Air bubbles in accreted ice

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SUMMARY

On the assumption that the concentration of air bubbles formed in freezing water is a function of the freezing rate, an expression for the concentration of air bubbles in accreted ice has been deduced. This expression has been confirmed by measurements of the bubble concentrations and size distributions in frozen bulk water and in ice accreted on rotating cylinders. Consequently, in both the wet and dry growth regimes it is the rate of freezing which essentially determines the bubble concentration. The size distribution of bubbles is determined by the amount of air available for bubble growth. This depends on the rate at which air diffuses out of the individual droplets during the freezing process. In the wet growth regime the freezing rate depends on the rate at which heat is dissipated from the accreting object by forced convection and also, depending on the fraction of unfrozen water, on the way in which the spongy deposits are finally frozen.

In the dry growth regime the freezing rate of the accreted droplets depends on their size and speed of impact, since these determine the extent to which the droplets spread, and on the temperature of the deposit.

The air bubble concentrations and size distributions were determined using ordinary optical microscopy so that only bubbles of radius greater than 1 μm were counted and sized. In the dry growth regime the visible bubble concentrations range from about $10^4$ to $10^6$ cm$^{-3}$, depending primarily on the deposit temperature. The mean radii of the bubbles in the deposits range from 1 to 4 μm. In the wet growth regime the bubble concentrations generally lie between $10^2$ and $10^4$ cm$^{-3}$ while the mean radii of the bubbles range from 10 to 50 μm. Consequently, the two growth regimes may be readily distinguished.

LIST OF SYMBOLS

- $c_i$: specific heat of ice
- $c_w$: specific heat of water
- $E(r)$: collection efficiency of cylinder for droplets of radius $r$
- $E(r, \theta)$: local collection efficiency of cylinder for droplets of radius $r$
- $f(r)$: frequency distribution of droplets
- $F$: freezing rate
- $\bar{F}$: mean freezing rate of droplet distribution
- $h$: average height of spread droplet
- $l$: depth of penetration of heat
- $L_f$: latent heat of fusion of water
- $n$: mean concentration of air bubbles
- $n(F)$: concentration of air bubbles formed at freezing rate $F$
- $N(r)$: number of air bubbles formed in droplets of radius $r$
- $r$: radius of droplet
- $r_b$: radius of air bubble
- $R$: radius of accreting cylinder
- $S$: spreading factor of droplet (ratio of radius of spread droplet to initial radius)
- $t$: variable time
- $t_f$: time of freezing of spread droplet
- $T_a$: ambient temperature
- $T_d$: temperature of ice deposit
- $T_m$: melting temperature of ice
- $T_w$: temperature of water sample
- $v_0$: impact speed of droplet
- $V$: airspeed
- $W$: liquid water concentration
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\( \theta \) \hspace{1cm} \text{cylindrical co-ordinate}

\( \theta_{m} \) \hspace{1cm} \text{maximum value of } \theta \text{ beyond which no deposition occurs}

\( \kappa_{i} \) \hspace{1cm} \text{thermal diffusivity of ice}

\( \rho_{i} \) \hspace{1cm} \text{density of ice}

\( \rho_{w} \) \hspace{1cm} \text{density of water}

\( \sigma \) \hspace{1cm} \text{surface tension}

1. INTRODUCTION

One of the characteristic features of hailstones is that they are commonly composed of alternate layers of clear and opaque ice. A sketch made by Volta in 1800, reproduced in the journal *Nubila*, is typical of the numerous drawings and photographs which now abound in the literature (see, e.g., Mason 1971). Coste (1940) put forward the view that the opacity of ice produced by riming is due to air bubbles released during the freezing of the individual droplets. This was substantiated by Macklin (1962) who carried out a microscopic examination of accreted ice deposits formed in the dry growth regime. He found that clear ice is formed only when the temperature of the deposit, determined by the balance between the rate of liberation of latent heat from the freezing droplets and the rate at which this heat can be dissipated to the surrounding air by forced convection, is close to 0°C. He inferred that the reason for this is that, in this circumstance, the manner of freezing of the accreted water is like that of a liquid film. This permits virtually all of the dissolved air to escape by diffusion and by the migration of bubbles to the surface. Opaque ice is formed when the rate of accretion of droplets is such that the deposit temperature falls below 0°C by at least a few degrees. However, opaque ice is also formed in the wet growth regime when the rate of accretion is sufficiently high, and the ambient (droplet) temperature is sufficiently low, for the deposit to become spongy (List 1959; Macklin 1961). The freezing is then more like that of bulk water. Bailey and Macklin (1968) have grown artificial hailstones in both the dry and wet growth regimes at low ambient temperatures, which appear equally opaque. The dependence of the opacity of accreted ice on the deposit temperature and on the liquid fraction of spongy ice has been depicted qualitatively by Brownscombe and Hallett (1967, Fig. 9).

The first systematic study of the size distributions of air bubbles in hailstones was made by List, Murray and Dyck (1972). They made planar cuts through the centres of a number of hailstones and then replicated the surfaces using formvar. The air bubbles which had been sliced produced holes in the replica and these were counted and sized. The planar concentration of bubbles and the planar size distributions thus obtained are statistically related to the volume concentrations and distributions (Wicksell 1925). List *et al.* found that the bubble size distributions are log-normal and that there are significant differences in the concentration and mean diameters of the bubbles in various hailstone layers. Using the same technique, List and Agnew (1973) examined the air bubble structure of accreted ice deposits grown in an icing tunnel. They conclude that the main factor affecting both the mean bubble diameter and the bubble concentration is the liquid water concentration, with a subsidiary dependence on the ambient temperature.

