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Nucleation in emulsified supercooled water

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A calorimetric technique was used to measure the nucleation rate of ice in supercooled H_2O and D_2O droplets in oil emulsions. The temperature dependence of the nucleation rate was determined for a wide range of temperatures and droplet volumes with use of emulsions stabilized by two different surfactants. The results are used to test quantitatively the theory of homogeneous nucleation for emulsified samples of water. The nucleation-rate measurements are also discussed in the context of theories which predict singularities in the thermodynamic functions of supercooled water.

INTRODUCTION

The discovery of large anomalies in the thermodynamic and transport properties of supercooled water[1–4] has stimulated recent interest in understanding the structure and behavior of metastable liquids. Angell[5] has parametrized the temperature dependence of many thermodynamic properties of water in terms of power laws which imply the existence of a singularity at approximately -45°C. One attempt to explain the fact that supercooled water behaves in many respects as if it were approaching a second-order phase transition has been advanced by Speedy[6,7] who proposed that there is a region in the P-V plane bounded by a spinodal curve on which liquid water becomes absolutely unstable. As the spinodal is approached, mean-field theories[8] suggest that the thermodynamic functions diverge. The theory of the thermodynamics of a metastable liquid in the vicinity of the spinodal is rather general and could be applicable to any strongly supercooled liquid; other explanations of the experimental data on water depend on the structure and properties of the tetrahedral hydrogen-bond network. Stanley and Teixeira[9] have developed a model in which the anomalous behavior of supercooled water is related to the percolation of fluctuating patches of four-bonded molecules.

Testing these theories is a considerable experimental challenge because the liquid-sample lifetime in the region of primary interest close to the spinodal or the percolation threshold is very short, due to nucleation and growth of the solid phase. The prevention of nucleation requires elimination of solid surfaces and the division of the sample into small droplets to minimize the effects of suspended heterogeneous nucleation centers. This goal can be accomplished by isolating small droplets in an immiscible fluid with a lower freezing temperature. Although some properties of the metastable fluid, including the nucleation rate,[10,11] can be determined from measurements on single drops, most quantitative thermodynamic measurements require a larger sample which can be obtained in the form of an emulsion with many droplets stabilized by a surfactant.[1,12,13] The experimental convenience of emulsified samples is somewhat offset by the complications introduced by possible effects of the surfactant, by the inevitible polydispersity of the droplets, and by the fact that emulsions are metastable systems which tend to phase separate and have time-dependent properties.[14] Extracting thermodynamic information about the droplets from measurements on emulsified samples also requires the assumption that the droplets are all in the same phase. In many measurements it is difficult to distinguish between a phase transition in some small fraction of the drops and a possible small change in the thermodynamic properties of the droplet phase. Despite these difficulties, emulsified samples offer the best opportunity to study strongly supercooled liquids at the limit of metastability where possible heterophase fluctuations,[15] transitions to a liquid-crystal-like state,[16,17] possible effects of a solid-liquid spinodal line,[7] or other exotic phenomena are most likely to occur. Since the nucleation rate imposes a practical limit on observations of the supercooled state in emulsified samples, it is important to understand the nucleation mechanism in these systems.

EXPERIMENT

The nucleation rate in emulsions can be conveniently determined by monitoring the release of heat of fusion as the droplets freeze. The measurements described below utilize an adiabatic calorimeter. The outside vacuum can was surrounded by a liquid-nitrogen bath. The temperature of the thermal shield was regulated by an analog feedback circuit whose set point was controlled by a computer. The sample cell was a brass container with a volume of approximately 1 cm^3 and heat capacity 2 J/K. A spiral coil of 0.002-cm-thick copper foil was used to reduce the internal thermal time constant of the cell to less than 60 sec. The cell had a vacuum-tight seal made with a small flange and a rubber *O* ring. A Manganin-wire heater was wrapped around the outside of the cell. The principal mode of heat transfer from the cell to the environment was radiation, with a thermal time constant of approximately 45 min. Thermistors with a room-temperature resistance of $10^4\ \Omega$ and a sensitivity of approximately $10^4\ \Omega/°\text{C}$ in the range -30 to -40°C were used to monitor the temperature of the sample cell and the thermal shield to within 10^{-4} K. The thermal drifts were sufficiently low that a heat input of 10^3 J/sec (corresponding to less than 10^{-6} g/sec of water freezing) could be detected easily.

