Automatic apparatus for nucleation investigations

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An automated apparatus serves repeatedly to detect and record the repeated formation of the crystalline phase in a single sample of a supercooled liquid. The technique is successfully applied to investigations of the nucleation of ice formation with silver iodide by repeatedly freezing and thawing a small volume of water in a U-shaped capillary tube.

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INTRODUCTION

A variety of techniques has been used in the past for the study of phase changes in many different systems. Single samples have been used to explore the nucleation of the crystalline phase in substances such as water,[1,2] metals,[3] and glass.[4] Emulsions of many tiny droplets have been used to study the nucleation properties of metals,[5,6] polymers,[7] and alkanes.[8] Observations of the freezing of a number of large drops held on a flat surface have also been used to study ice nucleation.[9,10,11] A comprehensive survey of techniques can be found in Zettlemoyer.[12]

These experiments have dealt with both homogeneous and heterogeneous nucleation. Some have used constant cooling rates, and others, a fixed temperature. These techniques require that the experimenter observe each nucleation event by eye, or monitor the nucleation process with a camera, a dilatometer, or some other recording scheme.

Often the observation techniques are tedious and become impractical for very large data samples. In addition, studies of heterogeneous nucleation using multiple sample techniques are often troubled by the variable population of nucleating material in each sample. Comparisons of nucleating ability between samples that are not identical cause uncertainty in determining what part of the variability in the freezing temperatures or times is attributable to the stochastic nature of the freezing process and what part to variations among the drops.

The single-sample methods have the advantage that the population of nucleating material is fixed. Many freezings of the same sample would then be equivalent to a single freezing of many identical samples. The single-sample methods may also be used to study how a nucleation

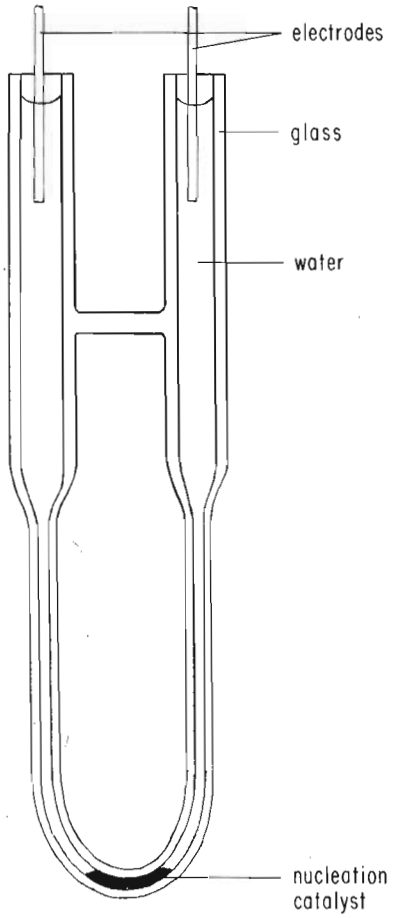

FIG. 1. U-shaped glass capillary tube with copper wire electrodes.

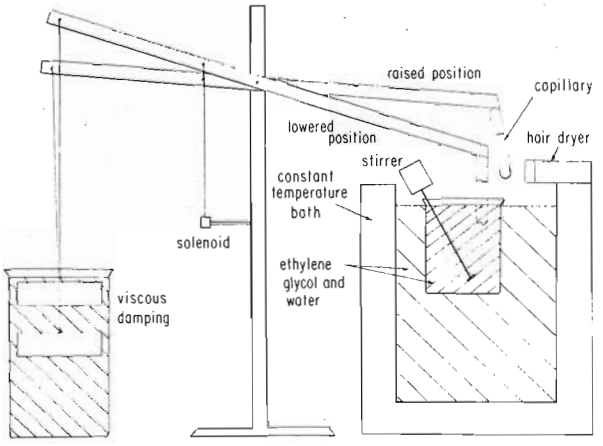

FIG. 2. Schematic diagram of apparatus.