In this paper we examine the problem of the formation of air bubbles in accreted ice, in order to ascertain the physical factors which determine the bubble concentrations and size distributions.

2. PROCESSES INVOLVED IN THE ACCRETION OF INDIVIDUAL DROPLETS

(a) The spreading and freezing of accreted droplets

The microphysical processes involved in the accretion of individual droplets have been
treated by Browncombe and Hallett (1967) on the surface of a hailstone, whose temperature is below 0°C, the droplet spreads and freezes. A convenient measure of the spreading is the ratio of the final radius to the initial radius, termed the spreading factor $S$. Macklin and Payne (1967) differentiate between two phases in the freezing process, the initial and subsequent freezing. The initial freezing occurs because the droplet is supercooled and it is assumed that in this phase a dendritic sheet grows through the droplets in the same manner as ice dendrites grow in bulk supercooled water (Macklin and Ryan 1965). The fraction of the droplet which can freeze in this way is $c_w(T_m - T_a)/L_f$, the remainder of the liquid in the droplet being warmed to 0°C. In the subsequent phase, the remaining liquid is frozen by the conduction of heat into the hailstone or into the boundary layer which surrounds it. For hailstone temperatures lower than $-1$ to $-2$°C, the former process dominates and the latent heat is conducted rapidly into the hailstone. This heat is then slowly dissipated through the air boundary layer until the frozen droplet cools to the mean temperature of the hailstone. The period of the subsequent freezing, $t_f$, is about ten times the period of initial freezing, while the cooling period is generally at least ten times $t_f$.

Macklin and Payne (1967) set up a simple model to determine $t_f$. The spread droplet is assumed to take the form of a pill-box of radius $Sr$ and height $h$ where

$$h = \frac{4r}{3S^2}$$  \hspace{1cm} (1)

Values of $h$ for different values of $r$ and $S$ are given in Table 2 of their paper. The value of $S$ depends on the droplet size and impact speed and the temperature of the deposit (Macklin and Payne 1969). The actual shapes of spread droplets are given in Fig. 3 of their paper and this model is not unreasonable for deposit temperatures higher than $\sim -10$°C, impact speeds greater than $\sim 10$ m s$^{-1}$ and spreading factors larger than $\sim 2$. At lower impact speeds and smaller spreading factors the shape is more like a spherical cap. Assuming the simple pill-box model, Macklin and Payne show that the time of subsequent freezing is given by the solution for linear flow of heat into a semi-infinite body of ice, initially at a uniform temperature $T_d$ and with its surface maintained at temperature $T_m$ (Carslaw and Jaeger 1959, p. 70). This ignores the movement of the growth front through the freezing droplet and a better solution is that given on p. 288 of Carslaw and Jaeger. The time of subsequent freezing is then given by

$$t_f = \frac{h^2}{4\lambda^2} \frac{1}{\kappa_i}$$  \hspace{1cm} (2)

where $\lambda$ is the solution of

$$\lambda e^{\lambda^2 \{1 + \text{erf}(\lambda)\}} = \frac{c_w(T_m - T_d)}{\pi^2 \{L_f + c_w(T_m - T_m)\}}$$  \hspace{1cm} (3)

This may be readily solved numerically. The values given by Eq. (2) differ from those calculated by Macklin and Payne by only 10%, the values of $t_f$ being now smaller.

A more serious defect in the calculation is that the flow of heat is one-dimensional. For an isolated droplet freezing on a surface there is lateral as well as normal heat conduction. Macklin and Payne (1967) show that, using the one-dimensional heat flow calculation, the depth of penetration of the heat into the surface, $l$, is given approximately by

$$l = \frac{2Sr}{2S^2}$$  \hspace{1cm} (4)

If the quantity $l/2Sr$ is significantly lower than unity then the one-dimensional model is
adequate. For hailstone growth $l/2Sr$ may be as high as about 4 so that the actual time
of subsequent freezing may be appreciably shorter than the value given by Eq. (2).

(b) The formation of air bubbles

The formation of air bubbles during the freezing of bulk water has been studied by
Carte (1961). He froze samples of water between glass plates at rates between $5 \times 10^{-4}$
and $1.3 \times 10^{-2}\text{cm s}^{-1}$, and then counted and sized the air bubbles produced. The con-
centration of bubbles increased from $3 \times 10^{3}$ to $8 \times 10^{5}\text{cm}^{-3}$, while the average radius
decreased from 300 to 40$\mu\text{m}$ over this range of freezing rates.

The average freezing rate, $F$, of a spread droplet during the subsequent freezing
phase is given by

$$F = \frac{h}{t_f}$$

(5)

For typical hailstone conditions values of the freezing rate range from $3 \times 10^{-2}$ to $1\text{cm s}^{-1}$.
These rates are considerably higher than those used by Carte. Further, for small values of
$h$, the air can diffuse out of the freezing droplet thereby limiting the size to which the bubbles
grow. There is a second major complication. Even for a single droplet size the impact
speed and collection efficiency vary locally over the surface of the accreting object. This
means that the values of the spreading factor, and hence the freezing rate, vary over the
surface and this affects the bubble concentration. In the case of a droplet distribution the
local impact speed and collection efficiency vary also for each droplet size.

