Thermal Shock as an Ice Multiplication Mechanism. Part I. Theory

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ABSTRACT

Thermoelastic theory is used to calculate thermal stresses in ice crystals of idealized shapes when a small area on one surface is warmed to 0°C, in simulation of riming of the crystal by a cloud droplet. It is shown that a typical riming event involving a 20 μm diameter droplet impinging on a 500 μm plate or column would need to occur at a temperature colder than -35°C before fracture could be expected. For a given ice crystal size, the thermal stresses increase with droplet diameter, and thin plates rimed by large droplets are the most sensitive to thermal shock, but still need to be colder than -10°C before fracture would occur. It is consequently concluded that the thermal shock mechanism is unlikely to be responsible for the proliferation of ice crystals in clouds at temperatures as warm as -4°C .

1. Introduction

A great deal of the research effort in cloud physics of the past ten years has been concerned with the discrepancy between the concentrations of ice nuclei and ice crystals found in some clouds. Since the ice crystals can sometimes outnumber the nuclei by several orders of magnitude (Koenig, 1968; Auer *et al.*, 1969; Hobbs, 1969; Mossop *et al.*, 1970), attempts at modifying these clouds by artificial means such as seeding with AgI are likely to be ineffective. It is therefore of some interest to investigate processes whereby ice particles can reproduce without consuming the relatively few nuclei known to exist in clouds. In more specific terms, this is normally thought to involve splintering or fracturing of the parent ice crystal, and this paper is concerned with a mechanism suggested by Hobbs (1969) and Hobbs and Farber (1972)—the fracture of a rimed ice particle by thermal shock. More recently, Hallett and Mossop (1974) have also tentatively suggested the same effect as one of several that could be responsible for the production of secondary ice crystals observed by them in their laboratory studies of the riming process.

The proposed mechanism is essentially as follows: When a falling ice crystal collects a smaller supercooled water droplet, the latent heat released by the droplet as it freezes warms the contact area to 0°C, while the extremities of the ice remain at the environmental temperature T_e . The temperature change

from T_e to 0°C occurs in a time no longer than it takes for the dendritic growth in the droplet to be completed, and this is of the order of milliseconds. Since the temperature change is also localized near the contact region, it constitutes a thermal shock which could be sufficient to fragment the ice crystal and produce the extra ice particles. By most thermal shock standards, the temperature changes involved are quite modest, being 40°C at most, yet the thermal and elastic properties of ice are such that thermal stresses merit consideration. Although ice has an elastic modulus and coefficient of thermal expansion which are typical of metals, it is quite brittle. In addition, the thermal diffusivity is more representative of that of an insulator, allowing large temperature gradients to exist for long times. The ice-water system is further distinguished by the relatively large amount of latent heat which is released at the freezing temperature. Taken in combination, these properties ensure that thermal shock of ice merits consideration as a possible fracture mechanism.

Thermal stresses in solids depend very much on the geometry of the situation, and to a lesser extent on the temperature boundary conditions. As a consequence, it is not possible for the results of a single analysis to give a general indication of the likelihood of fracture occurring. In this study, the problem has been approached by calculating the stresses for various idealized geometries likely to occur in clouds, and then comparing the predictions of the theory with the results of experiments on the cracking of large ice crystals. In these experiments, the details of which

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are given in the companion paper (King and Fletcher, 1976), small areas on the surface of large multi-grained ice crystals were warmed to 0°C, and the fraction which cracked as a function of their temperature was noted. There was good qualitative and quantitative agreement between the results of these experiments and the predictions of the theory. It should be emphasized that, from the point of view of ice multiplication, this method aims only to determine which set of circumstances is most likely to cause fracture of an ice crystal, and cannot decide on the nature, size or number of any secondary particles.

2. Assumptions

The stresses for the models of the following sections were calculated using the standard techniques of uncoupled, quasi-static, isotropic thermoelastic theory. This theory incorporates several simplifying assumptions, and comprehensive treatments of the subject and its limitations are given in Boley and Weiner (1960) and Nowacki (1962). It is sufficient to note that, for the present case, considering ice, the inverse coupling between the strain and temperature fields (i.e., the effect of the strains in modifying the temperature distribution) can be ignored for temperature changes $\lesssim 80^\circ\text{C}$. Similarly, neglect of the dynamic wave propagation terms is not a serious restriction because the temperature changes are experienced slowly on the time scale of elastic wave propagation. The well-known creep of ice at temperatures near the melting point can also be ignored since, at the strain rates of concern, ice behaves elastically.