Preliminary measurements were made on emulsions of water in heptane using sorbitan tristearate (STS) as a surfactant as used originally by Rasmussen and MacKenzie.[1] Because of the large density difference between water and heptane, these emulsions were unstable and experiments which lasted more than a few hours gave erratic results. To avoid this problem, the emulsions used in this study were made from petroleum jelly. The emulsions were prepared by dissolving 0.1—0.01 g surfactant in 5 g of molten petroleum jelly. Water was added and the mixture was either agitated by hand or stirred with a high-speed drill. The amount of surfactant, the degree of agitation, and the temperature (and therefore the viscosity of the petroleum jelly) all affected the size of the resulting water droplets, which could be made in the range of 2-μm electrons to 1 mm in diameter.[18] The surfactants and petroleum jelly were used as obtained from the manufacturer. The H_2O was distilled and deionized with a resistivity of 18 MΩ cm. The D_2O (99.9% isotopic purity) was purchased from Alfa Products; both the H_2O and D_2O were passed through a 0.2-μm filter. While the emulsion was still warm and fluid it was poured into the calorimeter sample cell, but it rapidly gelled and the water droplets remained suspended. The resulting emulsions were very stable and gave repeatable results even after several freezing and melting cycles of the water over a period of weeks.

The most interesting question about nucleation in these emulsions is whether the mechanism is bulk-homogeneous nucleation initiated by a thermal fluctuation of a critical nucleus as described by the theory of Turnbull and Fisher[19] or heterogeneous nucleation catalyzed by an impurity. The important features of homogeneous nucleation are as follows: (1) The lifetime of a droplet in the metastable state at a fixed temperature is a random variable with a Poisson distribution. (2) The average lifetime is a very rapidly varying exponential function of temperature. (3) At a fixed temperature the lifetime of a droplet is inversely proportional to the volume. Unfortunately, the phenomenological theories of heterogeneous nucleation[20] suggest that nucleation on a catalytic particle has the same qualitative properties, although the absolute rates may be very different. For emulsified samples, however, the most likely site of heterogeneous nucleation is the surfactant layer on the surface of the drop, which would be characterized by a nucleation rate which scales as the surface area of the drop rather than the volume. The role of the surfactant layer in nucleation can also be investigated by comparing the nucleation rate in emulsions made with different surfactants.

In order to determine the lifetime of a drop at a given temperature, the calorimeter could be operated in a mode in which the cell is rapidly cooled and then held at a fixed temperature. The power $P(t)$ required to keep the temperature constant is a direct measure of the rate of release of latent heat in the sample and, therefore, also the time dependence of the liquid-droplet population. The result of such an experiment is shown in Fig. 1(a). The emulsion was approximately 10% H_2O by volume, the surfactant was STS and the average droplet diameter was 6 μm. The cell temperature is $-37.8\,^{\circ}$C while the shield temperature is $-43\,^{\circ}$C. The variation of the power with time is approximately exponential with a best-fit time constant $\tau=2700$ sec. The accuracy of this approximation can be appraised by plotting $\ln[P_0-P(t)]$ versus time, where P_0 is the power required to keep the temperature constant after the sample is completely frozen; the slope of this plot gives the time constant. As can be seen in Fig. 1(b), there is actually a distribution of time constants which probably can be attributed to the polydispersity of the droplets in the emulsion. As discussed below, the nucleation rate is proportional to the droplet volume, so smaller droplets survive in the liquid state longer than larger drops. the data of Fig. 1 can, in principle, be deconvoluted to obtain a droplet-volume distribution, but the deconvolution procedure is numerically extremely unstable and sensitive to experimental noise. A measure of the polydispersity can be obtained, however, by fitting the data to a model assuming only two droplet sizes. This seems particularly appropriate, since for long times the data are, in fact, well described by a single time constant, which corresponds to a minimum droplet size. The results of this analysis shows that the droplet distribution ranges from a minimum size to approximately 4 times the minimum size , which corresponds to a factor-of-1.6 variation in the droplet diameter. This estimate of the polydispersity is consistent with estimates from microscopic examination, although the latent-heat data of Fig. 1 are