This may be formalized in the following way. For convenience, and later application,
we consider a rotating cylinder radius $R$ undergoing accretion at given air temperature
$T_a$ and airspeed $V$ in a constant liquid water concentration. The collection of droplets by
such a cylinder has been treated theoretically by Langmuir and Blodgett (1946). For a
given droplet radius $r$ there is a maximum cylindrical co-ordinate angle $\theta_m$ beyond which
no deposition occurs (Fig. 1). If we consider a time interval which is short compared with

![Figure 1. Schematic representation of the deposition of ice (hatched) on a cylinder of radius $R$ in a short time interval. $V$ is the airspeed and $\theta$ defines an arbitrary location on the cylinder, while $\theta_m$ is the maximum value of $\theta$ beyond which no deposition occurs for droplets of given radius.](image)
the time of rotation of the cylinder, then the number of droplets of radius \( r \) arriving at an arbitrary position on the cylinder is proportional to the local collection efficiency. The local collection efficiency, \( E(r, \theta) \), is approximately equal to \( E(r) \cos \left( \frac{\pi \theta}{2 \theta_m} \right) \), where \( E(r) \) is the overall collection efficiency for droplets of radius \( r \). Values of \( E(r) \) and \( \theta_m(r) \) have been calculated by Langmuir and Blodgett. On the basis of Carter's (1961) experiments, we assume that the concentration of air bubbles, \( n \), formed in the droplet is a function of the freezing rate, i.e. \( n = n(F) \). The number of bubbles formed in the ice deposited per unit length of cylinder in the short interval of time \( t \) at the location \( \theta, \theta + d\theta \) on the surface from droplets in the range \( r, r + dr \) is

\[
dN(r) = \frac{8\pi}{3} \frac{\rho_w}{\rho_i} n(F) E(r) \cos \left( \frac{\pi \theta}{2 \theta_m} \right) r^3 f(r) V R t d\theta d\theta
\]

where \( f(r) \) is the frequency distribution of droplets making up the liquid water and \( \rho_w \) and \( \rho_i \) are the densities of water and ice respectively. The freezing rate, \( F \), is dependent on the spreading factor since this determines the height of the spread droplet. Consequently \( F \) varies over the surface, i.e. \( F = F(r, \theta) \). The mean concentration of bubbles in the deposit is given by

\[
n = \frac{\int \int n(F) r^3 f(r) E(r) \cos \left( \frac{\pi \theta}{2 \theta_m} \right) d\theta d\theta}{\int \int r^3 f(r) E(r) \cos \left( \frac{\pi \theta}{2 \theta_m} \right) d\theta d\theta}
\]

For a rotating cylinder this is the mean concentration of bubbles in any volume of the deposit.

In Eq. (7), \( n(F) \) is the concentration of bubbles formed at a freezing rate \( F \) for a given solubility of air in the droplets. The layers of ice in a hailstone are likely to be formed at different heights in the cloud, i.e. at different temperatures and pressures. This affects the solubility of air in the droplets. The mass and volume solubilities of air in water at different levels in the cloud have been calculated for a number of severe storms, assuming adiabatic ascent. Typical values for the Cardiff storm, described by Macklin, Merlivat and Stevenson (1970), are given in Table 1. These have been extrapolated from the International Critical Tables. While the mass solubility is sensibly constant, the volume solubility changes by a factor of about 2 over the supercooled region of the cloud. This could affect the size of the air bubbles formed.

**Table 1. Mass and volume solubilities of air in supercooled droplets in the Cardiff storm**

<table>
<thead>
<tr>
<th>( T_d ) (°C)</th>
<th>( \rho ) (mb)</th>
<th>Mass solubility ( (g \ cm^{-2}) )</th>
<th>Volume solubility ( (ml \ cm^{-2}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>600</td>
<td>( 2\times 10^{-4} )</td>
<td>( 2.9 \times 10^{-3} )</td>
</tr>
<tr>
<td>-10</td>
<td>480</td>
<td>2.2</td>
<td>3.5</td>
</tr>
<tr>
<td>-20</td>
<td>390</td>
<td>2.3</td>
<td>4.3</td>
</tr>
<tr>
<td>-30</td>
<td>330</td>
<td>2.5</td>
<td>5.3</td>
</tr>
<tr>
<td>-40</td>
<td>280</td>
<td>2.7</td>
<td>6.5</td>
</tr>
</tbody>
</table>

In order to verify Eq. (7) and to obtain values of the air bubble concentration for various conditions, the following experiments were carried out.
3. The Freezing of Bulk Water

The purpose of these experiments was threefold: (i) to determine the dependence of air bubble concentrations and size distributions on freezing rate; (ii) to ascertain the possible effect of variations of the solubility of air on the bubble concentrations and size distributions; (iii) to compare the actual freezing times of large individual drops, freezing on a chilled surface, with those calculated from the one-dimensional model so that the effect of lateral flow of heat on the freezing rates could be ascertained.