Ice is mildly anisotropic in its elastic behavior. Depending on the stress system, the elastic parameters can vary by up to 30% with changes in orientation (Fletcher, 1970, p. 171), although 10% would be an average figure. This implies that the application of the isotropic thermoelastic theory is only accurate within these limits. We have used the elastic stiffness constants as found by Bass *et al.* (1957) for ice at -16°C . With the usual isotropic approximations (Fletcher, 1970, p. 168), these yield values of 6.3×10^4 bars and 3.5×10^4 bars for the Lamé constants λ and μ , respectively. In some situations, it is more convenient to use Young's modulus E and Poisson's ratio ν , which then take the values 9.3×10^4 bars and 0.32, respectively. The coefficient of thermal expansion was taken as $5.0 \times 10^{-5} (\text{°C})^{-1}$, which is an average over the values found by direct measurement and x-ray studies (Fletcher, 1970, p. 131). Any variations in the relevant elastic and thermal parameters due to temperature changes can be neglected within the range of interest.

3. General outline of method

As a first step in any thermoelastic problem, the temperature distribution is determined as a solution

of the Fourier equation

$$\kappa \nabla^2 T = \partial T / \partial t, \quad (1)$$

where κ is the thermal diffusivity of ice. In this study, T will always denote temperature deviations from the initial unstressed state. The temperature boundary conditions used on (1) were as follows. On the surface impacting the rimed droplets, the temperature was increased instantaneously by the supercooling ΔT in a circular region of radius a and left unchanged outside this region. For the remaining surfaces, the boundary conditions corresponded to either zero heat flow across them, or zero temperature change on them. Although neither of these is very realistic, and the true boundary condition probably lies somewhere in between, the exact nature of the boundary condition only plays an important role when the steady state is being approached, and we will see that the critical stresses are usually attained before this.

The stresses are obtained from the temperature field using the Duhamel-Nauman law (Sokolnikoff, 1956, p. 359):

$$\tau_{ij} = \lambda e_{kk} \delta_{ij} + 2\mu e_{ij} - \alpha(3\lambda + 2\mu)T \delta_{ij}, \quad (2)$$

where τ_{ij} and e_{ij} are elements of the stress and strain tensors respectively, δ_{ij} is the Kronecker delta with the usual summation convention applied, λ and μ are the Lamé elastic constants, and α is the coefficient of thermal expansion of ice. For stress equilibrium in the absence of any external forces,

$$\partial \tau_{ij} / \partial x_j = 0. \quad (3)$$

Differentiating (2), and using (3), along with the equation for small strains

$$e_{ij} = \frac{1}{2}(\partial u_i / \partial x_j + \partial u_j / \partial x_i), \quad (4)$$

yields the fundamental thermoelastic differential equation for the displacement u_i :

$$\mu \frac{\partial^2 u_i}{\partial x_k \partial x_k} + (\lambda + \mu) \frac{\partial^2 u_k}{\partial x_k \partial x_i} - \alpha(3\lambda + 2\mu) \frac{\partial T}{\partial x_i} = 0. \quad (5)$$

The solutions to Eqs. (2)–(5) are subject to the boundary condition of zero tractions on the external surfaces, i.e.,

$$\tau_{in} = 0, \quad (6)$$

where n is the direction perpendicular to the external surface.

Eqs. (5) and (6) cannot always be solved exactly, although quite good approximations can be made for certain geometries such as plates. These approximations usually involve solutions to (5) which satisfy average boundary conditions of the type described by (6), i.e., the total force on the side surfaces is zero, although it may be non-zero at particular points on it. A solution obtained under these approximations is

accurate for all points further from the sides than a few plate thicknesses (von Mises, 1945; Sternberg, 1954).

Quite general considerations show that the stresses vary considerably with time. At the instant of application of the temperature rise, the stresses are zero everywhere except near the warmed area, where they are compressive and of the order of $E\alpha\Delta T/(1-\nu)$. As the steady state is approached, the temperature gradients are minimal and the stresses diminish. At some intermediate time, the stresses are at a maximum and this maximum stress was used to calculate the supercooling necessary to cause failure, determined on the basis of the Griffith theory of brittle fracture.

Although theories of failure are numerous and not particularly successful (Nadai, 1950, Chap. 15), the Griffith theory has a fairly sound theoretical and experimental basis (Orowan, 1948; Brace and Bombolakis, 1963). It supposes that failure is due to stress concentrations around pre-existing flaws and micro-cracks, and a macro-crack is formed when the elastic strain energy becomes large enough to provide the extra surface energy needed. All the stress distributions of interest to this study were either biaxial (i.e., two-dimensional), or nearly so, and the Griffith criterion for determining the onset of cracking in a biaxial system can be stated as (Jaeger, 1956, p. 86)

$$\left. \begin{aligned} \sigma_1 &= S_0, & \text{if } 3\sigma_1 + \sigma_2 > 0 \\ (\sigma_1 - \sigma_2)^2 + 8S_0(\sigma_1 + \sigma_2) &= 0, & \text{if } 3\sigma_1 + \sigma_2 < 0 \end{aligned} \right\}, \quad (7)$$

where S_0 is the tensile strength in uniaxial tension, and σ_1 and σ_2 are the principal stresses with $\sigma_1 > \sigma_2$. There is considerable uncertainty in the value of S_0 . Hawkes and Mellor (1972) have attributed reported values of less than 10 bars to faulty testing techniques, and found the tensile strength of bubbly polycrystalline ice to be 20 bars for a wide range of strain rates. The value for clear ice is likely to exceed this, but in the absence of any reliable measurements, we have taken S_0 to be 20 bars. Hawkes and Mellor also find the uniaxial compressive strength to be about 90 bars for the strain rates of interest to us. This value is considerably less than 8 times the tensile strength as predicted by the Griffith criterion (7). Despite these deficiencies, we have used the Griffith model which, in any case, can be used to provide a relative figure for the supercoolings required for each situation.

