Droplet accretion during rime growth and the formation of secondary ice crystals

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SUMMARY

Laboratory experiments have been performed to study rime growth and its relation to secondary ice crystal production (the Hallett–Mossop process). The rime was grown in a wind tunnel on a fixed vertical fibre 0.5 mm in diameter. The range of conditions extended from \(-1.0^\circ\)C to \(-13^\circ\)C in temperature, from 20 cm s\(^{-1}\) to 200 cm s\(^{-1}\) in air speed, and liquid water content up to 1.5 g m\(^{-3}\). The droplet size distributions were 5 to 25 \(\mu\)m and 8 to 50 \(\mu\)m, peaking at diameters of 9 and 22 \(\mu\)m respectively. Under conditions favourable for secondary ice production, the accreting droplets spread out on the ice surface; individual frozen droplets formed only at the lower temperatures. A separate experiment showed that supercooled water droplets froze as cones on a flat surface above \(-10^\circ\)C. At temperatures between \(-1^\circ\) and \(-4^\circ\)C the spreading ratio of supercooled droplets on the basal surface of ice was less than on other faces, with lower molecular packing density. It is hypothesized that spreading takes place in a quasi-liquid layer which is thinner on the basal surface. Splinter formation by pressure build-up inside individual frozen droplets is therefore unlikely to be responsible for shatter; a new model is suggested in which thermal gradients give stresses leading to an ice crack at about \(-5^\circ\)C.

1. INTRODUCTION

On occasion, aircraft observations show ice crystal concentrations in clouds in excess, by as much as a factor of \(10^4\), of that expected by measurement of ice-forming nuclei by conventional techniques. Several mechanisms have been suggested to explain these observations:

(a) An early suggestion was that freezing droplets produced splinters by shattering under increased internal pressure resulting from the expansion of water as it transformed to ice by freezing symmetrically inwards. Earlier studies (summary in Mossop 1985) have shown that under atmospheric conditions, droplets <50 \(\mu\)m diameter do not shatter, while large droplets do not produce sufficient numbers of particles.

(b) There is some evidence that ice crystals fragment in clouds, possibly on collision (Hobbs and Farber 1972; Vardiman 1978). This was based on observations of stellar and dendritic fragments, although columnar and plate fragments were not observed.

(c) Fragmentation may take place during ice particle melt and evaporation. Knight (1979) pointed out that surface tension tended to pull water away from a uniform coating over a cylindrical ice surface which then accumulated at preferred places along the cylinder. With repeated melting and freezing, connecting bridges became thinner, eventually melted and broke. Recent experiments (Oraltay and Hallett, 1989, to be published) have demonstrated that dendrites and needles, both individually and as aggregates, break up on melting and to a lesser extent on evaporation, to give an enhanced particle concentration.

(d) Experiments reported in Hallett and Mossop (1974) and Mossop and Hallett (1974) showed that secondary ice particles were ejected during riming growth at temperatures between \(-3^\circ\)C and \(-8^\circ\)C with peak production at about \(-5^\circ\)C. The efficiency of the process depended on the concentration of large droplets \(\geq 24 \mu\)m. Further experiments (Foster and Hallett 1982; Heymsfield and Mossop 1984) showed that splinter production was a function of the ice surface temperature rather than ambient temperature. It was hypothesized that droplets could shatter when they froze on accretion, if a symmetrical
ice shell formed (Brownscombe and Hallett 1967). The pressure build-up inside the shell would lead to shatter, as in the case of an individual drop. This situation is optimized when droplets accrete at the tip of several droplets frozen in line, so that a balance occurs between heat flows into the ice and through the air. This process has been demonstrated in simulation experiments (Choularton et al. 1978, 1980).

The present experiments were planned to test the shell theory of secondary ice production. The riming process was simulated under controlled conditions of temperature, accretion velocity and drop size distribution which occur in the atmosphere. In particular the experiment was designed to show whether droplets spread out or froze individually as they accreted on an ice surface.

2. EXPERIMENTAL PROCEDURE

Accretion studies were carried out in a horizontal wind tunnel which enabled events to be continuously recorded by photography or video tape as conditions were changed. The essential parts of the apparatus are shown in Fig. 1. The chamber working section is 2.5 cm high by 20 cm wide and 200 cm in length. The top and bottom aluminium plates were maintained at a uniform temperature, monitored throughout the experiment by thermocouples. The target was a glass rod 0.5 mm diameter mounted vertically at the end of the working section. This was replaced by stainless steel wire 0.8 mm diameter maintained at a constant potential for investigation of electrical effects. Water droplets were produced by ultrasonic nebulizers with frequencies of 800 kHz and 100 kHz. The droplet size distributions are shown in Fig. 2.

