# On Freezing of Supercooled Droplets Shattered by Shock Waves

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## ABSTRACT

Supercooled water droplets in free fall were shattered by shock waves in a laboratory shock tube, and the fragments thus produced were examined for the presence of ice crystals. The experimental results show that the probability of formation of ice crystals by the shattering process is very small. It thus appears improbable that shock waves from lightning strokes or explosive charges can substantially increase the concentrations of ice crystals in a supercooled cloud by this mechanism.

## 1. Introduction

Laboratory studies have shown that freezing of supercooled liquids can be stimulated by mechanical or acoustic disturbances; the term "dynamic nucleation" has been applied to such phenomena. The existence of dynamic nucleation processes has led numerous investigators to suggest that natural or artificial acoustic disturbances may affect precipitation from supercooled clouds, by triggering freezing of hydrometeors. Goyer (1965) has reviewed much of the literature on this subject. He has suggested that shock waves from lightning discharges may produce local increases in precipitation, by increasing the numbers of ice crystals in the region surrounding the discharge channel. Others have proposed the use of explosive charges to modify clouds and precipitation processes.

The mechanism by which shock waves might stimulate freezing of hydrometeors is not clear. It is reasonably well established that dynamic nucleation of freezing in bulk water samples, in the laboratory, occurs when the disturbance induces cavitation in the liquid, i.e., the formation and collapse of cavities below the liquid surface (Chalmers, 1964; Hunt and Jackson, 1966; Gitlin and Lin, 1969). It is not clear that shock waves can induce cavitation in freely-falling hydrometeors. Koenig (1965) has suggested that shattering of supercooled droplets may stimulate freezing. He described experiments in which a water droplet, suspended in a small plastic loop, was blown out and shattered by a blast of air from a syringe; frozen particles were frequently observed among the fragments of the shattered droplet. Hanson *et al.* (1963) have studied the shattering of droplets by shock waves. Violent disruption of 1-mm diameter droplets resulted when the gas flow velocity behind the shock front was 15 m $\sec^{-1}$ or greater; the required velocity increased with decreasing drop size.

We report here the results of experiments in which free-falling supercooled droplets were shattered by shock waves. The droplet fragments were collected in a supercooled sugar solution in order to detect the presence of ice crystals among the fragments.

## 2. Experimental arrangement

### *a. Apparatus*

The experiments were carried out in a horizontal shock tube of rectangular cross section, 10 cm wide and 20 cm high. A drawing of the shock tube and the associated apparatus is shown in Fig. 1. The shock tube comprised two sections, a driver section, 1.2 m long, and a test section, 2.4 m long. The two sections were separated by one or more thin diaphragms of cellulose acetate. Shock waves were produced by pressurizing the driver section with compressed dry air, and then puncturing the diaphragm with a solenoid-operated needle. This resulted in almost instantaneous rupture of the diaphragm and movement of a shock front into the test section. The downstream end of the test section was open to the atmosphere.

The experiments were conducted in the test section at a point about 1 m downstream of the diaphragm, far enough to prevent contamination of the experiment by fragments of the diaphragm, yet also far enough from the open end of the tube to give a reasonable period of constant flow conditions (~7 msec).

An insulated cold box was built around the test section of the shock tube to allow operation at below-freezing temperatures. Refrigerant coils were mounted above and along both sides of the shock tube, but at

