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THE FREEZING BEHAVIOUR OF SUPERCOOLED WATER DROPS

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ABSTRACT. An electrodynamic containment system has been used to study the freezing behaviour of supercooled water drops, of radius range 25 to 90 μm. The drops were frozen at temperatures between 0 and -29°C in an environment whose relative humidity was approximately 90% with respect to ice. Freezing events were observed visually and photographically, and measurements were made of the accompanying fractional mass loss $\Delta m/m$.

The most common mode of freezing (70% of the drops studied) resulted in an apparently spherical ice particle. However, 18% exhibited spikes or other protuberances and the freezing of 3% was accompanied by the ejection of numerous ice particles. In each of these situations values of $\Delta m/m$ ranged from about 5 to 15%. A further 9% of the drops exhibited one or more secondary mass-loss events, occurring several seconds after the freezing process was complete; these were thus indicative of the ejection of ice particles.

Almost all of the values of $\Delta m/m$ were significantly in excess of those predicted on the basis of evaporation during freezing, suggesting that an additional mechanism of mass loss was also present. The measured freezing times were considerably shorter than the classical values—at least, for the larger drops freezing at warmer temperatures. Some visual observations were consistent with the "supersaturation wave" around a freezing drop, which has been predicted by Nix and Fukuta (1974).

RÉSUMÉ. *Le comportement en cours de gel de gouttelettes d'eau en surfusion.* On a utilisé un "récipient" électrodynamique pour étudier le comportement en cours de gel de gouttelettes d'eau surfondues, dont le rayon allait de 25 à 90 μs. Les gouttelettes étaient refroidies à des températures allant de 0 à -29 °C dans un milieu dont l'humidité relative par rapport à la glace était approximativement de 90%. Les péripéties du gel étaient observées directement et par photographie et l'on mesurait la perte partielle de masse $\Delta m/m$ qui accompagne le gel.

Le processus de gel le plus courant (70% des gouttelettes étudiées) conduisait à une particule de glace apparemment sphérique. Cependant, 18% montraient des spicules ou d'autres protubérances, et le gel de 3% était accompagné de l'éjection de nombreuses particules de glace. Dans chacun des cas, les valeurs $\Delta m/m$ allaient d'environ 5% à 15%. Un dernier groupe de 9% de gouttelettes présentaient une ou plusieurs pertes de masses secondaires, se produisant plusieurs secondes après que le processus de gel fut complet; il y avait donc là une preuve de l'éjection de particules de glace.

Presque toutes les valeurs de $\Delta m/m$ étaient significativement supérieures à celles prévues sur la base de l'évaporation pendant le gel, ce qui suggère la présence d'un mécanisme additionnel de perte de masse. La durée mesurée du gel était beaucoup plus courte que les valeurs classiques—au moins pour les plus grosses gouttes gelant à des températures supérieures. Quelques observations "à vue" étaient en accord avec "l'onde de sur saturation" autour d'une goutte en cours de gel, telle qu'elle a été prévue par Nix et Fukuta (1974).

ZUSAMMENFASSUNG. *Das Gefrierverhalten unterkühlter Wassertropfen.* Zur Untersuchung des Gefrierverhaltens unterkühlter Wassertropfen mit Radien zwischen 25 und 90 μm wurde ein elektrodynamisches Behältersystem benutzt. Die Tropfen gefroren bei Temperaturen zwischen 0 und -29°C in einer Umgebung, deren relative Feuchtigkeit gegenüber Eis etwa 90% betrug. Der Gefriervorgang wurde visuell und photographisch beobachtet; der damit verbundene relative Massenverlust $\Delta m/m$ wurde gemessen.

Die häufigste Art des Gefrierens (bei 70% der untersuchten Tropfen) führte zu einem sichtlich kugelförmigen Eispartikel. Doch zeigte sich bei 18% die Bildung von Stacheln oder anderen Auswüchsen; bei 3% war das Gefrieren mit dem Ausstoss zahlreicher Eispartikel verbunden. In all diesen Fällen bewegte sich $\Delta m/m$ zwischen 5 und 15%. Bei weiteren 9% der Tropfen zeigten sich ein oder mehr sekundäre Massenverlustvorgänge, die einige Sekunden nach Abschluss des Gefrierprozesses eintraten; sie liessen auf den Ausstoss von Eispartikeln schliessen.