Droplets cooled during fall at terminal velocity through a vertical precooling tower 1 m high before entering the working section. The liquid water content was calculated from the mass accretion rate. It was found that droplets carry some electric charge when they are produced and the effect of this charge was investigated in a separate experiment.

Two blower fans at the ends of the conditioner gave an air speed from a few cm s\(^{-1}\) to 300 cm s\(^{-1}\); visual observation of the droplet trajectory showed that the flow is laminar in the chamber, consistent with a Reynolds number of about \(10^4\) for an air velocity of

![Figure 1. Schematic of the wind tunnel system.](image-url)
200 cm s\(^{-1}\). A moisture conditioner precooled and saturated air at any desired temperature before it entered the chamber. Rime grew into the wind direction, up to a length of several centimetres. Observations were made on the growing tip of these elements after growth of about 1/2 to 1 cm from the support in order to minimize thermal and aerodynamic effects.

In order to understand droplet accretion behaviour, droplet spreading rates on different ice crystal facets were examined in a separate experiment. Spreading on the basal ice surface was first studied because this surface was relatively easy to obtain. Crystals in the form of thin dendrites were grown in the surface of slightly supercooled deionized water (by 1 degC) and removed with tweezers. The water droplets produced by the 100 kHz ultrasonic nebulizer fell at terminal velocities through the temperature conditioner onto this ice surface. The surface was then photographed under a microscope and a comparison made between the maximum of the size distribution of the spread and of the original droplets. Photographs of the side view of spread droplets gave a direct view of the cross-section and measurements of the spreading ratio. Similar experiments were carried out on an ice facet cut at an angle of about 45\(^\circ\) to the basal plane. This surface was chosen because it would be expected to have relatively higher surface energy associated with the lower molecular packing on the plane in this direction, which would be expected to enable more spreading to occur.

3. Observations

The experiments showed considerable variation of rime shape over the range of study. Photographs of the rime obtained at different temperatures (\(-1.5 \text{ to } -13.0 \text{°C}\)) and air speeds (0.6 to 1.7 m s\(^{-1}\)) are shown in Figs. 3 and 4. The observations can be summarized:

(a) Effect of temperature. The rime formed by small droplets (distribution S) is quite different from that formed by large droplets. At higher temperatures (\(>-3\)°C) rime developed as clear fingers with a smooth surface and blunt heads. As the temperature
Figure 3. Influence of air velocity and temperature on rime formed by small droplets (distribution S).
Figure 4. Influence of air velocity and temperature on rime formed by large droplets (distribution L).
decreased, branches appeared, becoming thinner as the temperature decreased further. Below $-8^\circ C$, some droplets froze as individual spheres.

Rime formed by larger droplets (distribution L) at temperatures higher than $-3^\circ C$ had a lumpy appearance and a glazed smooth surface. As the temperature decreased, the surface of the rime became rugged. At about $-8^\circ C$ and lower, individual frozen spheres were observed, and the rime became porous and opaque. In both cases, at higher temperatures the individual ice elements were transparent without bubbles.

(b) Effect of wind speed. The diameter of fingers formed by small droplets and the separation between them vary with the wind speed; the higher the wind speed, the larger the finger diameter and the smaller the separation (Figs. 5 and 6). At lower temperatures, because of the presence of branches, the finger size and separation are difficult to measure.

(c) The effect of electrical charge. When the stainless steel wire target was maintained at a constant voltage $>1000\text{ V}$, the rime appearance changed strikingly. The rime tip broadened, the effect increasing up to the highest voltage used, $5\text{ kV}$. The process was reversible, the rime diameter returning to its original size as the potential was removed, as shown in Fig. 7. The droplets produced by the ultrasonic nebulizer were usually electrically charged, which could affect both collision efficiency and spreading ratio. The amount of charge on the droplets was estimated by using a Millikan oil drop apparatus saturated with water vapour to prevent drop evaporation. The minimum detectable charge by the method is $\pm 10^{-17}\text{ C}$ (about 100 electron charges) for a droplet of $10\ \mu\text{m}$ in diameter. The observed highest charge carried by the droplets was about $10^{-16} \pm 10^{-17}\text{ C}$ per droplet. Both positive and negative charges were observed.
Consider the target to be electrically neutral. Using the simple image method, the electric force between the droplet of diameter 10\(\mu\)m and the target is

\[
\frac{1}{4\pi\varepsilon_0} \frac{q^2}{r^2} \approx 10^{-12}\text{N},
\]