(a) Experimental

The apparatus used for (i) and (ii) is shown in Fig. 2. It comprises an air-tight box, $29 \times 29 \times 30$ cm, constructed of aluminium 1-3 cm in thickness. Access ports to the interior of the box were fitted to the upper surface and to one of its sides. These were 16 cm in diameter and covered with 2-5 cm thick perspex so that visual observation of the interior of the box could be made. O-ring seals were used between the aluminium walls and the perspex ports to ensure airtightness. The box could be readily evacuated to a pressure of 0-5 atmospheres and pressurized to 2 atmospheres. The pressure was measured by a mercury manometer and the box was sufficiently airtight that the pressure could be maintained to within a few percent for a period of some hours. A microscope barrel was fitted through one side of the box so that cine-photographs of the freezing of water samples could be made. The camera used for this was capable of speeds between 12 and 64 frames per second. It was fitted with a small neon light which was pulsed at a known frequency so that time-marking pips were made on the side of the film. Accurate measurements of the framing rate were thereby obtained.

The water used in the experiments was singly distilled. No attempt was made to ascertain the effect, if any, of various impurities on the bubble concentration and size distribution. List et al. (1972), who studied the freezing of freely suspended water drops, found that there was little difference between the results for distilled de-ionized water, tap water and dilute solutions of NaCl. The water samples to be frozen were placed in small perspex tubes 2 cm diameter and 5 cm high, seated on a hollow copper block mounted inside the box. Liquid nitrogen was pumped through the block to lower its temperature and freeze the
TABLE 2. MASS AND VOLUME SOLUBILITIES OF AIR IN WATER FOR THE VARIOUS TEMPERATURES (T<sub>o</sub>) AND
PRESSURES (p) USED

<table>
<thead>
<tr>
<th>T&lt;sub&gt;o&lt;/sub&gt;(°C)</th>
<th>p (atmos.)</th>
<th>Mass solubility (g cm&lt;sup&gt;-3&lt;/sup&gt;)</th>
<th>Volume solubility (ml cm&lt;sup&gt;-3&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0·5</td>
<td>1·8 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>2·9 x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td>22</td>
<td>1</td>
<td>2·1</td>
<td>1·8</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>3·6</td>
<td>2·9</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>7·3</td>
<td>2·9</td>
</tr>
</tbody>
</table>

sample. The freezing rate was varied by changing the pumping rate of the liquid nitrogen. The freezing rate of a given sample was not constant through its volume but decreased with distance from the base of the container owing to the increasing thickness of ice through which the heat of fusion had to be conducted. The air bubble concentrations and size distributions were determined only for those sections of the sample in the field of view of the camera so that the corresponding freezing rates could be obtained. To vary the solubility of air dissolved in the water the experiments were conducted at room temperature (22°C) and with the box housed in a refrigerator or cold room maintained at 1°C. Pressures of 0·5, 1 and 2 atmospheres were used. The solubilities of air in water at these temperatures and pressures are shown in Table 2. Calculations were carried out to determine the time taken for the air in solution to attain 98% of the equilibrium value using the standard one-dimensional diffusion equation (Crank 1956, p. 45) and the water samples were allowed to stand in the box for this length of time (typically 2 to 3 hours) before freezing was initiated. Measurements were made of the oxygen dissolved in some of the samples using Winkler's method (Taylor 1958, p. 243) to ensure that in fact the times allowed for the samples to attain virtual solution equilibrium at the ambient pressure and temperature were sufficient. This proved to be the case.

The determination of the air bubble concentrations and size distributions were made in the following way. Thin sections of the ice samples were made by first cutting a rough section a few millimetres in thickness with a band saw in a cold room. One side of this was polished with a fine emery paper and placed polished surface down on a glass slide in a deep freeze unit at −25°C. Supercooled liquid diethyl phthalate at −15°C (the melting point of diethyl phthalate is −7°C) was poured over the section. The diethyl phthalate was nucleated with a piece of dry ice and allowed to freeze solid. This effectively glued the ice section to the glass plate. The section was then microtomed to a thickness of about 0·5mm for clear and transparent ice and to a thickness of only a few tenths of a millimetre for opaque ice. Following this, the glass slide was placed on a microscope stage which was maintained at −5°C. The purpose of this was to permit the diethyl phthalate to melt. This markedly improved the clarity of the field of view. The bubbles in the thin ice section were then photographed in transmitted light.

The reason for carrying out this relatively elaborate procedure to prepare the ice section for photomicroscopy was that very thin sections were found to be necessary to obtain sharp images of the bubbles. Sharp images of the bubbles could not be obtained in thick sections, particularly sections of opaque ice, because of the diffusion of the light by the bubble layers. Initially, the ice sections were prepared in the standard manner by melting them on to a warm glass plate. However, a simple calculation based on the diffusion of heat into a semi-infinite body with surface at constant temperature showed that, during the time taken to melt the ice section onto the warm glass plate (about 10 seconds), there was considerable penetration of heat into the section for the thicknesses used here. A section 1mm thickness, initially at −10°C, would be warmed to −2°C in this time.
Stehle (1966) has shown that air bubbles in ice migrate and change size under the influence of thermal gradients of this order of magnitude. Simple tests were carried out to check this. Small pieces of ice of varying opacities were placed on the microscope stage and one end melted using a warm brass plate. The air bubbles in the ice were observed through the microscope and, as the ice–water interface passed across the field of view, air bubbles near the interface were seen to migrate and change size. It was then obvious that the technique of melting the ice section on to the glass section could cause considerable changes in the air bubble concentrations and size distributions. Consequently, this technique was abandoned and the one using the diethyl phthalate adopted.