Fast alle Werte von $\Delta m/m$ überschritten beträchtlich jene Grenze, die sich auf der Grundlage der Verdunstung während des Gefrierens vorhersagen lässt, ein Hinweis darauf, dass ein zusätzlicher Vorgang von Massenverlust wirksam war. Die gemessenen Gefrierzeiten waren erheblich kürzer als die klassischen Werte — zumindest für die grösseren Tropfen, die bei höheren Temperaturen gefroren. Einige visuelle Beobachtungen stimmten mit der "Übersättigungswelle" um einen gefrierenden Tropfen zusammen, die von Nix und Fukuta (1974) vorhergesagt wurde.

1. INTRODUCTION

The freezing of supercooled water drops is a problem which, aside from its own intrinsic interest, may be of central importance in precipitation development, the rapid glaciation of some shallow supercooled clouds and cloud electrification. A major difficulty in assessing the

importance of drop-freezing in cloud physics has been the reproduction, in the laboratory, of conditions which accurately simulate those which will occur in the natural situation. It has generally proved impossible simultaneously to achieve the required conditions of thermal and solution equilibrium, ventilation, absence of mechanical supports and high-resolution observation, although the careful experiments of Kuhns (unpublished), Johnson and Hallett (1968), Hobbs and Alkezweeny (1968), Pitter and Pruppacher (1973), Bader and others (1974), and some others, have come close to achieving this objective over particular size ranges.

The experiments described in this paper were performed using individual supercooled drops suspended electrodynamically by means of a modified version of the technique devised by Wuerker and others (1959). It was hoped that all the required conditions could be met, with the possible exception of representative ventilation, and the size range studied (radius $25 < R < 90$ μm) involved drops sufficiently small for ventilation not to be a parameter of paramount importance. A main goal of this study was to determine the number of ice splinters which may be ejected from the drop during the freezing process. It was also hoped to measure freezing times and the evaporative mass loss associated with the freezing process.

2. Apparatus and experimental procedure

The drop production and suspension chamber is illustrated in Figure 1. Drops were produced by the bursting of bubbles at a water surface, using the technique described by Blanchard (1954). These were formed by forcing air through a drawn glass capillary tube immersed in the water. The water surface was kept clean by permitting the water to overflow continuously, as it was supplied from a header tank. The meniscus thus formed also centred the bubble (and the resulting drop) on the vertical axis of the apparatus. On bursting, the collapse of the bubble cavity produced an upward-moving jet which disintegrated into a series of drops. The top drop passed through the hole in the base of the diffusion chamber. Both the drop size and the height attained on ejection by this method were highly consistent for a given capillary. The vertical position of the water surface could be adjusted to deliver the drop to the appropriate height in the diffusion chamber. By applying a d.c. potential to the water surface the drop could be charged; this had the additional effect of accelerating the top drop whilst in the field region between water surface and earthed plate, and increased the height attained. The initial charge on the drop was measured using an induction ring mounted in the centre of the coolant reservoir.

Both distilled and tap water were used in these experiments. Distilled water was not so convenient because in this case the bubble invariably burst immediately on reaching the water–air interface, before the meniscus had centred it on the vertical axis of the apparatus. However, no difference was observed between the freezing behaviour of drops of either distilled or tap water, and it was possible in both cases to supercool them to -30°C for several seconds before they were heterogeneously nucleated.

The electrode configuration used to support the drop was arrived at after considerable experimentation. This was necessary since, as has been pointed out by Masuda and others (1970), although the behaviour of a particle held in a non-uniform alternating electric field is theoretically calculable by solving the equations of motion of the particle, an analytical solution is not generally obtainable. One exception to this is the electrode configuration used by Wuerker and others (1959) who have used a small experimental chamber machined to provide a known, circularly symmetric potential distribution. In this case, the equations of motion are a special case of the Mathieu differential equation, the solution of which leads to various conditions which must be satisfied for the stable containment of the charged particle.