\(\varepsilon_0\) being the permittivity of free space, and taking charge \(q\) as the maximum droplet charge 10\(^{-16}\)C observed in the experiment, and the distance between the target and the droplet as the drop radius = 5\(\mu\)m. Taking the air speed, \(U\), as 1 m s\(^{-1}\), the viscous force is 6\(\pi\eta rU \approx 10^{-9}\)N (\(\eta\) = viscosity of air). The electrical force is therefore negligible under these assumptions. This conclusion was verified experimentally. The charges on water droplets were modified by ionization from a polonium source mounted at the outlet of the nebulizer. The air was ionized by alpha radiation which gives a Boltzmann distribution of charge on the droplets. Examination in the Millikan apparatus showed that the droplets were neutralized when they passed through the unit, with charges between \(±10^{-17}\)C.

When these neutralized droplets were introduced into the working section to form rime, no obvious changes occurred under any condition of the experiment.

(d) **Spreading of individual droplets.** Photographs of droplets spreading on the ice basal surface are shown in Fig. 8. The spreading factor is insensitive to temperature below \(-4\)°C, but increases dramatically when the temperature is above \(-3\)°C. At very low temperatures, below \(-18\)°C, the droplets still spread significantly on the ice surfaces. At all temperatures, droplets freeze as cones, rather than individual hemispheres. The spreading ratio (radius to height) is greater on high index surfaces than on the basal plane at temperatures between \(-2\) and \(-5\)°C. Figure 9 shows the difference of spreading droplets on the basal surface and on the high index surface which makes an angle of
Figure 7. The effect of electrical potential on rime finger diameter. The arrowed region grew with high potential.
about 45° with the basal plane. Figure 10 shows a comparison of the average spreading ratios of droplets of 20–25 μm diameter at different temperatures and on different crystallographic ice surfaces.

The effect of impurity in the water was examined by spraying solutions of NaCl. No significant effect on spreading ratio was found for concentrations below 10⁻³M. With increasing concentration, greater spreading was observed; the effect of 0.1 M is shown in Fig. 10. The diameter distributions of spread droplets on the basal surface at various temperatures are shown in Fig. 11 with the original drop size distribution for comparison. The mode of the initial distribution increases from 22 μm to 40, 50 and 60 μm at surface temperatures −10, −2.0 and −1.7 °C respectively. There is a tendency for larger droplets to spread more for a given temperature.

About 500 droplets were measured for each curve. Data were fitted to a curve by a nonlinear regression method, using the equation

$$Y = x/(B_1 x^2 + B_2 x + B_3).$$

The maximum for each case is determined to give the mode of the distributions, which are given above. The overall deviation of the drop percentage is 0.1%, and the maxima of each case are insensitive to the coefficients to give an overall estimate of the diameter of ±5 μm.

4. DISCUSSION

The above observations are important in understanding the influence of rime growth on secondary ice crystal production. As mentioned above, shell fracture has been suggested as being responsible for the Hallett–Mossop process, with ice splinter production resulting from build-up of pressure within droplets freezing individually and connected with each other by a narrow bridge to reduce heat transfer. Choularton et al. (1978) showed an electron micrograph of a 15 μm diameter droplet with spike, indicating the pressure build-up inside the drop. However, this shell was formed at −8 °C, which is the lower temperature cut off of the process.

Mossop (1980) carried out an experiment in which the ice shell was weakened by ammonia to reduce splinter formation. The experiment showed reduction of secondary ice crystal production near −5 °C when NH₃ was injected into the cloud. Spike formation in these experiments was obtained at about −8 °C, with water drops of diameter 1–2 mm suspended at the interface between layers of carbon tetrachloride and liquid paraffin. It is pointed out that neither experiment demonstrated direct evidence of relation between spike formation and secondary ice crystal production.

In our experiment, no individual frozen droplets formed at all under the conditions in which the Hallett–Mossop process takes place. This result agrees with the experiment by Foster and Hallett (1982) in which no individual frozen droplets were observed in the region in which the maximum secondary ice crystal production was observed. Some individual ice spheres were observed at about −8 °C and below, which were formed by low impact velocity drops.