Some care was exercised to ensure that the bubble distributions obtained were truly representative. In preliminary experiments certain regions of the section were selected for photomicroscopy. However, it became evident that the observer tended to select regions where the bubbles were numerous and to avoid those where the bubble concentrations were low. To overcome this observer bias, a purely statistical effect, the glass plates on which the section was mounted were placed on a movable microscope stage and the photographs taken at regularly-spaced intervals over the section. The observer then played no part in selecting regions for photography.

The air bubble concentrations and size distributions were obtained by direct measurements on photographic prints of known magnification. Only bubble images which were in clear focus were measured. The depth of focus was determined from photographs of a thin metal blade taken at different positions relative to the objective lens and it is considered that the accuracy of the bubble concentrations measured is within ±20%. It should be noted that, because of the limitations of ordinary optical microscopy, only bubbles of radii greater than 1 µm were counted although undoubtedly smaller bubbles were present.

In the experiments on the freezing of large isolated drops, singly distilled water saturated with air at a temperature of 1°C at 1 atmosphere pressure was forced to flow, under a small pressure head, through a 26 gauge hypodermic needle to produce drops of radius 1.25 ± 0.10 mm. The drops were allowed to fall from varying heights on to a polished copper block 5 cm in diameter. The copper block was situated in a deep-freeze unit and its temperature, measured by a copper-constantan thermocouple embedded in the block 0.5 mm below the upper surface, could be varied from −2 to −30°C. Some experiments were conducted with the block surrounded by dry ice, giving a temperature of −80°C. On impaction the drops spread and froze. The advancing ice front could be readily seen as a difference of opacity in the spread drop. The freezing process was filmed using the 16-mm camera mounted above the block so that it looked down on the copper surface. The radii of the spread drops, and hence the spreading factor, were read from projected images of the film. The spreading factors ranged from 1.4 to 4 which covers the range of spreading factors of accreted cloud droplets (Macklin and Payne 1969). After freezing, the drops were removed from the copper block, photographed in profile to ascertain the height, and thin sections prepared for photomicroscopy in a manner similar to that described above.

\[(b) \text{ Results and discussion}\]

The dependence of the concentration of bubbles on freezing rate for the various temperature and pressure combinations used is shown in Fig. 3. Curves were fitted by computer, using standard numerical techniques, to each set of data. Although the data is scattered, there is a systematic dependence of the bubble concentration on mass solubility (Table 2), as is to be expected (see Carte 1961). This is more marked at the slow freezing rates.

The dependence of mean bubble radius, for each bubble distribution, on freezing rate is shown in Fig. 4. Again there is a solubility dependence at the low freezing rates
Figure 3. Dependence of the concentration of air bubbles in frozen bulk water on the freezing rate. The mass solubilities of air in water at the temperature and pressures used are given in Table 3. The lines shown are lines of best fit to the various sets of data.

Figure 4. Dependence of the mean radius of air bubbles in frozen bulk water on the freezing rate.

but it appears to be reversed in that larger bubbles are formed at the lower mass solubilities. However, there are a number of complicating factors. First, only visible bubbles (radius greater than 1\(\mu\)m) were counted and sized. Consequently, the actual frequency distribution of the bubbles was not fully determined. Second, after nucleation, the growth rate of a bubble depends on the density of the air enclosed, i.e. in the pressure inside the bubble. There are two contributions to the pressure, namely, the pressure due to the curva-
ture of the bubble, $2\sigma/r_b$, and the hydrostatic pressure, which in this case is essentially the ambient pressure. In an attempt to clarify this, the mass of entrapped air was calculated for the measured concentrations and distributions of bubbles and this compared with the corresponding mass of air in solution (Fig. 5). The fraction of the air entrapped appears to fall off with increasing freezing rate. This could be due either to a marked increase in the concentration of bubbles of radius less than 1$\mu$m or to a more rapid diffusion of air away from the freezing front due to the increase in local concentration gradients. This is discussed further in the next section. The numerically-fitted curves in Fig. 5 diverge at the lower freezing rates but this is probably due to scatter in the data, which is enhanced in this diagram because of the dependence of the mass of air on the cube of the radius.

Calculations of the freezing times of the drops frozen on the copper block were made on the assumption that the spread droplets were cylinders of height $h$ and radius $Sr$ and that the heat conduction was one-dimensional. The depth of penetration of the heat into the copper block was calculated from Eq. (4), inserting the values of the physical constants for copper. In Fig. 6 the ratio of the values of the measured time of freezing to the theoretical values is plotted against $l/2Sr$. For small values of $l/2Sr$ the ratio approaches unity while for large values it is seen that the ratio tends to a value of about 0.3.

4. ACCRETION ON ROTATING CYLINDERS

Measurements of the air bubble concentrations and size distributions were made in samples of accreted ice formed on rotating cylinders. The reason for using cylinders was that accurate determinations could be made of the deposit temperature and, as already indicated, detailed calculations of the local collection efficiencies and impact speeds for droplets have been made by Langmuir and Blodgett (1946).
TABLE 3. Mass and Volume Solubilities of Air in Supercooled Droplets in the Icing Tunnel (\( p = 1 \) atm.)