The electrode configuration used in this apparatus was finally chosen for its ease of construction and flexibility of operation and was a simplified version of that employed by

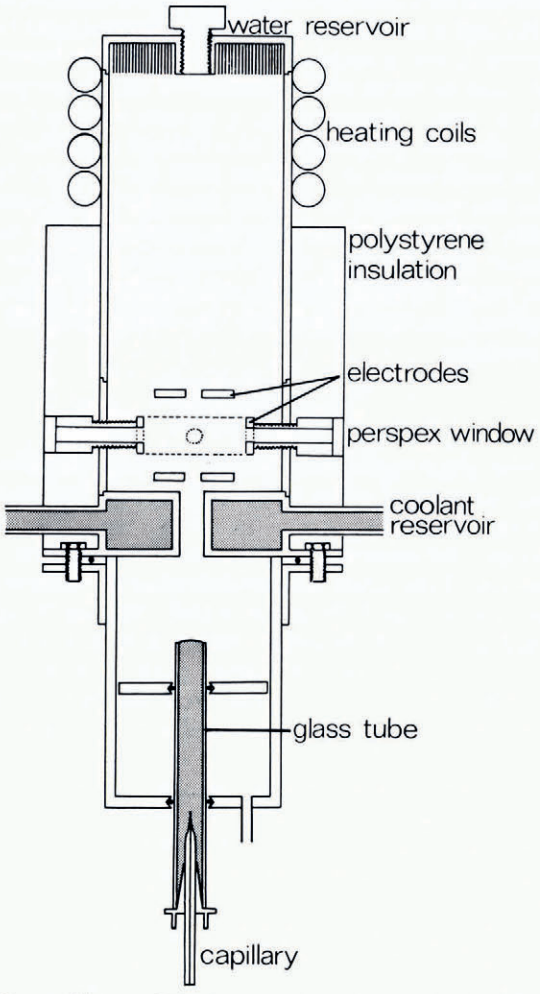

Fig. 1. Diagram of the drop production and suspension chambers.

Wuerker and others. It consisted of three coaxial electrodes, the top and bottom electrodes being flat circular discs with a small hole in the centre and between which a d.c. potential was applied, the lower electrode being earthed, whilst the middle electrode was cylindrical and had an a.c. potential applied between it and earth. It had four small holes equally spaced around the cylindrical surface and was supported by four ebonite cylinders which were hollow, two with perspex end-plates to permit illumination and observation, one connecting the electrode to a transformer, and the fourth containing a thermocouple which was thus located at the same level in the diffusion chamber as the supported drop. This apparatus permitted drops in the radius range 10 to 100 μm to be stably suspended.

The diffusion chamber, which had a volume of about 1 l, was of the type used by Hallett and Mason (1958). It was employed in an effort to produce large supersaturations which would render visible any ice particles ejected during the freezing of a drop. In fact, the presence of the upper electrode prohibited the achievement of a supersaturation, the measured relative humidity in the suspension region being about 90% with respect to ice.

Illumination was provided by a mercury arc lamp, condenser lens, heat filter, and auxiliary lens. Observation was through a microscope mounted at right-angles to the incident illumination. With this arrangement it was a simple matter to distinguish between the liquid and solid states. The microscope could be fitted with a calibrated vernier eyepiece to measure visually the diameter of the frozen drop. Alternatively, a 35 mm camera was used.

The signal from the induction ring was fed to a voltage amplifier, the output from which could be displayed on an oscilloscope or, together with the voltages applied to the electrodes and the output from the thermocouple meter, fed through the necessary allied circuitry to a multi-channel ultra-violet recorder so that these parameters might be constantly monitored during each observation of drop freezing, and subsequently analysed.

Wuerker and others (1959) showed that the maximum a.c. potential difference V_{ac}, for which a drop of charge-to-mass ratio Q/m may be stably confined within their electrode system is given by the equation

$$\bar{V}_{ac} = \frac{A\Omega^2 z^2}{16}\frac{Q}{m} \qquad (1)$$

where $\bar{V}_{ac}$ is the peak value of the applied alternating potential difference of angular frequency Ω, A is a dimensionless constant of value 0.908 and z is the spacing of the d.c. electrodes. To determine whether this expression was valid for our electrode system, drops of known charge were introduced into the apparatus and allowed to evaporate whilst the a.c. potential was held constant. The size of the drop was monitored as it evaporated, using the calibrated vernier eyepiece and microscope, and the size at which the drop became unstable was noted. Assuming an insignificant fraction of the initial charge to have been lost during evaporation, values of A were determined from the measured charge and the final size and found to approximate closely the theoretical value, ranging from 0.89 to 0.91. In view of the difficulty in determining the size of the drop at precisely the moment of instability, the agreement is satisfactory.

