The fits are obtained by matching the curves at $P = 0.5$. These values are remarkable because they correspond to more than 10 orders of magnitude increase in the nucleation rate when the nucleus is at the surface relative to when the nucleus is immersed in the bulk. The reduction in the parameter $f$ is in qualitative agreement with the thermodynamic arguments of Djikaev et al.[3] for homogeneous nucleation: that is, the free energy barrier for formation of a critical ice germ is lower near the water−air (or water−oil) interface than when the ice germ is immersed in the bulk water away from the interface. Furthermore, $f$ differs for the water−air and water−oil systems, matching qualitative expectations.[7] However, more precise evaluation of the dependence of $f$ on the properties of the surrounding medium (air, various oils, etc.) will be necessary for detailed comparison with the thermodynamic arguments. This will require additional work because careful determination of all interfacial free energy differences is required, including those for the ice-forming nucleus. Finally, the role of thermodynamics must be decoupled from possible changes in the kinetics of ice formation, as discussed next.

The fit of classical nucleation theory with the kinetic rate determined from best estimates of the activation energy for self-diffusion and other properties of water[9] is excellent when the ice-forming nucleus is immersed in the undercooled water. When the ice-forming nucleus is at the surface, however, it appears that the experimental probability distributions are narrower than the theory suggests (Fig. 3, thin black curves). A reduced variance in freezing temperature can be explained in the context of the theory as an increased kinetic growth rate, i.e., increased molecular jump frequency. When the second fitting parameter $f_k$ is included we can estimate $f_k = 10^8$, $f = 0.394$ for the ice-forming nucleus at the air−water interface and $f_k = 10^6$, $f = 0.387$ at the oil−water interface (Fig. 3, thin grey curves). Note that only the low-undercooling portion of the probability distribution is fit to the theory since these are samples representative of the surface freezing mode alone. Such large enhancements in the kinetic growth rate must be regarded as somewhat speculative at this time, but they do agree qualitatively with observations of homogeneous nucleation at droplet surfaces in molecular dynamics simulations.[10,11] Chushak and Bartell[10] speculate that: "One factor favoring nucleation near the surface would be the greater freedom of motion and, hence, a larger nucleation prefactor." In other words, the kinetic rate coefficient may be larger at the surface than in the bulk. For example, a factor of 2 decrease in the activation energy for a molecule jumping from the liquid to the solid results in more than a factor

of $10^3$ increase in the kinetic rate coefficient. Furthermore, the kinetic rate coefficient as typically formulated in classical nucleation theory, i.e., via viscosity, has been shown to severely underestimate the actual values in some situations.[22]

## Summary

We have presented experimental evidence for greatly enhanced ice nucleation rates at water surfaces relative to bulk water. Although only a limited number of results are able to be shown in the context of this letter, the phenomenon is observed for all materials we tested (silicate glasses and crystalline solids).[12] In all cases, the freezing temperature for the surface mode is approximately 4−5 K higher than that for the bulk-water mode. Therefore, we expect that the phenomenon is quite general and likely is of importance for ice formation in the atmosphere. It remains to be seen whether a theoretical description of the surface-enhanced crystallization can explain the surprisingly robust change of 4−5 K in freezing temperature. Furthermore, implications of this freezing mechanism for atmospheric process will need to be more fully explored.

## References and Notes

(1) Bartell, L. S.; Chushak, Y. G. In *Water in Confining Geometries*; Buch, V., Devlin, J. P., Eds.; Springer: Berlin, 2003; Chapter 16.

(2) DeMott, P. In *Cirrus*; Lynch, D. K., Sassen, K., Starr, D. O'C., Stephens, G., Eds.; Oxford: New York, 2002; Chapter 5.

(3) Djikaev, Y. S.; Tabazadeh, A.; Hamill, P.; Reiss, H. *J. Phys. Chem. A* **2002**, *106*, 10247.

(4) Ewing, G. E. *J. Phys. Chem. B* **2004**, *108*, 15953.

(5) Shaw, R. A.; Lamb, D. *Geophy. Res. Lett.* **1999**, *26*, 1181.

(6) Vali, G. In *Nucleation and Atmospheric Aerosols*; Kulmala, M., Wagner, P., Eds.; Pergamon: New York, 1996.

(7) Tabazadeh, A.; Djikaev, Y. S.; Reiss, H. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 15873.

(8) Jensen, E. J.; Toon, O. *Geophys. Res. Lett.* **1992**, *19*, 1759.

(9) Pruppacher, H. R.; Klett, J. D. *Microphysics of Clouds and Precipitation*, 2nd ed.; Kluwer Academic Pub.: Norwell, MA, 1997; Chapters 7 and 9.

(10) Chushak, Y. G.; Bartell, L. S. *J. Phys. Chem. B* **1999**, *103*, 11196.

(11) Chushak, Y. G.; Bartell, L. S. *J. Phys. Chem. A* **2000**, *104*, 9328.

(12) Durant, A. J.; Shaw, R. A. *Geophys. Res. Lett.*, to be submitted.

(13) Shaw, R. A.; Kostinski, A. B.; Larsen, M. L. *Quart. J. R. Met. Soc.* **2002**, *128*, 1043.

(14) We neglect morphological changes that might occur at the surface of the nucleus throughout the experiment because little evidence for such changes has been observed.

(15) Vali, G. *J. Atmos. Sci.* **1971**, *28*, 402.

(16) Vonnegut, B.; Baldwin, M. *J. Clim. Appl. Meteor.* **1984**, *23*, 486.

(17) Seeley, L. H.; Seidler, G. T.; Dash, J. G. *Rev. Sci. Inst.* **1999**, *70*, 3664.

(18) Heneghan, A. F.; Wilson, P. W.; Haymet, A. D. J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 9631.

(19) Turnbull, D.; Fisher, J. C. *J. Chem. Phys.* **1949**, *17*, 71.

(20) McDonald, J. E. *J. Atmos. Sci.* **1964**, *21*, 225.

(21) Battezzati, L.; Castellero, A. *Nucleation and the Properties of Undercooled Melts*; Trans Tech Pub.: Zurich, Switzerland, 2002; Chapter 3.

(22) Bartell, L. S. *Annu. Rev. Phys. Chem.* **1998**, *49*, 43.