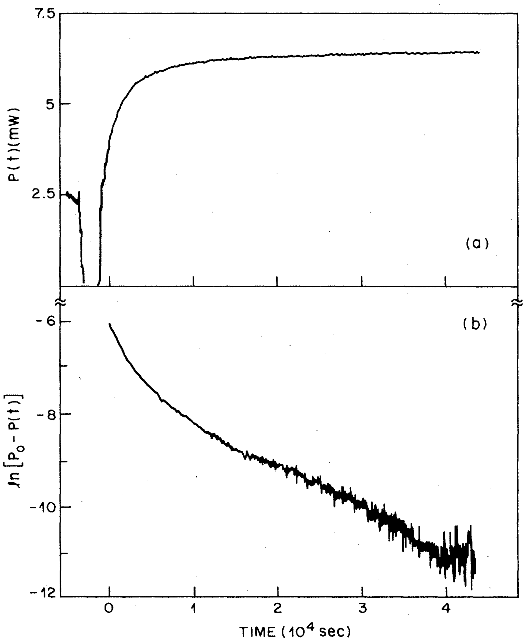

FIG. 1. (a) Power required to maintain the sample cell at $-37.5\,^{\circ}$C as a function of time. After an initial transient, the population of liquid drops decays approximately exponentially. (b) $\ln[P_0-P(t)]$ as a function of time, showing the distribution of time constants.

probably a more reliable quantitative measure.

The temperature dependence of the time constant can be measured by monitoring the release of latent heat $Q(T,t)$ as the temperature T of the sample is slowly decreased,[21] with $\tau(T)=(Q_0-Q)/Q$, where Q_0 is the total latent heat emitted by the sample. Since τ varies by more than an order of magnitude per degree, the temperature dependence of the time constant can be determined quite accurately despite the uncertainty due to the polydispersity of the emulsified samples. Using this technique the time constant can be determined in a range of temperatures for which τ varies from a few minutes to several days.

Measurements have been carried out for a wide range of droplet volumes and for two different surfactants, sorbitan tristearate and sorbitan trioleate (STO); these surfactants were chosen on the basis of their extremely low solubility in water.[14] The nucleation rate per unit volume J is related to the droplet lifetime by $J=1/(\tau V_d)$, where V_d is the average droplet volume. For the 300-μm droplets, approximately one-third of the sample nucleated at temperatures between -10 and $-25\,^{\circ}\mathrm{C}$ via a heterogeneous mechanism. In these samples the onset of homogeneous nucleation was clearly characterized by a region of strong temperature dependence in the nucleation rate. The rate of heterogeneous nucleation implies a concentration of approximately 2×10^4 nuclei per cubic centimeter, despite the purity of the water and the filtration process. For 60-μm droplets, this level of contamination causes less than 1% of the droplets to nucleate on an impurity.

A plot of the nucleation rate as a function of temperature is shown in Fig. 2. For the STS emulsions the nucleation-rate data for droplet volumes which vary by a factor of 10^6 form a smooth curve as a function of temperature, while the STO emulsions have a higher nucleation rate and the data for the two droplet sizes do not form a smooth curve. If the STO data in Fig. 3 are replotted in terms of a nucleation rate per unit area, the data for both droplet sizes do form a smooth curve. The fact that the nucleation rate scales with the droplet surface area suggests that nucleation is catalyzed at the surface in these emulsions. For the STS emulsions, however, the nucleation rate scales with the volume and seems to be determined by the properties of bulk water. The measurements of the nucleation rate per unit volume can be parametrized by