A typical variation of temperature along the vertical axis of the apparatus, and therefore passing through the suspension point of the drop, which is at the centre of the electrode configuration, is shown in Figure 2. The temperature gradient at this point is about 0.2 deg mm^{-1}, so that the temperature difference across the vertical extremities of a drop in a typical experiment is about 0.02 deg.

This system was used to study the freezing behaviour of drops of radius R ranging from 25 to 90 μm at temperatures between 0 and −30°C. The drops could be retained at the suspension point throughout the freezing process—and for many minutes before and after freezing, if required—and their charge-to-mass ratio could readily be determined, in about two seconds, using Equation (1) at any selected times during its period of suspension. The values of Q/m obtained by measuring the d.c. field required for levitation were less accurate than those obtained from measurements of V_{ac}, but were in reasonable agreement with them, differing by not more than 10%.

Having optimized the environmental parameters within the diffusion chamber, the electrode potentials were adjusted to approximately those required to accommodate the charge-to-mass ratio of the incoming drop. The drop would usually settle in an oscillatory mode slightly away from the equilibrium position. The potential across the d.c. electrodes was adjusted to bring the drop to the equilibrium position, where it would be stably supported. Its charge-to-mass ratio was determined, as described previously. This measurement would take several seconds, sufficient for drops in the size range studied to reach thermal and solution equilibrium. The drop would slowly evaporate, necessitating a gradual reduction in the d.c. potential required to maintain the stable equilibrium position.

Several techniques were employed to nucleate the drop to ascertain whether the method of nucleation affected the manner in which the drop froze. Drops supercooled to below approxi-

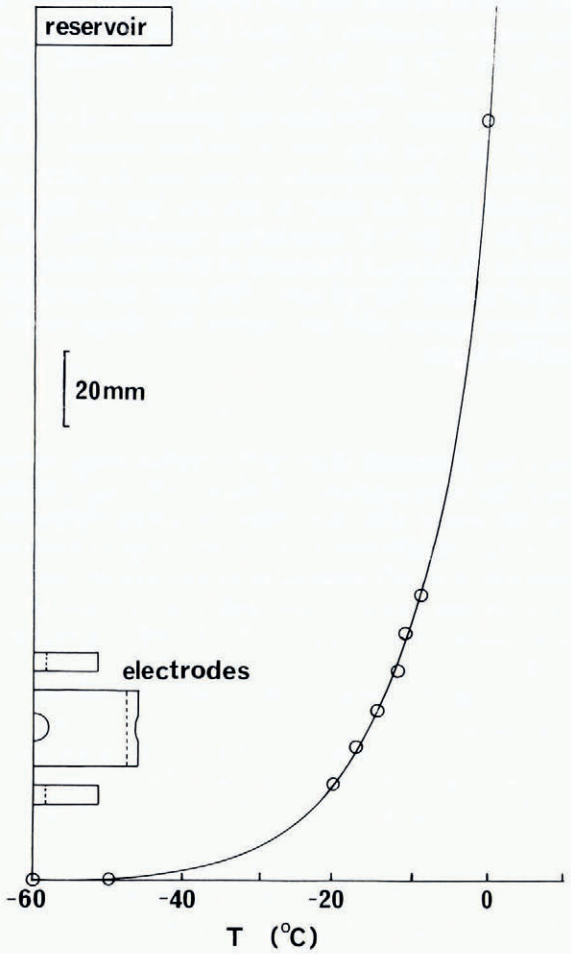

Fig. 2. Typical variation of vertical temperature gradient in the suspension chamber.

mately −15°C often were self-nucleated, presumably by impurities within the drop. At higher temperatures, drops were nucleated either with small ice crystals produced by a cold metal rod, or by the introduction of a small quantity of silver iodide into the chamber. This latter method could only be used towards the end of a period of observation prior to dismantling the apparatus since considerable contamination resulted. In either case, the mass and charge of the nucleating particle were negligible compared to the mass and charge of the drop. No distinction was observed in the manner in which a drop froze for the various methods of nucleation.

Immediately the drop was frozen, its charge-to-mass ratio was again determined. The change in charge-to-mass ratio on freezing resulted in the drop being displaced from the equilibrium position, to which it could be restored by adjustment of the d.c. potential difference. It would have been most desirable to determine the charge on the frozen product, but it was found impossible to return the drop through the induction ring, either by merely switching off the electrodynamic field or by applying a suitable d.c. voltage pulse to propel the frozen drop out of the containment field.