The time that the riming droplet takes to freeze depends on the supercooling and the crystal geometry, so the final stage in the theoretical treatment of this study deals with a calculation to determine whether the droplet contains sufficient latent heat to maintain the assumed temperature distribution up to the time at which the critical stress is attained.

4. Models studied

In clouds, depending on the temperature regime, the ice crystal shapes can vary from columns to thick plates or stellar dendrites. In addition, there are variations in scale caused by the droplet size distribution and, to a lesser extent, by the amount by which the droplet spreads on impact. This last effect is only important at temperatures close to 0°C , and the spreading factor, defined as the ratio of the radius of the spread drop to its initial radius, is unlikely to exceed 2 for the droplet sizes and impact velocities of interest to us (Macklin and Payne, 1969). The situations we have modeled are shown in Fig. 1. The hatched areas are warmed by an amount ΔT and the temperature on the remaining boundaries is left unaltered. They correspond, respectively, to (i) a large crystal, (ii) a thin plate, (iii) a thick plate, and (iv) a long column. In most cases, hexagonal symmetry has been replaced by circular symmetry and the column has been regarded as a rectangular beam. The important case of extreme crystalline forms such as hollow columns and sheaths, which are known to be the dominant growth mode at the critical temperature around -5°C , are also treated in qualitative fashion. We will also consider the case of a sphere whose surface is subjected to a sudden rise in temperature. This is of little interest to cloud physics, but can yield some useful information on fracture strengths when taken in conjunction with the experimental results of Part II of this study.

FIG. 1. The thermoelastic models studied. The characteristic length (or diameter) of the ice crystal is $2b$, the length (or diameter) of the warmed area is $2a$, and the thickness of the crystal is h , with the origin of coordinates at the center of the warmed area.

5. Semi-infinite solid (large crystal)

Ono (1969) has shown that the onset of riming of ice crystals occurs when a particular dimension of the crystal exceeds a fairly well-defined length. This critical dimension corresponds to the minor axis being greater than $90\text{ }\mu\text{m}$ for columns, and the diameter greater than $400\text{ }\mu\text{m}$ for plates. Since a typical riming situation involves a droplet about $20\text{ }\mu\text{m}$ in radius, and the stresses decrease in a distance of the order of two droplet radii, the semi-infinite model can provide a reasonable basis for examining stresses in such cases.

The solutions to Eqs. (1)–(5) for the semi-infinite geometry were obtained by a Hankel-Laplace transform method. This technique is not significantly different from the one used by Bailey (1958). Consequently, the details of the solution are omitted here, and the expressions for the stress fields, which are cumbersome, are presented in Appendix A. These have not previously been published in the open literature.

The temperature and stresses were calculated to 5% accuracy by numerical integration of (A4)–(A7) using Simpson's rule. The computed values of $\tau_{\theta\theta}$ and τ_{rr}

FIG. 2. Azimuthal stress $\tau_{\theta\theta}$ in a semi-infinite solid, as a function of z/a and r/a for various values of the time parameter $\omega = \kappa t/a^2$. The isopleths are in bars $(^\circ\text{C})^{-1}$.

FIG. 3. As in Fig. 2 except for the τ_{rr} .

are shown in Figs. 2 and 3 as a function of the dimensionless time $\omega = \kappa t/a^2$. For axial symmetry, the only other non-zero stresses are τ_{rz} and τ_{zz} , which are quite small for all times [less than $1\text{ bar } (^\circ\text{C})^{-1}$] and are not shown. Initially, both $\tau_{\theta\theta}$ and τ_{rr} are compressive near the warmed area, as expected. As the thermal wave propagates outward, τ_{rr} decreases in magnitude near $z=0$, but becomes more compressive in the regions away from the drop, while $\tau_{\theta\theta}$ develops a tensile stress of $2.3\text{ bars } (^\circ\text{C})^{-1}$ on the boundary near $r=a$ as the steady state is approached. At this time, there is a discontinuity in this stress, equal to $E\alpha\Delta T$ at the boundary of the heated area.

Since the semi-infinite model probably best represents the riming situation that occurs most frequently in clouds, and the tensile stress of $2.3\text{ bars } (^\circ\text{C})^{-1}$ is quite large, it is important to know whether this stress is a direct consequence of the temperature discontinuity near the droplet edge. This discontinuity is artificially maintained by the applied boundary conditions for all times, whereas, in a real situation, the surface temperature is probably smoothed out considerably after a time of the order of $\omega=1$. The question of the exact magnitude of the steady-state

stress under more realistic boundary conditions is considered in Appendix B, where it is shown that $\tau_{\theta\theta}$ is unlikely to exceed $0.2 \text{ bar } (^{\circ}\text{C})^{-1}$. This is quite small, and consequently will not be considered further.