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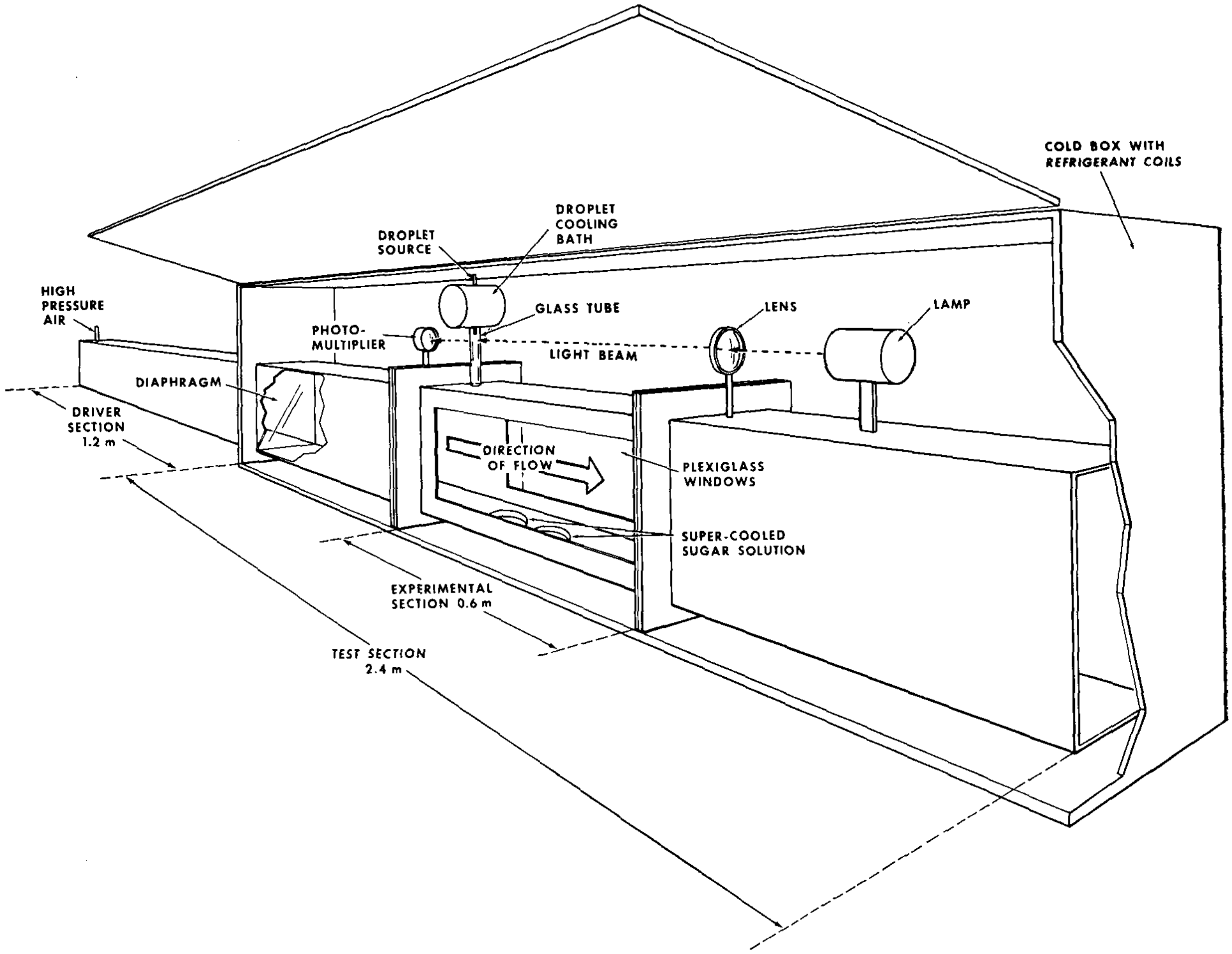

FIG. 1. Shock tube and associated apparatus for droplet shattering and ice crystal detection experiments.

least 10–15 cm from it. This separation minimized temperature gradients in the tube and reduced the possibility of frost formation in the tube, which would have made a clean experiment impossible. The metal construction of the shock tube (3-mm sheet steel) also helped to reduce temperature gradients in its interior. The maximum temperature difference observed between the shock tube and the bottom of the cold box (the coldest spot) was 3C.

Droplets were introduced through an aperture in the top of the shock tube. The water supply for the droplets entered through 0.5-mm bore Teflon tubing or, alternatively, a drawn glass capillary, and was cooled just before introduction by an independently controlled cold bath. Water purified by repeated vacuum sublimation was injected into the tubing from a hypodermic syringe, producing droplets 2.2–2.8 mm in diameter. The droplet source was mounted about 15 cm above the shock tube. The intervening space was spanned by a length of glass tubing, so that ice crystals from the cold box could not inadvertently enter the shock tube.

Before entering the shock tube, a falling droplet interrupted a collimated light beam striking a photomultiplier. The signal thus generated activated delay circuits which triggered the diaphragm-puncturing solenoid and, when necessary, light sources for photography of the shattering process.

The bottom of the shock tube was fitted with a removable panel with apertures in which could be mounted two 6-cm diameter, flat-bottomed dishes, each containing a thin layer (1–3 mm) of sugar solution. These dishes were mounted with their rims flush with the shock tube interior, to minimize aerodynamic disturbances. The sugar solution concentration (450 gm sucrose in 650 gm $H_2O$) was such that it froze spontaneously at −11 to −12C. The temperature of the sugar solution was maintained between −9 and −10C by another independently controlled cold bath. When the solution was at or below −7C, any ice crystal contacting it grew to a diameter of several millimeters within 1 min, so that the total number of ice crystals produced in any experiment could readily be determined. The sides of the shock tube were fitted with large flush-mounted Plexiglas windows to allow observation of the sugar solution and of the drop-shattering process.