Several checks were made to ensure that the results obtained were not spurious or grossly unrepresentative of the natural situation. It should be stressed that the a.c. electric field at the suspension point was *zero*. The d.c. field was typically around 5 V m^{-1}, a modest value. The charge carried by each of the drops was close to 3×10^{-13} C which is about one-tenth of the Rayleigh instability threshold. The electrical pressure in the drop surface was therefore two orders of magnitude less than that due to surface tension, and could be neglected. Although the field gradient at the suspension point was not zero, the force between the induced dipole-field gradient is of the order of one per cent of the direct field-charge force for drop charges around the 3×10^{-13} C used in our experiments. The frequency of the a.c. field was 50 Hz, whereas the vibrational frequency of the drops, determined from the Rayleigh equation, was in excess of 12 kHz for all sizes. We may feel confident, therefore, that the electrodynamic containment system did not subject the drops under investigation to any significant unrepresentative forces.

3. Results

The freezing of some one thousand drops in the radius range 25–90 μm at temperatures varying from 0 to −29°C has been studied. Of this number, 45% of the freezing events were discounted, usually for the reason that nucleation occurred within one second of the drop entering the chamber, giving insufficient time for the drop to achieve equilibrium with its environment or any measurement of charge-to-mass ratio to be made. Of the valid freezing events observed, accurate measurements were made on 76 drops of (1) their size, (2) their initial charge, (3) their charge-to-mass ratio prior to and following freezing, and (4) the environmental temperature.

The 549 freezing events regarded as acceptable could be subdivided, on the basis of visual observation, into several categories as shown in Table I. In the great majority of cases (377 drops) freezing was completed within a fraction of a second of nucleation, as revealed by the fact that the charge-to-mass ratio Q/m, which changed abruptly on nucleation, then remained constant. The measured change in d.c. potential required to restore the frozen drop to its equilibrium position indicated that Q/m increased typically by between 5 and 15%. During and after the freezing event there were no visible products of freezing ejected from the drop, which itself showed no gross departure from sphericity. That this was so was confirmed by the fact that the drop frequently rotated about a vertical axis.

Though this was the most common mode of freezing, there were three significant departures. In some 18% of freezing events (though very much more frequently for drops which nucleated and froze within one second of entering the chamber) various surface irregularities were formed. These ranged from small bulges to spicules up to one drop radius in length. Such a deformed drop always orientated itself in the electrodynamic field with the deformation

Table I. Frequency of occurrence of various modes of freezing

Mode of freezing	*Number of drops*	*Increase in (q/m) %*	*Temperature range °C*
"common"	377	5 to 15	0 to −29
spikes and bulges	98	5 to 15	−5 to −25
splinters	19	5 to 15	≈ −15
secondary mass loss	53	4 to 12†	−1 to −15
Rayleigh freezing	2*	decrease	−10
drop splitting	1	≈5	−8
Total	549		

* out of 100 drops in a separate study.
† per event; some drops exhibited multiple recoils.

uppermost. As in the previous case, the increase in charge-to-mass ratio was in the region of 10% and there was no visible production of secondary particles throughout the range of sizes and temperatures investigated.

Visible splinters were observed, however, for 19 of the drops studied. They could be readily identified as ice, owing to the characteristic specular reflection from their surfaces. Since they evaporated some twenty drop diameters from the surface of the freezing drop and their visible lifetime was only about one second it was impossible to determine precisely the number of splinters ejected per freezing event. A rough estimate is that this figure lay between 20 and 50. Although visual observations of this rapid and infrequently occurring phenomenon could be misleading, and photographs of this effect were not obtained, it appeared that the splinters were produced over a wide area of the surface of the freezing drop, being then rapidly swept upwards in the electric field. The increase in Q/m of the parent drop was around 10%.

The third significant variation of freezing mode was identical to that of the majority of drops, as originally described, but with the additional effect that, at various times after the original nucleation of the drop, the by now completely frozen drop exhibited secondary step-changes in the charge-to-mass ratio, again always increases. 53 of the drops studied exhibited this secondary change, of which roughly half experienced one such event, whilst the other half exhibited a series of such events up to six in number, over a period of up to a few minutes.

The increase in Q/m per event was usually in the range 4 to 12%, with 20% being a typical overall value for drops which exhibited multiple events.