It is probably worth noting that the stresses are really only in doubt for long times: at $t=0$ there will be a discontinuity in the temperature (in terms of the length scale employed here), so that the stresses of Figs. 2 and 3 are probably accurate up to a time of the order of $\omega=1$.

An inspection of the Griffith fracture criterion (7) shows that it is difficult to produce fracture when both $\tau_{\theta\theta}$ and τ_{rr} are compressive and of the same magnitude, so that although the compressive stresses at $t=0$ are quite large, they are unlikely to cause failure. In considering stresses on the surface, the most likely possibility of fracture occurs near $r/a \approx 1.2$ when $\omega=10^{-2}$. Here $\tau_{\theta\theta} \approx 0$ and $\tau_{rr} \approx 2 \text{ bars } (^{\circ}\text{C})^{-1}$, and the Griffith condition predicts that about 80°C of supercooling would be required. It was previously noted that the Griffith theory may not be particularly accurate in predicting the required compressive stresses, but even if the value of 80 bars for the compressive strength is taken, a supercooling of about 40°C is still required.

For stresses other than those on the surface, both $\tau_{\theta\theta}$ and τ_{rr} are tensile on the z axis at a depth of $0.6a$ and, when $\omega=10^{-2}$, about $0.6 \text{ bar } (^{\circ}\text{C})^{-1}$. Although not shown, τ_{zz} is also tensile and of the same magnitude at this depth, so that a state of triaxial tension exists. Such a stress system is likely to cause fracture, needing about 35°C of supercooling, but the tensile region is so localized that it is difficult to know whether any cracks will propagate over extensive distances.

Simple arguments can be used to show that droplets freezing at -40°C contain sufficient latent heat to maintain the contact area of 0°C up to a time of the order of $\omega=10^{-1}$. This result is independent of the droplet size, and indicates that the critical stress can be achieved within the time limits imposed by the physics of the riming situation.

To sum up, it would appear that the temperature would need to be below -35°C for the collision between a small droplet and a large crystal to cause cracks of any type.

6. Thin plate

The semi-infinite model is adequate when the dimensions of the splashed area are small compared with the dimensions of the ice crystal. The impact of a large cloud droplet, on a thin plate, or the plate section of a capped column, cannot be described by that model, and will be discussed in this section. Ono (1969) found that, for cloud crystals which approximate thin plates, most were less than $50 \mu\text{m}$ thick, a dimension which is comparable with that of the larger cloud droplets. Consider the collision be-

tween a large cloud droplet and an ice crystal of comparable thickness and diameter 10 times its thickness. The time constant for temperature variation through the thickness of the plate is then about 4×10^{-2} of the time constant for variation in the plane of the plate. Consequently, after a short interval, the temperature is effectively uniform throughout the thickness, yet away from the droplet it has not changed significantly in the radial direction. For such a system, a state of plane stress, in which the only non-zero stress components are τ_{rr} and $\tau_{\theta\theta}$, will exist, and those stresses are, according to Boley and Weiner (1960, p. 290)

$$\tau_{rr} = \alpha E \left[\frac{1}{b^2} \int_0^b T r dr - \frac{1}{r^2} \int_0^r T r dr \right], \quad (8)$$

$$\tau_{\theta\theta} = \alpha E \left[\frac{1}{b^2} \int_0^b T r dr + \frac{1}{r^2} \int_0^r T r dr - T \right], \quad (9)$$

where a is the radius of the warmed area, b the radius of the plate, and E is Young's modulus for ice. These expressions are obtained within the framework of the plane-stress formulation so that they are only accurate at distances more than a plate thickness away from the edge $r=b$.

If we impose the usual conditions that $T=\Delta T$ for $r < a$ and $T=0$ at $r=b$, then the temperature distribution, assuming only radial heat flow, is (Carslaw and Jaeger, 1959, p. 207)

$$T(r, t) = \begin{cases} \Delta T, & \text{for } r \leq a \\ \pi \Delta T \sum_{n=1}^{\infty} \frac{J_0(\rho_n b) J_0(\rho_n a) U_0(\rho_n r) \exp(-\kappa \rho_n^2 t)}{J_0^2(\rho_n a) - J_0^2(\rho_n b)} + \Delta T \log(b/r) / \log(b/a), & \text{for } r > a \end{cases} \quad (10)$$

where

$$U_0(x) = J_0(x) Y_0(b) - J_0(b) Y_0(x), \quad (11)$$

J_0 and Y_0 are the zero-order Bessel functions of the first and second kind, and the ρ_n are solutions of

$$U_0(\rho_n a) = 0. \quad (12)$$

The integrals in (8) and (9) can be evaluated analytically and, denoting them by I_1 and I_2 respectively, we find

$$I_1 = \int_0^b T r dr = \Delta T \left[2 \sum_{n=1}^{\infty} \frac{J_0(\rho_n b) \exp(-\kappa \rho_n^2 t)}{\rho_n^2 [J_0(\rho_n a) + J_0(\rho_n b)]} + \frac{(b^2 - a^2)}{4 \log(b/a)} \right], \quad (13)$$

for $r \leq a$

FIG. 4. Radial stress τ_{rr} in a thin plate with $a/b=0.4$ for various values of the time parameter $\omega = \kappa t/b^2$.