In the later experiments on a rotating needle (Choularton et al. 1980) individual frozen droplets were observed along with protuberances. These observations are in apparent contradiction to our present results, where neither protuberances nor individual frozen droplets were observed in this particular temperature range, −3 to −8 °C. This difference also raises questions as to the carry-over of either experiment to the atmosphere. Graupel particles do not, generally, show the structure of ice fingers of Figs. 3 and 4. Two effects are important here: first, in the atmosphere, growth conditions of
Figure 8. Spread of droplets on basal surface of ice at different temperatures. The spreading ratio is nearly constant below $-3^\circ C$, but increases above $-3^\circ C$. Drops freeze as cones with a sharp tip on the top.
Figure 9. Spread of droplets on basal (a, b, c, d) and a high index ice surface (45° to the basal plane) (e, f, g, h) at -3°C. The spreading ratio is higher on high index surfaces.
Figure 10. Spreading ratio (radius/height) as a function of temperature for droplet diameter 22 μm falling at terminal velocity. Each point on the full lines represents the mean of 100 droplets; fewer droplets for the dashed line; the bars represent standard deviations. Full lines — basal plane. Dashed line — 45° to basal plane.

an individual particle change quite rapidly as it falls so that opportunity for growth under constant conditions over a significant part of its history is small. Second, particles falling beyond a Reynolds number ~200 oscillate, so that the angle of attack changes with a frequency 10–100 Hz or greater. Similarly, rime growing from fog at the surface of the earth is subject to turbulent fluctuation of wind speed and direction, which would tend to spread out the accretion direction.

It was estimated that the oscillation acceleration of graupel particles is a few g (Hallett and Mossop 1974). The acceleration of the rotating needle in the Choularton et al. rotation accretion experiment is ~50g, and there is cause for concern that droplets undergo outward trajectories under this flow and could easily give rise to the shapes observed.

The electrical charge carried by a droplet is about 10⁻¹⁶C which is about 0.1% of the Rayleigh limit (10⁻¹²C for a droplet of 10 μm in diameter). Thus, the effect of the electrical charge on spreading is also negligible. By contrast when the voltage on the rime target is raised to above 10³V, the electric field near the target surface will be above ~10⁴V m⁻¹, with a corresponding surface charge of about 10⁻⁴C m⁻², and the value of the electrostatic stress will be close to that of the surface tension force. In this case, the electrical charge will significantly increase the spreading ratio, as shown in Fig. 7.

Recalling the hypothesis that there is a transition layer on an ice surface (first suggested by Faraday 1860) we hypothesize the following interactions. Beaglehole and Nason (1980) using optical ellipsometry observed a transition layer at temperatures above −5 °C on the prism plane; Furukawa et al. (1986) observed the presence of such a layer above −4 °C on the prism surface and −2 °C on the basal surface. For higher index
surfaces, this temperature would be expected to be even lower as there is a lower surface molecular density and a greater probability for molecular mobility. In our spreading experiment, the contact angle of the drops on the basal surface rapidly reaches zero when the temperature is raised above $-2^\circ$C. These observations show that water droplets spread more on high index faces at temperatures around $-3^\circ$C, which is consistent with the observations of Furukawa et al. on the basal and prism plane of ice. The spreading rate of droplets into such a shallow layer is a complex process and has been analysed in detail by Gennes (1985) for a non-freezing situation. Bulk flow is preceded by a foot which is itself preceded by an adsorbed layer. In the present case, upward freezing of the foot would become important as the outward spreading rate decreased to the upward freezing rate.

A question arises when the temperature decreases: why do supercooled water drops still spread on an ice surface where the transition layer no longer exists? It is suggested that this results from the relatively long freezing time compared with the drop deformation time. Suppose a drop of diameter 10 $\mu$m starts freezing when it touches the ice surface at $-5^\circ$C; the released latent heat will be rapidly transferred to the surroundings, raising the ice surface temperature near the drop to 0 $^\circ$C in $10^{-4}$ second. The deformation time may be estimated from drop size and impact velocity; it is of the order of $10^{-4}$ second for an impact velocity of 100 cm s$^{-1}$. The freezing time estimated by Hallet (1964) is about $10^{-3}$ second for 10 $\mu$m droplets. Therefore, the drop will spread on the ice surface on which a temporary transition layer forms at the higher temperature caused by released latent heat before the freezing is complete. If the impact velocity decreases to 1 cm s$^{-1}$ and temperature decreases to $-10^\circ$C, the freezing time will be shorter than the deform-
ation time, and the drop freezes as an individual hemisphere on a flat surface. The observed increased spread of NaCl solution droplets and the lowering of the critical temperature for wetting is consistent with these ideas, as solute rejected on freezing would be expected to lower the equilibrium melting point and extend the transition layer to lower temperatures.