Two rare occurrences are perhaps worthy of mention. On one occasion a drop neatly split in half very shortly after freezing, the two halves being fused together at a point on the rim of each hemisphere. No secondary particles were observed, and the charge-to-mass ratio increased by 5%. Secondly, on two occasions out of approximately one hundred observations in a separate study, drops which were allowed to evaporate down to the Rayleigh limit and which were not artificially nucleated, froze on disrupting. Under these circumstances, the charge-to-mass ratio decreased. No secondary particles were observed.

Unfortunately the small size and confined location of the drops made it extremely difficult to obtain good photographs of these various types of freezing event. However, Figure 3 gives some indication of the size and shape of bulges which occurred during some freezing events, and of one frozen drop in which freezing has apparently occurred along clearly defined planes. Analysis of the evidence indicated that there was no apparent connection between the various types of freezing event and temperature, drop-size, or the manner of nucleation.

On freezing, the charge-to-mass ratio of the drop increases, that is, either the charge increases or the mass decreases or a combination of both occurs. It is difficult to see how charge might be gained by the freezing drop, particularly in view of the fact that reversing the polarity of the drop charge and d.c. suspension potential produces no apparent change in the pattern described above. If we assume therefore that the charge on the frozen drop is the same before and after freezing, then the change in charge-to-mass ratio is directly attributable to a change in the mass of the drop, which can be calculated. Since charge may in fact be lost during the freezing process, this change Δm in the mass of the drop must be regarded as a minimum value. In Figure 4 we present measured values of the minimum fractional mass loss $\Delta m/m$ for 76 drops of radii R ranging from 30 to 90 μm frozen at temperatures T between 0 and −29°C. The initial mass was determined either from the measurement of charge-to-mass ratio and the initial charge of the drop, or from a direct measurement of drop size immediately after nucleation using the calibrated vernier eyepiece. Both techniques were used for a number of drops and the agreement between the two results was excellent. It is seen from Figure 4 that values of $\Delta m/m$ lie typically in the range 5 to 15%. Subsidiary studies demonstrated that the errors in $\Delta m/m$ resulting from loss of charge or mass by the drop prior to nucleation were negligible: these experiments were performed using evaporating charged drops at temperatures above 0°C.

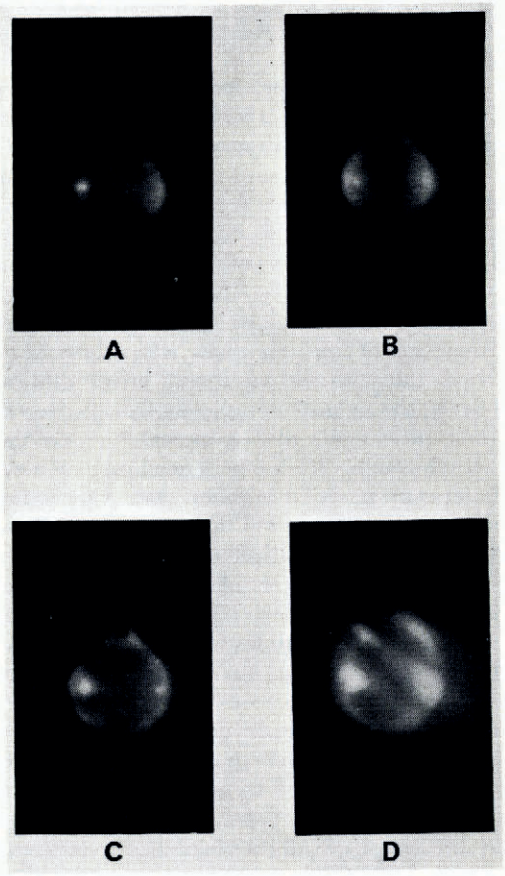

Fig. 3. Four frozen drops supported in the electrodynamic field, showing: A, *approximate sphericity;* B, *slight bulge;* C, *large bulge;* D, *a drop which had apparently frozen along clearly defined planes. All the drops have a radius of approximately 75 μm.*