To determine the approximate number of droplet fragments produced, and the region in which they fell on the bottom of the shock tube, a strip of white paper was mounted on the shock tube bottom. Ink droplets from a separate drop dispenser were introduced on the same path that the supercooled water droplets followed. Shock strength and the time delay between droplet introduction and diaphragm rupture were then adjusted to obtain complete disruption of the droplets and deposition of most of the fragments in the sugar solution trays.

### b. *Test procedure*

A well-defined experimental procedure was found necessary to minimize the possibility of contamination of the experiment by spurious sources of ice crystals. When the shock tube and cold box had reached the desired operating temperature, the interior of the tube was thoroughly cleaned with a vacuum cleaner and a diaphragm installed. The sugar solution trays were then mounted in place. A "rest period" of at least 10–15 min followed, before the experiment was carried out. This allowed ample time for the sugar solution to reach the desired temperature. Equally important, this also allowed time for evaporation of any minute ice crystals which might have remained after the cleaning process. Since many preliminary experiments had shown the difficulty of eliminating extraneous ice crystals, dry (control) and wet runs were performed on a randomized basis. In dry runs, the shock tube was fired manually, and no droplet was introduced. In wet runs, a single droplet was introduced and shattered by the shock wave. The sugar solution trays were inspected just prior to each run, to verify that no spontaneous nucleation had occurred to confound the experiment. After each run, the sugar solution trays were left unmolested for 2 min, to allow ample time for formation of visible crystals from any ice crystals formed in the experiment.

After this sequence of events, the driver section of the shock tube was retracted, the experimental section again vacuumed, and a new diaphragm installed. If seeding of the sugar solution had occurred, the trays were removed, cleaned and refilled. If no seeding had occurred, the trays were often left undisturbed. Even though we made sure, by intentional seeding, that the seeding properties of the sugar solution did not change after standing for eight hours in the shock tube, the solution was replaced at least every two to three hours.

When the system was thus prepared for the next run, the foregoing sequence of events, including the rest period, was repeated.

### c. *Operating conditions and limitations*

Shock-tube temperatures were measured at a point on its upper surface about 30 cm upstream from the experimental section. The temperature at this point, which was 1–2C warmer than the experimental section itself, varied from −2.5 to −6C. The droplet source was maintained between −6 and −8C. The ink drop shattering experiments had shown that the optimum distribution of drop fragments over the sugar solution trays occurred when the driver section was pressurized to 180 mm Hg, and when the shock intercepted the droplet trajectory at a point just below the mid-point of the tube.

The water used for the droplet supply froze spontaneously at −8 to −10C in bulk samples (several cubic centimeters). In small bore capillary tubing, it could be supercooled below −17C, while in the shock tube set-up, itself, the droplet supply frequently froze at −9C or below. Freezing of the supply was much more frequent when drops were introduced through a glass capillary than when Teflon tubing was used.

The shock tube itself could be cooled to −12C. At this temperature, however, numerous ice crystals were observed in most runs, wet or dry. Thus, the conclusions drawn in this paper are strictly applicable only for air and drop temperatures warmer than −10C.

The history of the droplet environment, from the time of arrival of the shock front until the fragments reached the sugar solution trays, was very complicated. Measurements in the shock tube showed that the pressure jump across the shock wave was about 85 mm Hg, in good agreement with elementary shock tube theory. The gas flow velocity behind the front was calculated to be about 24 m sec$^{-1}$. These flow conditions remained practically constant for about 7 msec. At this time, rarefaction waves from both ends of the tube arrived almost simultaneously, reducing the pressure to roughly an equal amount below atmospheric, a condition which persisted for another 7 msec. Thereafter, a complex series of compression and rarefaction waves ensued, producing steadily decreasing oscillations in pressure until final equilibration was obtained. The shock wave raised the air temperature about 10C, so that for 7 msec the droplet environment was above freezing. The ensuing rarefaction wave then reduced the temperature to about 10C below the initial temperature for another 7 msec. Thereafter, the temperature oscillated with the pressure, but with rapidly decreasing amplitude.