$$\begin{aligned}
 I_2 &= \int_0^r T r dr = \Delta T r^2/a \\
 &= \pi \Delta T \sum_{n=0}^{\infty} \frac{J_0(\rho_n b) J_0(\rho_n a) \exp(-\kappa \rho_n^2 t)}{J_0^2(\rho_n b) - J_0^2(\rho_n a)} \\
 &\quad \times \left[\frac{2 J_0(\rho_n b)}{\pi \rho_n^2 J_0(\rho_n a)} + \frac{r U_1(\rho_n r)}{\rho_n} \right] \\
 &\quad + \frac{\Delta T}{2} \left[\frac{r^2 \log(b/r)}{\log(b/a)} + \frac{r^2 - a^2}{2 \log(b/a)} \right], \quad (14) \\
 &\quad \text{for } r > a.
 \end{aligned}$$

Results for $a/b=0.4$ are shown in Figs. 4 and 5 for various values of the dimensionless time $\omega = \kappa t/b^2$. The stress τ_{rr} is compressive throughout, is a maximum near the warmed area, and becomes slightly more uniform as the heat diffuses out. In contrast, $\tau_{\theta\theta}$ shows some unusual behavior, having a discontinuity at $r=a$ when $t=0$, smoothing out as time progresses until there are fairly large tensile stresses on the edges as the steady state is approached. These edge stresses can be ignored for two reasons: first, we have already mentioned that the plane stress solution is not accurate near the edge, and second, these stresses would again be sensitive to changes in the boundary conditions—if there were no heat flow across $r=b$, the equilibrium state of the crystal would be one of uniform temperature and zero stress.

FIG. 5. As in Fig. 4 except for the azimuthal stress $\tau_{\theta\theta}$.

Although the tensile values of $\tau_{\theta\theta}$ which occur initially would not be affected by such changes in the boundary conditions, only those stresses which occur after about $\omega=10^{-2}$ can be considered. Prior to this, there may be temperature variations through the thickness, and the assumption of radial displacements is not valid. The tensile stresses which occur after this time, however, of the order of 1.8 bars $(^\circ\text{C})^{-1}$, are probably quite realistic, since there are good physical reasons for expecting them outside the warmed area. Heating of the central region produces displacements in the positive radial direction, moving neighboring points at the same radius further apart in the azimuthal direction—a situation equivalent to the application of a tensile $\tau_{\theta\theta}$ stress.

The tensile values of $\tau_{\theta\theta}$ vary with the ratio a/b approximately as $(1+a^2/b^2)$, and, since the model is not accurate for a/b ratios $\gtrsim 0.8$, departures from the values shown in Fig. 5 amount to 40% at most for a wide range of droplet sizes. On the basis of these calculations and the Griffith criterion, it is therefore expected that a supercooling of 10–12°C would be required to produce fracture, with less perhaps for a particularly large drop.

The heat balance condition requires that the latent heat of the drop exceed the sensible heat required to warm the ice under the drop from T_e to 0°C . When $T_e = -12^\circ\text{C}$, this condition is met by all drop-crystal pairs for which a/h is greater than 0.1, where h is the plate thickness. This is not a severe constraint in terms of riming of thin plates.

7. Thick plate

The most frequently observed thick plate crystals in the cap cloud studied by Auer and Veal (1970) were of the order of 100 μm in diameter and 40 μm thick. For plates of these dimensions, riming by droplets up to 20 μm diameter is effectively described by the semi-infinite model, but collision with larger cloud droplets requires a separate description because bending stresses must be considered. These arise when a body which is heated on one surface attempts to accommodate the expansion near the warmed area by bending away from it. These stresses were not important for the previous two problems. In the first, the semi-infinite geometry prevented any bending behavior, and in the second, the temperature was considered to be uniform throughout the thickness, so that no bending stresses would arise.

The solution is obtained under certain assumptions. The usual Euler-Bernoulli approach supposes that surfaces parallel and normal to the median plane before deformation remain so after it, and we will further assume that the plate is not so thick that plane-stress theory cannot be utilized. Boley and Weiner (1960, pp. 325, 406) have shown that the solution obtained under these assumptions is the first-

order approximation to the complete three-dimensional one, obtainable only as an infinite series of separate solutions. The neglected terms are of second-order magnitude and it is estimated that the solution used here is accurate to 20% everywhere except near $r=a$.