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>Mass solubility (g cm(^{-3}))</th>
<th>Volume solubility (ml cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( 3.5 \times 10^{-5} )</td>
<td>( 2.9 \times 10^{-2} )</td>
</tr>
<tr>
<td>-10</td>
<td>4.6</td>
<td>3.5</td>
</tr>
<tr>
<td>-20</td>
<td>5.8</td>
<td>4.3</td>
</tr>
<tr>
<td>-30</td>
<td>7.5</td>
<td>5.3</td>
</tr>
</tbody>
</table>

(a) Experimental

The icing tunnel used for these experiments was that described by Bailey and Macklin (1968). The method of injection of water droplets into this tunnel and the measurements of the droplet sizes distributions and of the liquid water concentrations in the tunnel have been discussed fully by Carras and Macklin (1973). In the present experiments two droplet distributions were used, one having a median volume radius of 15μm and a maximum radius of 33μm, and the other having a median volume radius of 30μm and a maximum radius of 80μm. The liquid water concentration was varied between 1 and 10 g m\(^{-3}\). The water used for the experiments was again singly distilled and the experiments were carried out at air temperatures between −5 and −30°C and at airspeeds of 15 and 33 m s\(^{-1}\).

Detailed calculations, similar to those of Macklin and Payne (1969), were carried out to determine the extent to which the droplets had reached thermal and air solution equilibrium in the time that they took to reach the working section of the tunnel. These showed that all of the droplets in both distributions had virtually attained thermal equilibrium by the time they reached the working section and that the smaller distribution had reached 96%, and the larger distribution 91%, of the equilibrium solution values. Values of the solubility for the icing tunnel conditions are given in Table 3.

The deposits were grown on a 2.5cm brass cylinder which spanned the tunnel section and which was rotated at 30 r.p.m. As described by Carras and Macklin (1973), a thermistor was attached to the inner surface of the cylinder and electrical contacts from the thermistor to the laboratory were made by a system of slip rings and brushes. The output was fed directly to a chart recorder so that the cylinder temperature could be continuously monitored. The ice accretions on the cylinder were grown to a thickness of about 1-2cm. By varying the liquid water concentration slightly during an experimental run it was possible to maintain the temperature of the deposit constant to within ±0.7 degC.

The range of liquid water concentrations used permitted growth in both the dry and wet growth regimes. The bubble concentrations and size distributions in spongy ice deposits are determined, to an extent depending on the fraction of unfrozen water, by the manner in which the deposits are finally frozen (see, e.g., Knight and Knight 1968, 1973). In the present experiments the growth of the spongy ice accretions was terminated at the desired radius by turning off the sprays. The spongy deposits were then allowed to freeze solid in the airstream. This meant that the rate of heat transfer from the deposit during the complete freezing was approximately the same as that during its growth. The determination of the air bubble concentrations and size distributions were made in the manner already described.

(b) Results and discussion

The air bubble concentrations in dry growth deposits using the smaller droplet distribution and an airspeed of 33 m s\(^{-1}\) are shown in Fig. 7. For a given ambient temperature,
Figure 6. The ratio of the measured freezing times \( t_{f, \text{exp}} \) to the theoretical freezing times \( t_{f, \text{th}} \) for large isolated drops as a function of \( I/2Sr \).

The concentration increases systematically with decreasing deposit temperature. To compare this data with that deduced from Eq. (7), values of the freezing rate \( F(r, \theta) \) were computed for appropriate droplet radii at a number of locations on the cylinder. To do this, values for the spreading factor \( S(r, \theta) \) had to be obtained. The components of the impact

Figure 7. Bubble concentrations in ice deposited on the rotating cylinder as a function of the deposit temperature for various values of the ambient temperature. The data are for the smaller droplet distribution and an airspeed of 33 m s\(^{-1}\). The theoretical values deduced from Eq. (7) are shown as dashed lines.
speeds normal to the cylinder surface were calculated for the $r$, $\theta$ values from Langmuir and Blodgett (1946) and the spreading factors for different deposit temperatures obtained by interpolation and extrapolation of the experimental data of Macklin and Payne (1969). Values of the height, $h$, of the spread droplets were calculated using the simple model described by Eq. (1). The freezing times, and hence freezing rates, were determined from the one-dimensional heat conduction equation and these then corrected, to take into account the lateral flow of heat, using the data in Fig. 6. The concentration of bubbles formed at the various freezing rates were read from the appropriate mass solubility curve in Fig. 3. The calculated values so obtained are also shown in Fig. 7 and, given the complexity of the problem, the agreement is reasonable. A second series of experiments were conducted using the larger droplet distribution at an airspeed of 15 m s$^{-1}$. Using larger droplets at a lower airspeed produced a significant change in the height $h$ of the spread droplets and hence in the freezing rates. The data, together with the corresponding calculated values, are shown in Fig. 8 and again there is good agreement. This justifies the assumption that the bubble concentration is primarily a function of the freezing rate over a wide range of conditions.

Following Browncombe and Hallett (1967, Fig. 9), an attempt was made to depict the air bubble concentrations in wet growth deposits as a function of the liquid fraction of spongy ice but this resulted in a complete scatter of the data. To relate the bubble concentrations obtained in the two growth regimes calculations were made of the appropriate freezing rates. In the dry growth regime, the mean freezing rate, $F$, was readily determined for the overall droplet distribution for each deposit temperature since the values of $F(r, \theta)$ had already been calculated. In the wet growth regime, the freezing rate was determined from the rate of heat transfer from the cylinders. The heat transfer coefficient could be ascertained quite accurately from the critical liquid water concentration, the liquid water concentration for which the deposit temperature just reaches 0°C (see Carras and Macklin 1973). The dependence of the air bubble concentration on the mean freezing rate is shown in Fig. 9. Data for both droplet distributions are included. The wet growth data is no longer scattered and both the wet and dry growth data agree with the data obtained from frozen bulk water.