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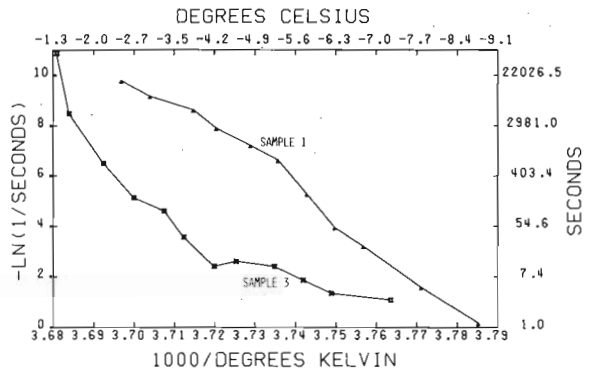

FIG. 3. Relationships between average time intervals observed for ice nucleation to occur and temperature for sample 1 (silver iodide) and sample 3 (silver-copper iodide).

catalyst changes with repeated freezings[1] or to investigate long-term changes in the nucleating behavior of a substance. Typically, these single-sample investigations involve a relatively small number of observations because of the long time periods often required to observe and record each nucleation event. Obtaining large, statistically significant data samples and the study of very low nucleation rates have been impractical using the single-sample methods. We describe here an apparatus that is designed to overcome these problems by automating the single-sample method. This apparatus represents only one specific use of the general technique.

I. DESIGN AND OPERATING PRINCIPLE

The apparatus detects and records a nucleation event in a single sample of supercooled water, thaws and recools the sample, and repeats the process indefinitely. In all experiments reported here, silver iodide or silver-copper iodide was used as a nucleation catalyst. A small sample (10 mg) of the nucleation catalyst is held in the bottom of a U-shaped, thin wall, glass capillary tube of inner diameter 0.5 mm (Fig. 1). Distilled water fills the entire capillary tube, and only the bottom few centimeters are immersed in a stirred water-glycol bath whose temperature, monitored by an electronic thermometer accurate to ±0.02 °C, is held constant by a thermostat to within ±0.1 °C of some fixed temperature below freezing. The capillary tube is held at the end of a 1-m wooden arm (Fig. 2).

When immersed in the bath, the temperature of the capillary and the water in it rapidly comes to equilibrium with the temperature of the bath. Tests made by filling the capillary with a salt solution and determining its temperature by measuring the ac resistance between the two electrodes as a function of time show that the capillary cools to within 0.1 °C of the bath temperature in about 8 s.

In nucleation experiments, as the capillary is cooled to the temperature of the bath, its resistance between the electrodes rises to a value characteristic of the bath temperature and remains constant as long as the water remains supercooled. Depending on the temperature and the nucleation material, the water may remain in the supercooled condition for periods ranging from tens of seconds to days or even weeks. Because ice is a poorer electrical conductor than liquid water, a very large increase in resistance occurs when the water in the cooled portion of the capillary suddenly turns to ice. The freezing of the water takes no more than a few seconds, and an electric circuit actuated by the sudden increase in electrical resistance activates equipment that lifts the capillary out of the bath, melts the ice by blowing warm air from a hair dryer on the capillary, and then returns the sample to the cold bath. Typically, an interval of the order of 20 s elapses from the time that the sample freezes, is thawed, and is reimmersed and brought back to the temperature of the bath.