We will give only an outline of the derivation of the solution, since it is a lengthy, but quite straightforward process, and a general method is given by Boley and Weiner (1960, p. 379). The interested reader can find the details in King (1973). The deformation of the plate is characterized by displacements of the median plane, u and w , in the radial and z directions respectively, both being averaged over the plate thickness, i.e., the deformation of the plate is considered to be made up of bending of the plate as a whole (w) together with expansion within the "plane" of the plate (u). As would be expected from a description of this type, the stresses due to u and w can be evaluated separately and are associated with the forces and moments generated by the temperature distribution. The forces arise from the volume expansion averaged over the plate thickness (and are consequently zero for temperature distributions which are asymmetric with respect to the median plane), while the bending moments are a direct consequence of asymmetries in the heating. The force-like stresses are just those which we have considered in the previous sections: these are compressive near the warmed area and are generated rapidly. In opposition to these, the bending stresses are tensile near the warmed region (i.e., $z < 0$, where z is measured from the median plane as in Fig. 1c), compressive for $z > 0$, and attain their maximum values after a delay characterized by the thickness of the crystal. This delay is approximately given by the time required for the heat to diffuse half-way across the crystal thickness so that the temperature asymmetry is also maximized.

Fig. 6 shows τ_{rr} on the z axis as a function of $\omega = t/b^2$ for the case when $a/b = 0.5$, $h/b = 0.5$. The combined effects of instantaneous compressive stresses near the warmed area and delayed tensile ones due to bending result in a maximum tensile value for τ_{rr} of about 1.5 bars $(^\circ\text{C})^{-1}$, occurring at a depth of $0.4h$ at times between $\omega = 10^{-3}$ and $\omega = 10^{-2}$.

The azimuthal stress $\tau_{\theta\theta}$ is slightly smaller than τ_{rr} , its maximum value being 0.8 bar $(^\circ\text{C})^{-1}$ for $a/b = 0.5$, increasing to 1.0 bar $(^\circ\text{C})^{-1}$ for $a/b = 0.75$. Both stresses are at a maximum on the z axis, are fairly insensitive to changes in a/b and h/b , and the stressed regions are essentially confined to those underneath the warmed area. Decreasing the ratio h/b to 0.1 affects the values of both stresses by less than 10%.

On the basis of these calculated stresses, it is expected that a thermal shock of 14°C would be required to induce fracture of a thick plate by riming with large cloud droplets. Since the maximum stress is felt some time before the steady-state temperature is

FIG. 6. Radial stress τ_{rr} on the z axis of a thick plate with $a/b = 0.5$, $h/b = 0.5$ for various values of the time parameter $\omega = kt/b^2$.

attained, any variations in the temperature boundary conditions do not affect these conclusions. It also means that the heat balance relation between droplet and ice substrate imposes no severe restraints on the droplet size.

8. Other geometries

a. Solid columns

The semi-infinite model adequately describes the riming of columns whose minor axis is considerably larger than the droplet diameter. For riming situations involving droplets comparable in size with the crystal width, we can make some general statements about the magnitudes of the stresses without solving the problem exactly.

This problem is a two-dimensional one, i.e., the stresses vary only with depth and distance along the major axis, and the axial stress τ_{xx} can be described by (Boley and Weiner, 1960, p. 309)

$$\tau_{xx} = \alpha E \left[-T + \frac{1}{A} \int_{-h/2}^{h/2} T dA + \left(\int_{-h/2}^{h/2} T z dA / \int_{-h/2}^{h/2} z^2 dA \right) \right], \quad (15)$$

where A is the cross-sectional area normal to the major axis, z is measured from the undistorted median or central plane, and the crystal is of depth h . This expression is obtained under the same approximations and assumptions used in the thick-plate analysis of Section 7. Consequently, under the warmed area, the spatial and time variations of the two stress systems are very similar but there is an important difference in magnitude. Because the column is not restrained

FIG. 7. Radial stress τ_{rr} in a sphere for various values of the time parameter $\omega = \kappa t / b^2$.

across its width, this extra degree of freedom allows for a reduction in the magnitude of the stresses over the comparable thick plate ones. This reduction factor is $(1-\nu)$, where ν is Poisson's ratio. For ice, $\nu = 0.32$, so that the maximum stress experienced by a column is unlikely to exceed 1 bar $(^\circ\text{C})^{-1}$, necessitating a temperature change of 20°C to induce fracture.

b. Hollow columns, needles and sheaths

These crystals are especially worthy of investigation because their growth regime in clouds lies between -4 and -6°C , and corresponds with the narrow temperature window in which Hallett and Mossop (1974) observed secondary ice production to occur in the laboratory. Hollow needle-like crystals would be most sensitive to thermal shock on those parts where the walls are thinnest. Under these circumstances, tensile stresses could arise in two ways. First, in a way analogous to that of the thin plate of Section 6, expansion near the droplet boundary could produce tensile stresses of the order of 1.5 bars $(^\circ\text{C})^{-1}$. Second, bending stresses for hollow columns will be slightly higher than for solid ones of the same diameter. Although the moment of inertia,

$$\int_{-h/2}^{h/2} z^2 dA,$$

is considerably less, this reduction in strength of the hollow column does not have the pronounced effect that it does in isothermal situations where the moments and tractions are applied externally. In the thermal case, the stresses are generated within the material by bulk expansion, so that the driving force is related to the volume of material attempting to expand; this fact is reflected in the integral

$$\int_{-h/2}^{h/2} T z dA.$$

These two effects, the decrease in driving force and decrease in strength, are self-compensating to the extent that the maximum stress experienced by a hollow cylinder is only about 15% higher than that of a solid one.