Figure 8. Bubble concentrations in ice deposited on the rotating cylinder as a function of the deposit temperature for various values of the ambient temperature. The data are for the larger droplet distribution and an airspeed of 15 m s$^{-1}$. The theoretical values deduced from Eq. (7) are shown as dashed lines.
The reason for the fairly marked change in the bubble concentration, by a factor of at least 5, in going from the dry to wet growth regimes is that the freezing rate in the dry growth regime is very sensitive to deposit temperature at temperatures near 0°C. This is seen from the values of the deposit temperature corresponding to the freezing rates indicated on the figure. (There is a range of deposit temperatures corresponding to a given freezing rate because of the ambient temperature dependence. There is also a dependence on the droplet size. The values of the deposit temperature shown are for the smaller droplet distribution. Deposit temperatures for the larger distribution are displaced slightly towards slower freezing rates.) As the wet growth limit is approached, the bubble concentrations in the dry growth regime fall slightly below, by a factor of about 1.5, the line for bulk water. This is considered to be due to the diffusion of air out of the spread droplets during the freezing since, at these higher temperatures, the height of the spread droplets is small and the freezing times comparatively long. An approximate calculation, based on the time-dependent diffusion equation for air diffusing in bulk water (Crank 1956, p. 45) confirmed this.

Within the scatter of the data, there is no splitting of the dependence of bubble concentration on freezing rate with ambient temperature. Consequently, the ambient temperature is not an independent physical variable determining the concentration of bubbles. Its only relevance is that it enters the effective latent heat $L_f + c_w(T_a - T_m)$ during the freezing of the droplets. This affects the freezing rate and hence the concentration of bubbles that are formed.

Typical distributions of bubble sizes are shown in Fig. 10. In the dry growth regime two extreme examples are given. There is a slight shift in the distributions towards larger bubbles in going from the former to the latter but in both cases most of the bubbles are less than a few microns radius. The distributions in the wet growth regime are far more spread
Figure 10. Typical bubble distributions (left to right) for the dry and wet growth regimes, and for frozen bulk water. $F$ is the mean calculated freezing rate for the droplet distribution while $F$ is the measured freezing rate for the bulk water samples.

Figure 11. Dependence of the mean bubble radius on the mean freezing rate for both wet and dry growth regimes. The line shown is that for bulk water taken from Fig. 4. Deposit temperatures corresponding to values of the freezing rate are shown.
and range up to several tens of microns radius. For comparison, two distributions obtained from frozen bulk water are included in the figure. These are much more sharply peaked, as is to be expected given the more well-defined conditions under which the bubbles grew. Following List, Murray and Dyck (1972) and List and Agnew (1973), the distributions were plotted on log-normal paper. This resulted in linear relationships similar to those obtained by these authors with a similar separation between the data for the wet and dry growth regimes. It seems, however, that the latter simply reflects the differences in bubble size with the differing freezing rates in the two regimes.

The values of the mean bubble radius are shown as a function of mean freezing rate in Fig. 11. Data for both droplet distributions are included. Again there is reasonable agreement between the values for bulk water and for the accreted ice samples in the wet growth regime and in the dry growth regime at high freezing rates (low deposit temperatures). The departure of the mean bubble radius in dry growth accreted ice from that in frozen bulk water is far more marked as the wet growth limit is approached than is the departure of the concentrations (Fig. 9). It is apparent that approximately the same concentrations of bubbles are nucleated at the same freezing rates but that the diffusion of air from the spread droplets at higher deposit temperatures grossly affects the bubble growth rate. In fact the data indicate that at deposit temperatures near 0°C, the mean bubble radius is smaller, by a factor of 5 to 10, than the values in frozen bulk water. This is a factor of $10^3$ to $10^3$ in volume. This is obviously the reason for the formation of clear ice near the wet growth limit, as found by Macklin (1962). In the wet growth regime the mean bubble radii and concentrations revert to the bulk water values and the ice becomes transparent or even opaque again.

Values of the ratio of the mass of air entrapped to the mass of air in solution were calculated for each distribution and are shown as a function of freezing rate in Fig. 12. There is a similar fall-off with freezing rate as for the bulk water data (Fig. 5). However,

![Figure 12](image-url)

Figure 12. Fraction of air entrapped in accreted ice deposits, deduced from the air bubble concentrations and size distributions, as a function of the freezing rate. The large crosses represent the values measured by Winkler's method for oxygen determination.
AIR BUBBLES IN ACCRETED ICE

the fall-off is more marked at freezing rates between $5 \times 10^{-3}$ and $10^{-1}$ cm s$^{-1}$ which are those appropriate to clear ice. To ascertain the actual fraction of air entrapped in the ice, the following experiments were carried out. Ice was accreted on a rotating cylinder of 0.6 cm diameter at known liquid water concentrations and ambient temperatures. The corresponding deposit temperatures and hence freezing rates were deduced from the data on the 2.5 cm diameter cylinders. These samples were then analysed using Winkler's method for the determination of oxygen in solution. (The reason for using small diameter cylinders for these experiments was to obtain large samples for analysis.) The values of the fraction of air entrapped, deduced from the oxygen values, are also displayed on Fig. 12. These show the same general trend as the calculated curve. However, in the dry growth regime there is evidently more air entrapped than the air bubble distributions and concentrations indicate. This could be due to the presence of sub-micron bubbles or to air entrapped in fissures in the ice. The latter seems more probable in the case of clear ice.