The simplest method of recording the data is to use a counter that records how often the sample freezes during a given time period. Thus, the average nucleation rate can be determined. This method of data recording is ap-

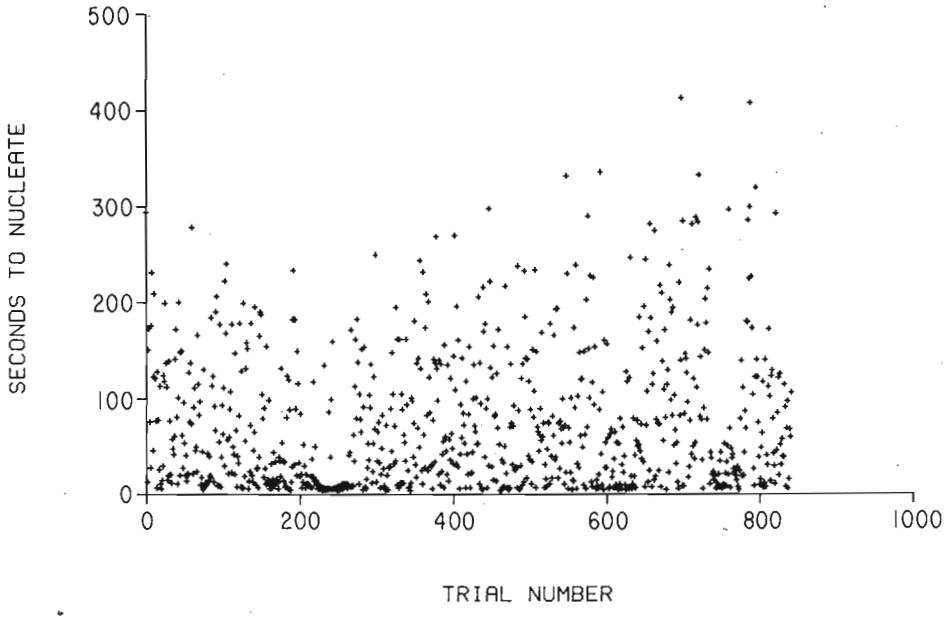

FIG. 4. Time series of time intervals observed for ice nucleation catalyzed by sample 1, silver iodide at −5.5 °C.

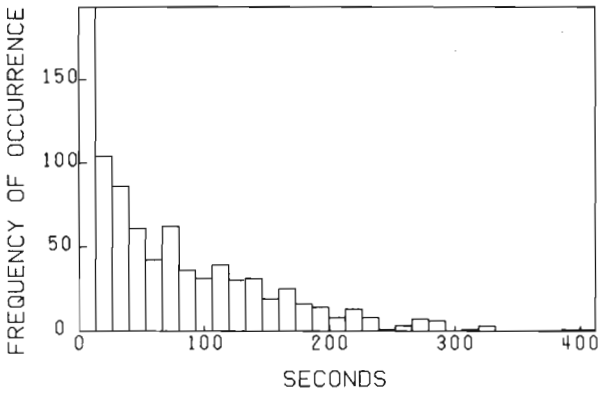

FIG. 5. Histogram of frequency of occurrence of time intervals observed for ice nucleation catalyzed by sample 1, silver iodide at −5.5 °C.

propriate for determining how the nucleation rate changes with temperature.

A more elaborate method of recording data can give the various lengths of time the sample takes to freeze. As the sample is returned to the bath, the time is recorded on a punch clock. The time that elapses before nucleation of the supercooled water takes place is obtained by taking the difference between adjacent times and then subtracting the time needed to withdraw and to thaw the sample and then return it to thermal equilibrium in the bath.

II. RESULTS AND APPLICATIONS

The results of repeated freezings of two water samples nucleated with silver iodide and one sample with silver-copper iodide illustrate typical ice nucleation behavior (See Figs. 3–6).

Sample 1 (Figs. 3–5) is a silver iodide dispersion precipitated by dilution from a saturated solution of potassium iodide, iodine, and silver in water. Sample 2 (Fig. 6) is a silver iodide dispersion precipitated by dilution from a saturated solution of silver iodide and potassium iodide in water. Sample 3 (Fig. 3) consists of silver-copper iodide (3 AgI · CuI) collected from the flame guard of an acetone burner used for cloud seeding. The crystal size is highly variable, but is typically 5–10 μm in samples 1 and 2 and slightly larger in sample 3.