At the terminal velocity of graupel particles of 1 m s$^{-1}$, the ratio of the kinetic energy to the surface energy of the droplets is of order 0.01, which is far too low by itself to cause spreading under conditions of these experiments (Hallett and Christensen 1984). It is therefore concluded that the spreading observed comes about as a result of the nature of the ice surface and results in a reduction of energy of the system.

There is a further consideration in that the freezing of a cloud droplet 10–20 μm diameter is probably quite different from a millimetre drop. The large drop freezes as bulk water with dendrites growing throughout the bulk liquid as shown by Hallett (1964). Those studies also showed that both the radius of the dendrite tip and the dendrite separation decreased with increasing supercooling, being 30 μm at −2 °C and 20 μm at −5 °C. Thus for cloud droplets, the size of the dendrite tip is of the same order as that of the droplet and a quite different freezing process would be expected to take place. This is difficult to observe under the conditions of accretion in the tunnel, but it implies that a shell will not form.

From these considerations, the shell theory is unlikely to be the mechanism of the Hallett–Mossop process. We must therefore consider other mechanisms. Thermal shock was for a long time considered a possible fracture mechanism. King and Fletcher (1976) proposed a model of the thermal shock which led to a negative result. We consider a different model which involves an ice cylinder formed by the individual deformed droplet rather than the ice substrate. Supposing the temperatures of the original droplets, ice particle and ambient air are the same, the solidification starts on the liquid–ice interface, and then continues up to the surface. The surface will be warmed up to near 0 °C as latent heat is released. In the extreme case, the temperature difference between ice substrate and new surface is equal to the degree of supercooling. Subsequently, the surface temperature falls and leads to contraction. Such an idealized process is shown in Fig. 12. According to the classical theory of thermal expansion the upper surface size change is proportional to $r\Delta T$, where $r$ is the diameter of the cylinder and $\Delta T$ is the temperature change. When the overall temperature falls to ambient, this gives a shear stress, $\gamma = G(\pi r / h)\Delta T$, where $h$ and $r$ are the height and base radius of the spread droplets. Using Young’s modulus $E = 9.3 \times 10^4$ bar; $G = (E/2)(1 + \nu)$; Poisson’s ratio $\nu = 0.32$; coefficient of thermal expansion $\alpha = 5 \times 10^{-5}$ K$^{-1}$ (Fletcher 1970) and a critical shear strength $\gamma_c \approx 10$ bar, the calculated value of the stress at −5 °C is just enough to cause ice failure. At above −3 °C, the accreted droplet rapidly spreads to a thin layer and freezes upward without a large stress build-up. Therefore, the Hallett–Mossop

![Figure 12. Simpistic model of drop break-up during freezing and differential contraction on an ice surface.](image-url)
process will not occur at temperatures above $-3\,^\circ C$. As temperature decreases, the shear stress of the ice layer increases. The ultimate strength of ice depends on the way in which ice is formed, the shape and size of the specimen, and the way in which the stress is applied. In the temperature range of interest ($0 \sim -10\,^\circ C$), the freezing time differences vary by a factor of 100. In addition, the solubility of air in supercooled water increases with decrease of temperature, so that smaller and more concentrated air bubbles will be formed at lower temperatures because of higher freezing rates and air concentrations (Johnson and Hallett 1968; Bari and Hallett 1974). These bubbles will make the ice more plastic, as will air incorporation into the ice lattice at a molecular level. The importance of this process is evident from the role of NH$_3$ in Mossop's experiment. The probability of crack formation will therefore be reduced, leading to a lower limit for the shatter process. A possible shatter site is shown in Fig. 13.

To complete the discussion, we explain the effect of electric charge on riming rate which was shown in the experiment in Fig. 7. The charged ice target can collect water droplets more efficiently. Calculation shows that electrical forces on a water droplet larger than $10\,\mu m$ in diameter in a non-uniform electric field may increase to the same order as that of the viscous force. In the case in Fig. 7, the estimated field strength is $10^5$ to $10^6 Vm^{-1}$, the electric force applied to the water droplets near the target is about $10^{-9} N$, of the same order as the viscous force. This means that the trajectories of the droplets will be considerably affected and collision efficiency will increase. Because the local field near surfaces of ice particles could be much stronger than the external field, particularly near sharp corners of the particles, the field strength required to influence collision efficiency will be lower than the above value. This result agrees with Latham
(1979) who found a threshold field of $10^5 \text{V m}^{-1}$ for increasing growth rate, which increased rapidly in the presence of even larger fields. Once the droplet has accreted, the spread rate is enhanced by the effective reduction in surface tension by the surface charge, which reduces the probability of secondary ice production in such strong electric fields.

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