The expansion-type stresses are likely to be the more important ones, but a temperature change of 12 – 15°C would still be needed to produce failure. Thus although these extreme crystalline forms are fragile mechanically, they are not especially susceptible to fracture by thermal shock.

c. Sphere

Finally, we conclude with the case of a sphere of radius b whose surface is subjected to a sudden temperature rise ΔT . Although it is of limited usefulness in terms of cloud physics applications, the clear-cut nature of the spherical geometry and application of the thermal shock renders it useful as an experimental check, and this aspect will be used in the companion paper. This problem can be solved exactly, and has been studied in detail (Nowacki, 1962, p. 238) and we state the results here for the sake of completeness. The temperature is

$$T(r, t) = \sum_{n=0}^{\infty} \frac{2\Delta T(-1)^{n+1}}{r} \sin(n\pi r/b) e^{-\kappa n^2 \pi^2 t/b^2}, \quad (16)$$

and the stresses can be obtained from

$$\tau_{rr} = \frac{2E\alpha}{3(1-\nu)} [P(b, t) - P(r, t)], \quad (17)$$

$$\tau_{\phi\phi} = \tau_{\theta\theta} = \frac{E\alpha}{3(1-\nu)} [2P(b, t) + P(r, t) - 3T(r, t)], \quad (18)$$

where

$$P(r, t) = \frac{3}{r^3} \int_0^r T(r, t) r^2 dr \quad (19)$$

$$= \frac{6\Delta T b^3}{\pi^3 r^3} \sum_{n=1}^{\infty} (-1)^n \left[\frac{n\pi r}{b} \cos(n\pi r/b) - \sin(n\pi r/b) \right] \times e^{-\kappa n^2 \pi^2 t/b^2}. \quad (20)$$

The stresses for ice are given in Figs. 7 and 8. They show that τ_{rr} is tensile, being a maximum at the center when $\omega = \kappa t / b^2$ is 0.058, when its value is 2.6

FIG. 8. As in Fig. 7 except for the azimuthal stress $\tau_{\theta\theta}$.

bars ($^{\circ}\text{C}$) $^{-1}$. The azimuthal stresses $\tau_{\theta\theta}$ and $\tau_{\phi\phi}$ are compressive on the surface, but tensile for $r/b < 0.8$, also attaining a maximum value of 2.6 bars ($^{\circ}\text{C}$) $^{-1}$ when $\omega = 0.058$.

9. Summary and conclusions

Although the stress systems of the various models we have studied have shown considerable differences, the preceding analyses allow us to discern some general trends in the behavior of ice under thermal shock. A small droplet impacting on a crystal whose dimensions are much greater than those of the drop will produce compressive stresses near the warmed area, and mildly tensile ones in a localized region at a depth of 0.6 of the droplet radius. These arise instantaneously, and probably require 35°C of supercooling to initiate cracking. As the drop and crystal become more comparable in size, tensile stresses due to bending arise. These occur after a delay characterized by the thickness of the crystal, and are again localized in the sense that they occur below the drop and at a depth of approximately one-quarter of the crystal thickness. It was calculated that temperature changes of about 20°C should be sufficient to cause failure under these circumstances. When a large droplet impinges on a thin plate, the stresses can be tensile outside the warmed area, occur almost instantaneously, and are not localized in that they exist through the depth of the crystal and out as far as the crystal edge. These require the least supercooling and the crystal can probably be induced to crack by temperature of 10°C or more.

Although the progression toward ease of fracture with droplet size is in accordance with the laboratory and field evidence linking the larger cloud droplets with the ice multiplication mechanism (Mossop *et al.*, 1970; Hallett and Mossop, 1974), several other aspects of the problem need consideration before any final conclusions can be drawn.

First, the condition that the macroscopic failure stress be exceeded in some region of the crystal constitutes only one of several conditions that should be investigated for ice multiplication mechanisms. Nucleation of cracks, their propagation over extensive distances, fragmentation of the crystal, and ejection of ice splinters are all aspects that have not been considered in this theoretical treatment, but are likely to impose further constraints on the system and make it more difficult to produce extra ice particles.