Curve A in the figure provides a theoretical relation between the evaporative mass loss $\Delta m/m$ and temperature T derived from the expression

$$\frac{\Delta m}{m} = \frac{L_f D \Delta\rho (1 - C_w \Delta T / L_f)}{K_a \Delta T + L_v D \Delta\rho} \qquad (2)$$

which follows from considerations of the heat losses during freezing resulting from conduction and evaporation. L_f is the latent heat of fusion, L_v that of sublimation, K_a the thermal conductivity of the air in the vicinity of the drop, D the diffusion coefficient of water vapour molecules in air, C_w the specific heat of water, ΔT the degree of supercooling of the drop prior to nucleation and $\Delta\rho$ the difference between the saturation vapour density at 0°C and the actual vapour density in the chamber around the suspension point. $\Delta\rho$ was calculated on the basis that the relative humidity close to the drop was 90% with respect to ice for all measurements; in fact, the predicted values of $\Delta m/m$ are insensitive to the value of relative humidity. It is evident that almost all experimental points lie above the curve, indicating that either the evaporative mass loss was greater than predicted or some additional mechanism of mass loss was present. To underline this point we also present (curve B) in Figure 4 values

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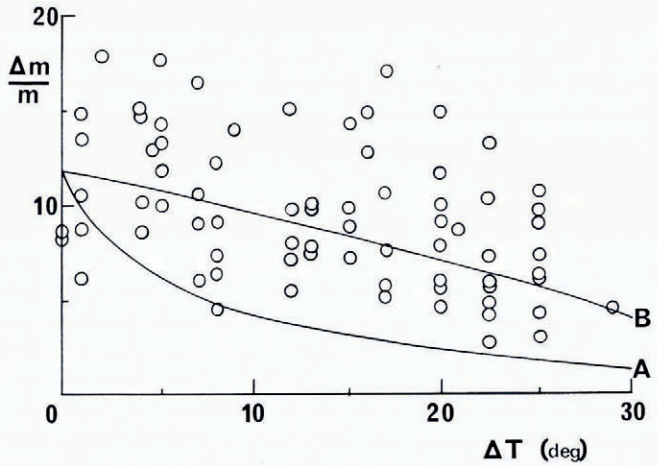

Fig. 4. Variation of the measured values of percentage mass loss, $\Delta m/m$ with degree of supercooling ΔT. Curve A is the calculated variation of evaporative mass loss for a drop in an environment of 90% relative humidity with respect to ice. Curve B is the maximum evaporative mass loss assuming no conduction between a drop and its environment.

of mass loss which would occur if thermal conduction was negligible (i.e. $\Delta m/m \rightarrow L_f(1-C_w\Delta T/L_f)/L_v$). Even with this extreme and unrealistic assumption many measured values of $\Delta m/m$ lie above the theoretical curve. There will also exist some evaporative mass loss as the frozen drop rapidly cools down towards the air temperature T_a. However, this effect is small, increasing the values of $\Delta m/m$ derived from Equation (2) by factors of only about 1.01 at -2°C and 1.1 at -20°C.

Figure 5 shows that the fractional mass loss on freezing is insensitive to the radius R of the drop. Further measurements, not presented here, yielded the reassuring findings that the values of $\Delta m/m$ did not depend upon either the initial charge carried by the drop or its initial charge-to-mass ratio.

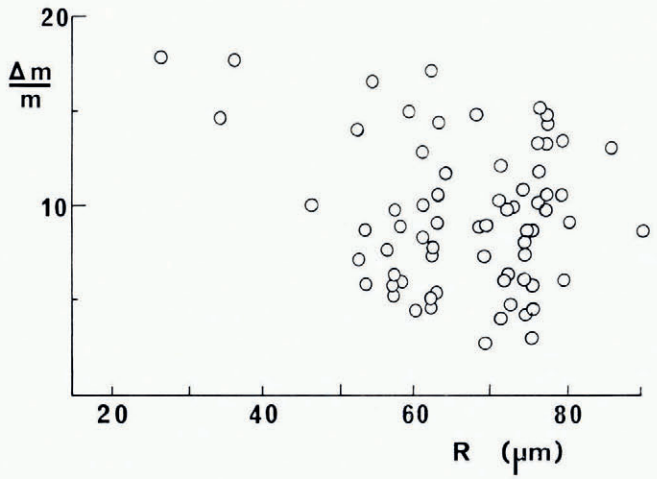

Fig. 5. Variation of measured values of percentage mass loss $\Delta m/m$ as a function of drop radius R.