The method of counting nucleation events was used to obtain the average nucleation time at various temperatures for samples 1 and 3 (Fig. 3). In this case, there is about a threefold increase in the nucleation rate for every 1 °C drop in temperature. The temperature range covered is from −1.3 °C to −9.1 °C. Low nucleation rates, such as one event per week, can easily be studied using this apparatus. The large data samples that can be obtained permit a better estimate of the mean freezing time over a wide range of temperatures.

Figure 4 is a time-series plot of the freezing times for sample 1, silver iodide at −5.5 °C. Note the variability in the freezing times, with the shorter times being the more common. Figure 5 is a histogram of the relative frequency of occurrence of freezing times of various lengths. To a first approximation, the frequency decreases exponentially with longer freezing times.

As found by Dorsey,[1] repeated freezings of a single sample may have some effect on the sample's freezing behavior. Changes in the nucleating ability with time can be seen in both time-series plots (Figs. 4 and 6). Figure 6 was obtained using sample 2 at −8.2 °C. In Fig. 4, note the concentration of nearly all short times between trial numbers 220 and 270, and the overall trend toward longer freezing times. Figure 6 shows change in behavior near trial number 650. The freezing times become consistently longer and remain longer for the remainder of the run.

Some samples of silver iodide were greatly affected by the repeated freezing–thawing cycles. It was found that nucleation rates could either increase or decrease, often in very erratic jumps, but sometimes in a repeated pattern. Some samples showed the strange behavior of jumping back and forth between low and high nucleation rates,

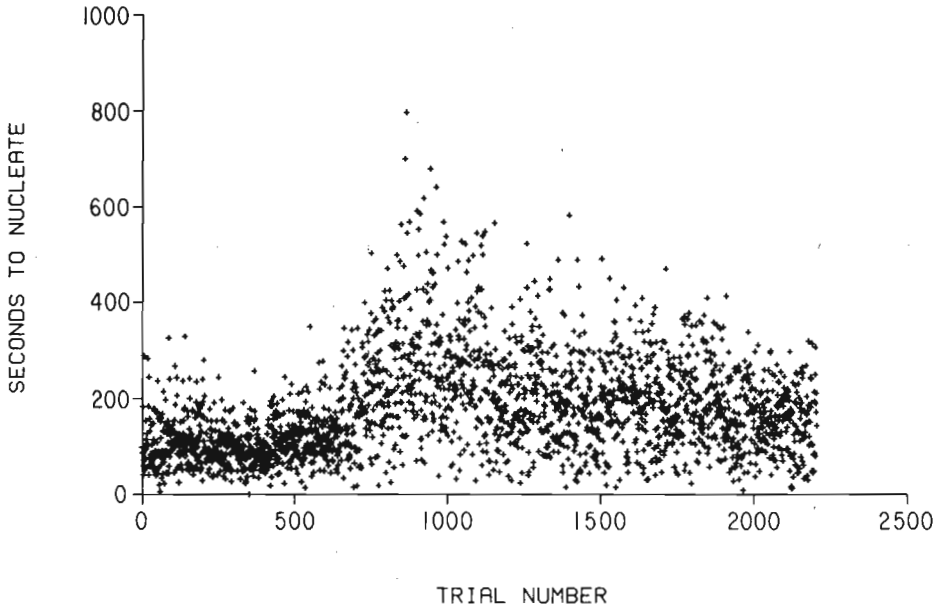

FIG. 6. Time series of time intervals observed for ice nucleation catalyzed by sample 2, silver iodide at −8.2 °C.

remaining in each of these modes for periods of the order of several hours.

The effect of repeated freezing is different for each given sample. Tests, such as those involving the time-series plots, must be run on each sample to determine the magnitude of the changes in nucleating ability.

The automatic apparatus has proved to be useful for investigations of nucleation kinetics and for the detection of changes in the nucleation catalyst. It can readily be adapted to nucleation studies with other substances and with other detection methods.

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