## 3. Results

The primary problem encountered in this study was the elimination of extraneous ice crystals. With the entire apparatus operating below freezing, there were many possible sources of ice crystals. Some of the measures taken to eliminate spurious sources of ice crystals were described in the preceding section. In spite of these precautions, experimental days could usually be divided into two classes: "clean" days and "dirty" days. On dirty days, seeding of the sugar solution was observed from time to time, apparently occurring with roughly equal probability in wet and dry runs. On clean days, no ice crystals were detected in

TABLE 1. Results of droplet shattering experiments.

| Ice crystals observed? | Type of run Wet | Dry |
|---|---|---|
| Yes | 8 | 6 |
| No | 27 | 29 |

either wet or dry runs. We were thus led to suspect that shattering of supercooled droplets in our experiments did not lead to ice crystal production, and that freezing, when observed, resulted from some uncontrolled factor in the experiments.

A statistical evaluation of the data supports this hypothesis. The results of 70 experiments carried out under the above conditions are shown in Table 1, which shows the number of runs in which ice crystals were or were not observed for both wet and dry runs. In 9 of the 14 runs which seeded the sugar solutions, only a single ice crystal was observed. Multiple crystal formation (up to a maximum of three crystals) occurred in one wet and four dry runs.

The increased frequency with which wet runs produced ice crystals is not statistically significant. The chi-square test shows that results with an asymmetry equal to or greater than those in Table 1 occurs with a probability near 0.5 in a purely random process, thus supporting the null hypothesis that the occurrence of ice crystals is independent of the droplet shattering process.

A more quantitative estimate of the frequency of ice crystal production by droplet shattering can be obtained. The last 22 consecutive runs in the series of 70 runs described above produced no ice crystals; 10 of these runs were wet runs. (This abrupt cessation of freezing, in both wet and dry runs, occurred when the glass capillary used for droplet introduction was replaced by Teflon tubing.) An examination of the ink drop shattering experiments showed that about 4500 fragments were obtained from a single droplet, and that about 1200 of these would be expected to fall into the sugar solution trays. If only one of these 4500 fragments were frozen, the probability of its being detected would thus be 4/15; it would go undetected with probability 11/15. The probability of not detecting such an event, if it did occur, in 10 runs is thus $(11/15)^{10}$, or about 0.045. We can thus conclude, at the 5% significance level, that the number of ice crystals produced by the drop shattering process is less than 1%.

## 4. Discussion

There is one important question that must be resolved before drawing final conclusions from the results presented above: Is it possible that the increased temperature behind the shock wave could have melted any ice crystals formed by the droplet shattering process? It was mentioned in Section 2 that, for about 7 msec following shock wave passage, the gas temperature is about 10C warmer than the shock tube temperature. Immediately thereafter the gas is cooled about 10C below the shock tube temperature, so that only the first 7 msec are critical. Shock tube temperatures varied between −2.5 and −6C, with the great majority of the runs being carried out below −4C. (There appeared to be no correlation between shock tube temperature and ice crystal formation. The 22 consecutive runs with no ice crystal formation, mentioned above, were all carried out at temperatures below −4C.) Thus, the peak gas temperature in the majority of cases was +6C or lower.

Photographic studies showed that droplet disruption occurred 1–2 msec after passage of the shock wave. Thus, the droplet fragments were immersed in a warmer environment for about 5 msec. Appreciable warming in this time interval could occur only for quite small droplets, since the lower surface-to-volume ratio of larger fragments would preclude rapid temperature changes. Moreover, the effects of evaporative cooling could partially counteract warming by heat conduction.

Most experiments here were run with droplets supercooled to about −8C. Nucleation of the ice phase at this temperature would result in rapid freezing of about one-tenth of the droplet mass, since the heat of fusion of ice is about 80 cal $\text{gm}^{-1}$. Pruppacher (1967) reports that the linear velocity of ice crystal growth at −8C is near 3 cm $\text{sec}^{-1}$. In 1 msec, then, ice crystal growth could propagate across a 30 $\mu$ droplet. For smaller droplets, one may assume that nucleation and freezing will bring the droplet temperature to 0C in a time much smaller than 5 msec. Since remelting of one-tenth of the droplet mass would require about 8 cal $\text{gm}^{-1}$, the quantity of heat, $\Delta q$, which must be added is given approximately by

$$\Delta q = 32\pi r^3/3 \text{ [cal]}, \tag{1}$$

where $r$ is the droplet radius.

Heat transfer to hydrometeors takes place by conduction and by transfer of latent heat of evaporation. The rate of heat transfer, $\Delta q/\Delta t$, to a small spherical droplet is given by

$$\Delta q/\Delta t = 4\pi r(k\Delta T - LD\Delta\sigma), \tag{2}$$

where $k$ is the thermal conductivity of air, $\Delta T$ the temperature difference between the air and the surface of the droplet, $L$ the heat of vaporization of water, $D$ the coefficient of diffusion of water in air, and $\Delta\sigma$ the difference between the water vapor density at the surface of the droplet and that in the surrounding atmosphere. When $\Delta\sigma$ is positive, evaporation takes place, and the droplet is cooled.