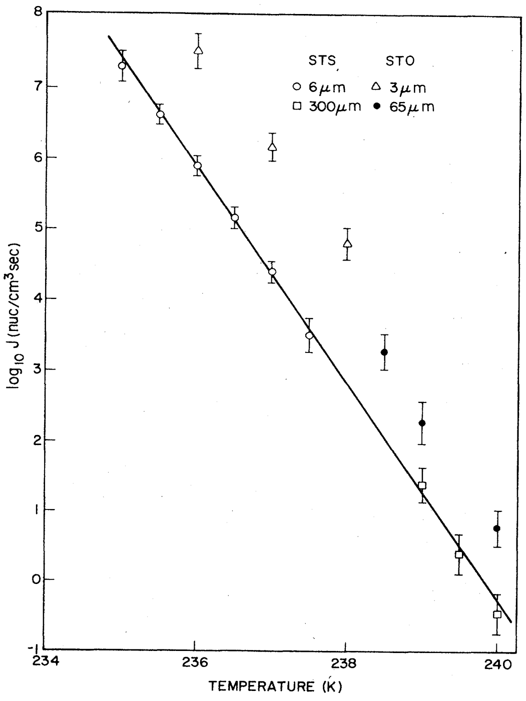

FIG. 2. Log of the nucleation rate per unit volume as a function of temperature for STS and STO emulsions of H_2O for two values of the mean droplet diameter.

$$\log_{10}[J(\text{nucleation/cm}^3\,\text{sec})]=365.7-1.525T \qquad (1)$$

with T the absolute temperature in degrees Kelvin and $235<T<240$ K. These rates agree within a factor of 2 with previous measurements on isolated drops.[10] Similar measurements on D_2O droplets in STS emulsions with mean droplet sizes of 8 and 55 μm can be parametrized by

$$\log_{10}[J(\text{nucleation/cm}^3\,\text{sec})]=369.4-1.505T \qquad (2)$$

with $240<T<246$ K.

DISCUSSION

A simple theory of homogeneous nucleation based on the rate of growth of small nuclei of the solid phase was first described by Turnbull and Fisher. Small nuclei do not grow spontaneously because the surface energy required for their formation is greater than the gain in free energy per unit volume. The energy balance between the surface and volume terms is most disadvantageous for nuclei of a certain critical radius r_c which depends on the surface tension γ and the free-energy difference between bulk water and ice, $\Delta G_{\mathrm{sl}}=L\;\Delta T/T_m$, where L is the latent heat of fusion per unit volume, ΔT is the amount of supercooling, and T_m is the equilibrium melting temperature. Nuclei of the critical size $r_c=2\gamma/\Delta G_{\mathrm{sl}}$ constitute a bottleneck which determines the nucleation rate. The rate at which nuclei grow larger than the critical size is given by

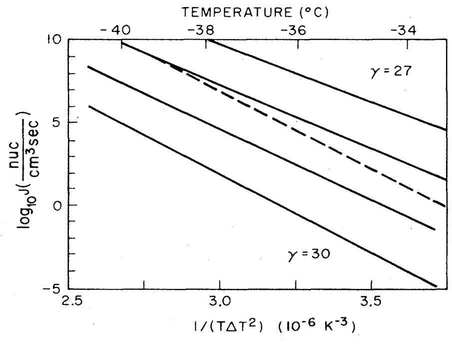

FIG. 3. Log of the homogeneous nucleation rate from Eq. (3) as a function of $1/[T(\Delta T)^2]$, for $\gamma=$ 27, 28, 29, and 30 mJ/m^2. Dashed line denotes STS data of Fig. 2.

$$J=\frac{NkT}{h}e^{-\Delta G_f/T}\exp\left[-\frac{16\pi\gamma^3}{3(\Delta G_{\mathrm{sl}})^2T}\right], \tag{3}$$

where ΔG_f is the energy barrier associated with viscous flow,[22] and N is the number of molecules per unit volume.

The only free parameter in Eq. (3) is γ, which determines the absolute rate as well as the temperature dependence of the rate as illustrated by the solid lines in Fig. 3. For $T=236$ K a best fit to the STS data of Fig. 2 gives $\gamma=28.3$ mJ/m^2 for H_2O, but the temperature dependence of the rate cannot be fitted without invoking a temperature dependence of γ with $d\gamma/dT=0.1$ mJ/m^2 K. If this rate of change is extrapolated to 0°C, one obtains a value of 31.9 mJ/m^2 which is consistent with the measured value of the equilibrium ice-water surface tension.[23] At $T=-37\,^\circ$C the critical nucleus has a radius of 12 Å and contains approximately 250 molecules. One can also extrapolate Eq. (2) to conclude that a maximum nucleation rate of 10^{25} nucleations/cm^3 sec occurs at approximately 170 K, but this estimate depends not only on the surface tension but also on the extrapolation of the Arrhenius behavior of the viscosity up to values of 10^5 P.