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4. Discussion

The freezing time τ_f of a supercooled drop may be defined as the time from the instant of nucleation until the drop is completely solidified. Johnson and Hallett (1968) constructed a simple model of drop freezing, viewed as a quasi-steady-state process, and showed that the freezing time may be given by the expression

$$\tau_f = \frac{\rho_w L_f R^2}{3F} \frac{(1 - \Delta T C_w / L_f)}{(K_a \Delta T + L_v D \Delta \rho)} \tag{3}$$

where ρ_w is the density of water, C_w its specific heat capacity, R the drop radius, and F a ventilation factor. Nix and Fukuta treated the problem of the freezing of a stationary drop as a non-steady-state process, deriving the evolution with time of the temperature and vapour density fields. However, their predicted values of τ_f are in good agreement with those determined from Equation (3). In our experiments, with the drop suspended motionless in the electric field, the ventilation is by free convection and F involves the Grashof number (Gr). However, for the ranges of drop-size and temperature employed F varies only from about 1.0 to 1.1. Equation (3) predicts that the freezing times for the largest, warmest drops utilized would be several seconds and should therefore be measurable; for example, with $R = 90$ μm and $\Delta T = 2°C$, $\tau_f \approx 10$ s. It was quite clear from visual observation of the drops that their charge-to-mass ratio stopped changing well within one second of nucleation. If we assume that during freezing the rate of evaporative mass loss is approximately constant, as is predicted on the classical theory and is a consequence of the fact that the surface temperature is at or close to 0°C throughout this process, we are forced to the conclusion that the freezing times for the drops studied in our experiments were substantially shorter (perhaps typically by an order of magnitude) than those predicted. This conclusion is underlined by the observation, made in subsidiary experiments on evaporating warm drops, that the position of the drop in the field changed constantly as long as its charge-to-mass ratio was changing.

It is clear from Figures 4 and 5 that the fractional mass loss $\Delta m/m$ is generally greater than that predicted on the classical picture of evaporation during freezing. This additional mass loss could be due either to enhanced evaporation or the ejection of water or ice from the freezing drop. The variability in the individual measurements of $\Delta m/m$ suggests that the ejection of mass is the more likely explanation. Again, it should be stressed that the scatter in the results is not attributable to inaccuracies in the experimental technique—a series of experiments showed that in a reproducible situation, such as the evaporation of charged drops down to the Rayleigh bursting threshold, results were consistent to a high level of accuracy. It is not possible to state unequivocally whether ice or water was ejected during freezing. However, since ice splinters were very readily visible on the few occasions when they were observed it appears more likely that the additional mass loss is due to the ejection of water droplets.

The observation of ice particles produced by several drops supercooled to −15°C, which evaporated some twenty drop diameters from the surface of the parent drop, is consistent with the magnitude and extent in space of the supersaturation wave proposed by Nix and Fukuta (1974). Further evidence on this point has been provided by the recent photographs of Magono and Iwabuchi (in press). The reason that ice particles were not observed at higher temperatures is probably that the maximum supersaturation was insufficiently high. The possibility that the observed ice particles were due to the activation of hitherto quiescent ice nuclei by the supersaturation wave, rather than originating from the freezing drop itself, can be discounted on the grounds that such transient fluctuations in the ice nuclei concentration in the vicinity of the drop are incompatible with the clean, stable environment in the chamber.

The observed production of spikes, bulges, and ice splinters, together with the occurrence of secondary mass losses, which together account for 30% of the observations, are suggestive

of ice particle ejection from the freezing drop. Johnson and Hallett (1968) concluded that the production of spikes was dependent on the formation of a strong ice shell during symmetrical heat transfer to the environment, and as such was unlikely to occur when drops of raindrop size were ventilated at their terminal velocity. On the other hand, Pitter and Pruppacher (1973) reported that a noticeable fraction of the drops of radii between 200 and 350 μm frozen in a vertical wind tunnel developed pronounced knobs or spikes. It seems clear that ventilation is not the only factor involved in the production of protuberances during freezing. It appears probable that the absence of realistic ventilation of the drops used in the present experiments did not seriously affect their freezing behaviour.

The observations which appear most strongly indicative of the ejection of ice splinters are those of secondary recoils, some of which were multiple events, occurring many seconds after freezing was complete. Thermal stresses would have decayed to insignificant values by this time, and could not be responsible for these observations, but huge mechanical stresses associated with the production of an ice shell can persist for very long periods and could provide an explanation. It may be relevant to mention that Gold (1967) made measurements of the time required to produce large cracks in ice as a result of the application of stress. Times of many hours were found when the stress was low, decreasing rapidly as the stress increased. However, accurate measurements of the numbers of ice particles ejected during these secondary recoils must be made before it can be established whether this process might be important in ice particle multiplication in supercooled clouds.

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