Elimination of $\Delta q$ between (1) and (2) gives the following expression for the radius of the largest droplet for which the rate of heat transfer is sufficient to melt any ice which may have been formed:

$$r^* = [0.375(k\Delta T - LD\Delta\sigma)\Delta t]^{\frac{1}{2}}. \tag{3}$$

The values of the constants in (3), as given by Mason (1957) are: $k = 5.8 \times 10^{-5}$ cal cm$^{-1}$ (°C)$^{-1}$ sec$^{-1}$, $L = 597$ cal gm$^{-1}$, and $D = 0.226$ cm$^2$ sec$^{-1}$. If the air in the shock tube is saturated with respect to liquid water at −8C (the temperature of the droplets), $\Delta\sigma$ is about $2.2 \times 10^{-6}$ gm cm$^{-3}$. Then, with $\Delta T = +6$C and $\Delta t = 5$ msec, one obtains a critical radius of about 3 $\mu$.

Microscopic examination of the ink spots on white paper, formed by shattering of ink droplets, showed an apparent lower limit to the spot size, no spot being smaller than ~50 $\mu$ in its smallest dimension. The technique would have detected spots at least an order of magnitude smaller. It appears, then, that surface tension effects prevented formation of droplets small enough to be warmed appreciably in the time allowed in the shock tube experiments.

Furthermore, if the dew point of the air in the shock tube were below about −10C, the evaporative cooling term in (2) and (3) would exceed the heat conduction term, and a net heat loss would occur for droplets of any radius. Since the supercooled sugar solution, at −10C, was observed to evaporate slowly in the shock tube, the dew point must have been below −10C. We are therefore convinced that any ice crystals formed in the shattering process would have survived to seed the sugar solution, and would have been observed.

We conclude, therefore, that shattering of droplets by shock waves, in the temperature range covered by these experiments, produces few if any ice crystals, and that shock waves from lightning discharges or explosive charges will have little effect on ice crystal concentrations in a cloud via this mechanism. These results contradict those of Koenig (1965), but are in agreement with more recent work by Edwards *et al.* (1969). The latter authors suspended droplets, at −10C, on a thermocouple junction, and shattered them with shock waves from explosive charges; no evidence for freezing was found. Evans (private communication) has reported that these experiments were also carried out on falling droplets, with the same negative result.

In retrospect, it is not surprising that agitation or shattering does not stimulate freezing. Nucleation occurs when a statistically improbable configuration of water molecules, the critical embryo, is created in some small volume of the liquid. At the molecular level, the impulse from a mechanical disturbance is almost certainly small in comparison with the thermal motion, and should not be expected to stimulate formation of the critical embryo. The mere process of creation of many small droplets from a larger body of water does not lead to nucleation. For instance, we have bubbled air through water supercooled to −4C for extended periods. Bursting of the air bubbles at the surface, a process known to create a spray of fine droplets, showed no tendency to stimulate ice formation.

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## REFERENCES

Chalmers, B., 1964: *Principles of Solidification.* New York, Wiley, 86–89.

Edwards, G. R., L. F. Evans and S. D. Hamman, 1969: Nucleation of ice by mechanical shock. *Nature*, **223**, 390–391.

Gitlin, S. N., and S.-S. Lin, 1969: Dynamic nucleation of the ice phase in supercooled water. *J. Appl. Phys.*, **40**, 4761–4767.

Goyer, G. G., 1965: Effects of lighting on hydrometeors. *Nature*, **206**, 1203–1209.

Hanson, A. R., E. G. Domich and H. S. Adams, 1963: Shocktube investigation of the breakup of drops by air blasts. *Phys. Fluids*, **6**, 1070–1080.

Hunt, J. D., and K. A. Jackson, 1966: Nucleation of solid in an undercooled liquid by cavitation. *J. Appl. Phys.*, **37**, 254–257.

Koenig, L. R., 1965: Drop freezing through drop breakup. *J. Atmos. Sci.*, **22**, 440–451.

Mason, B. J., 1957: *The Physics of Clouds.* Oxford, Clarendon Press, p. 444.

Pruppacher, H. R., 1967: Interpretation of experimentally determined growth rates of ice crystals in supercooled water. *J. Chem. Phys.*, **47**, 1807–1813.