For comparison with Fig. 9 of Brownscombe and Hallett (1967), each sample of accreted ice was classified visually as clear, transparent or opaque. The results for both droplet distributions are shown in Fig. 13 and, within broad limits, the two diagrams are similar. Whether spongy ice containing a high percentage of unfrozen water remains clear or transparent depends on how it is finally frozen.

![Figure 13: Dependence of the visual opacity of accreted ice on the deposit temperature in the dry growth regime and on the liquid fraction of water in the wet growth regime. The full lines represent the demarcation between clear (C), transparent (T) and opaque (O) ice for the present data while the dashed lines are those of Brownscombe and Hallett (1967).](image)

5. COMPARISON WITH PREVIOUS WORK

No direct comparison of the present results with those of previous workers can be made. Carte (1961) states that he did not count small bubbles and it is also likely that the concentrations and size distributions he obtained were affected by the proximity of the walls of the cell in which he froze his water samples. Consequently, the mean radii he obtained were larger and the concentrations smaller than those obtained here. List, Murray and Dyck (1972) and List and Agnew (1973) measured the planar concentrations and size distributions of the air bubbles in natural hailstones and artificial hailstones respectively. However, they show that the mean planar bubble radius should be the same, to within some eight per cent, as the mean volume bubble radius which was determined in the present investigation. There is in fact general agreement between the two sets of experimental data in this regard.

List and Agnew (1973) conclude that the main factor affecting both the bubble concentration and size is the liquid water concentration. This is based on experiments made
at two different liquid water concentrations (2 and 4g m\(^{-3}\)) and ambient temperatures between \(-5\) and \(-20^\circ\)C. At the higher liquid water concentration the deposits they obtained were spongy while at the smaller concentration the deposits were dry, at least at the lower ambient temperatures. Measurements of the surface temperature of one of the deposits growing at an ambient temperature of \(-20^\circ\)C, using an infrared radiometric microscope, gave values between \(-2\) and \(-10^\circ\)C, the surface temperature decreasing as the radius of the stone increased from 2.4 to 3.1cm (Fig. 8 of their paper). It is evident that their conclusion is of limited validity. The liquid water concentration is important in so far as it determines whether the ice deposit grows wet or dry. But this is also determined by the rate of heat transfer from the accreting object. Even in the wet growth regime the bubble concentration and size are determined by the freezing rate, i.e. by the rate of heat transfer rather than by the liquid water concentration. In the dry growth regime the liquid water concentration is only one of many factors which determine the deposit temperature and hence the rate of freezing of the droplets.

6. Conclusions

The essential factor which determines the concentration of air bubbles in ice formed by accretion is the freezing rate. In the dry growth regime the freezing rate of the individual droplets is controlled by the deposit temperature while in the wet growth regime the freezing rate is governed by forced convection processes and, in the case of spongy ice, on the manner in which the deposits are finally frozen. The size distribution of the bubble is determined by the amount of air dissolved in the accreted droplets. In both growth regimes the concentrations of bubbles is comparable with those in bulk water frozen at the appropriate freezing rates. At temperatures close to \(0^\circ\)C in the dry growth regime, the droplets spread considerably and freeze relatively slowly. This permits a significant fraction of the dissolved air to escape by diffusion before the bubbles have time to grow. This reduces only slightly the concentration of bubbles formed but reduces significantly the size of the bubbles and hence the volume of the air entrapped. Consequently, clear ice is formed.

The physical variables which determine the freezing rate in the dry growth regime are the droplet size and impact speed (since these partly determine the height of the spread droplet) and the deposit temperature. It is of interest to note that these are the same variables which determine the density of rime (Macklin 1962). The relation between these variables and the environmental or growth parameters of the accreting object in the cloud is complex, as shown schematically in Fig. 14. The dependence of the impact speed on ambient temperature and pressure is only slight and this has been indicated by dashed lines. The pressure is important in determining the deposit temperature because the diffusivity

![Figure 14](image_url)  
Figure 14. Schematic dependence of the physical parameters \(r\), \(v_0\), and \(T_0\) which determine the density and bubble structure of dry growth accreted ice deposits, on the environmental or growth parameters of the accreting object.
of water molecules is incorporated into the heat balance equation (see Ludlam 1958; Macklin and Payne 1967, Eq. (1)). The shape is also important as it affects the aerodynamic flow around the object and hence the impact speed and heat transfer coefficient.

In the dry growth regime the visible bubble concentrations range from about $10^5$ to $10^6 \text{cm}^{-3}$, depending primarily on the deposit temperature. The mean radii of the bubbles in the deposits range from 1 to 4\(\mu\)m. In the wet growth regime the bubble concentrations generally lie between $10^5$ and $10^6 \text{cm}^{-3}$ (unless spongy ice is quenched in the manner described by Knight and Knight 1968, 1973) while the mean radii of the bubbles range from 10 to 50\(\mu\)m. Consequently, the two growth regimes may be readily distinguished. Application to hailstone growth will be made in a subsequent paper.

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