Although one might expect that the nucleation rate of D_2O should be the same as H_2O, but shifted by the 4 °C difference in the melting temperatures, this assumption yields a nucleation rate which is several orders of magnitude slower than the observed rate. This discrepancy can be understood in terms of the differences between the latent heat of fusion and the solid-liquid surface tension for the two isotopic species. If we assume that the energy barrier for viscous flow for D_2O is the same as for H_2O and use the value $L=313$ J/cm^3 for the latent heat of fusion and $T_m=276.9$ K for the melting temperature, a best fit of Eq. (3) for the D_2O nucleation-rate measurements of Eq. (2) yields $\gamma=26.3$ mJ/m^2 at $T=241$ K, with the same temperature dependence as the surface tension of H_2O. This value of the surface tension is in accordance with the estimate based on the similarity argument

$$\frac{\gamma_{\mathrm{H_2O}}}{L_{\mathrm{H_2O}}}\approx\frac{\gamma_{\mathrm{D_2O}}}{L_{\mathrm{D_2O}}}\,.$$

Measurements derived from the temperature dependence of the nucleation rate and solid-liquid surface tension provide important constraints on the theoretical descriptions of supercooled water. Despite the fact that the thermodynamic response functions and relaxation times of supercooled water are anomalously large and can be described surprisingly well with power laws which imply a divergence below $-45\,^\circ$C, there appears to be no corresponding anomaly or singular behavior in the temperature dependence of the nucleation rate of H_2O or D_2O. Since the temperature dependence of the nucleation rate is determined by the surface tension, this implies that γ is a much weaker function of temperature than most other thermodynamic parameters in the metastable region. In fact, if the surface tension is extrapolated to low temperatures, one finds that even at 0 K it has dropped to only one-half of its value at the triple point. This implies that there is always a substantial free-energy barrier to nucleation, and supports the notion that there is no spinodal line which separates the metastable liquid from the crystalline state. If there were a spinodal line at a temperature T_s, however, a mean-field analysis[24] suggests that the free-energy barrier to nucleation behaves similarly to other thermodynamic functions, i.e., it should vanish as a power of $T-T_s$. Because of the extreme sensitivity of the nucleation rate to the size of the free-energy barrier, this type of power-law behavior would be very easy to detect experimentally and would manifest itself in pronounced curvature in Fig. 3. The fact that the free-energy barrier to nucleation and the surface tension are smooth and slowly varying functions of temperature in the same temperature range in which other thermodynamic properties obey power laws is a puzzle which requires explanation within the spinodal stability limit model of supercooled water.[25]

SUMMARY AND CONCLUSION

Emulsions of water in petroleum jelly and sorbitan tristearate are a convenient experimental system for investigating the properties of supercooled water. The degree of supercooling of sufficiently small drops appears to be limited by thermodynamic fluctuations which cause homogeneous nucleation, and not by heterogeneous effects. Stable emulsions can be produced with a wide variety of droplet sizes, and large samples of dispersed water can be held in the strongly supercooled regime (e.g., $-36\,^\circ$C) for days without freezing. This system may facilitate more precise determinations of the thermodynamic and transport properties of metastable liquid water than have been previously possible.

We have used this technique to measure the temperature dependence of the nucleation rate over 8 orders of magnitude. The nucleation rate in STS emulsions agrees with previous determinations on larger single drops[10] and can be described with the standard theory of homogeneous nucleation with a temperature-dependent surface tension (see, however, Ref. 26). There have been no previous measurements of the nucleation rate in D_2O, but the results obtained here are consistent with the H_2O results if the thermodynamic parameters are scaled appropriately. Although the temperature dependence of the nucleation rate in STO emulsions is similar to STS emulsions, the absolute rates and the volume dependence of the rate in these emulsions suggest that the nucleation process is more complicated. The nucleation rate in both emulsions is many orders of magnitude slower than the rates observed in emulsified samples in Ref. 27. As suggested by the authors, the high nucleation rates they observe may be due to heterogeneous nucleation initiated by the lanolin which they used as a surfactant.

If the anomalies of supercooled water can be explained in terms of a percolation of ice-like patches of 4-coordinated hydrogen-bonded molecules, the results presented here suggests that the fluctuating clusters contain less than 250 molecules, since larger patches would presumably become unstable to nucleation of the solid.

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