Second, any extrapolation of the theory to describe microphysical processes should err on the conservative side. This applies particularly to the value used for the uniaxial tensile strength of ice which, for crystals in clouds, could exceed the macroscopic value of 20 bars used in this study. The first requirement for crack initiation and propagation is that the elastic strain energy stored in the body be sufficient to provide

the free energy of the new surfaces. In general terms, this implies that $\tau > (4\gamma E/d)^{1/2}$, where τ is the critical stress, γ the surface free energy of ice, E Young's modulus, and d the length scale of the stressed domain. With appropriate values for ice, and taking the stressed region to be confined to a volume with dimensions of the riming droplet, we find that 50 bars is probably a more realistic value for the tensile strength. This suggests that the temperature changes for failure could be at least a factor of 2 greater than those calculated above, shifting the critical temperature regime even further away from -4 to -6°C where one would look for these effects to be important.

Further consideration shows that for microscopic bodies, the temperature change need not be as abrupt as the step function assumed in the theoretical analyses. The time scale for establishing the temperature change is approximately a/v , where v is the dendritic growth velocity and is of the order of 1 cm s^{-1} for typical cloud supercoolings. Against this, the time scale for removal of heat by diffusion goes as a^2/κ , so that the temperature change is only abrupt provided $a/v \ll a^2/\kappa$. This condition is met by droplets with $a < 100 \mu\text{m}$, so that the riming of an ice particle by a droplet of this size or smaller would generate less abrupt temperature changes than we have modelled, with a consequent reduction in thermal stresses.

In discussing thermal shock mechanisms, we have only considered the classic riming situation, but there are other ways in which temperature changes could arise in cloud particles. Since the quasi-static thermoelastic theory is a linear one, it predicts that if the body is cooled rather than warmed, the compressive stresses we have calculated become tensile, and *vice versa*. There is an important distinction between the two cases, however. In the warming case, the compression stresses which generally occur initially could be ignored because ice is difficult to crack in compression. When the body is cooled, these stresses become tensile, and a temperature difference of 5°C would probably be sufficient to cause fracture. There are several ways in which a crystal can be cooled, but all rely on the collision between two ice particles, one of which is in temperature equilibrium with the cloud, and the other has been warmed in some way, for example by excessive riming. However, such events would be unusual because collisions between similar sized ice particles in clouds are rare, and we can probably rule out the possibility of fracture occurring in this manner on the basis of the time-scale involved.

On the whole, the theoretical evidence suggests that thermal shock mechanisms are unlikely to be responsible for the extra ice particles found in clouds near 0°C . Results of thermal shock experiments on large ice crystals which lend support to these conclusions will be presented in the companion paper (King and Fletcher, 1976).

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APPENDIX A

Time-Dependent Temperature and Stresses in a Semi-Infinite Solid

If the functions f , g and h are defined as

$$f(\eta, z, t) = e^{\eta z} (\eta z/4 + \eta^2 \kappa t/2) \operatorname{erfc}(z/2\sqrt{\kappa t} + \eta\sqrt{\kappa t}) - e^{-\eta z} (\eta z/4 - \eta^2 \kappa t/2) \operatorname{erfc}(z/2\sqrt{\kappa t} - \eta\sqrt{\kappa t}), \quad (\text{A1})$$

$$g(\eta, z, t) = e^{-\eta z} [(0.5 + \eta^2 \kappa t) \operatorname{erf}(\eta\sqrt{\kappa t}) + \eta\sqrt{\kappa t}/\pi e^{-\eta^2 \kappa t}], \quad (\text{A2})$$

$$h(\eta, z, t) = e^{-\eta z} \operatorname{erfc}(z/2\sqrt{\kappa t} - \eta\sqrt{\kappa t}) + e^{\eta z} \operatorname{erfc}(z/2\sqrt{\kappa t} + \eta\sqrt{\kappa t}), \quad (\text{A3})$$

then the expressions for the time-dependent temperature and stresses are

$$T(r, z, t) = \frac{a\Delta T}{2} \int_0^\infty J_0(\eta r) J_1(\eta a) h(\eta, z, t) d\eta \quad (\text{A4})$$

$$\begin{aligned} \tau_{rz}(r, z, t) &= \frac{E\alpha a \Delta T}{(1-\nu)} \int_0^\infty J_1(\eta a) J_1(\eta r) \\ &\times [(\eta z - 1)g(\eta, z, t) - f(\eta, z, t) - h(\eta, z, t)/4 + \eta\sqrt{\kappa t}/\pi \\ &\times \exp[-(z^2/4\kappa t) - (\eta^2 \kappa t)] - z\eta^3 \kappa t e^{-\eta z}] d\eta \quad (\text{A5}) \end{aligned}$$

$$\begin{aligned} \tau_{zz}(r, z, t) &= \frac{E\alpha a \nabla T}{(1-\nu)} \int_0^\infty J_1(\eta a) J_0(\eta r) \\ &\times [f(\eta, z, t) + \eta z g(\eta, z, t) - \eta^2 \kappa (\eta z + 1) e^{-\eta z} t] d\eta \quad (\text{A6}) \end{aligned}$$

$$\begin{aligned} \tau_{rr}(r, z, t) &= \frac{2E\nu\alpha a \Delta T}{(1-\nu)} \int_0^\infty J_1(\eta a) J_0(\eta r) \\ &\times [g(\eta, z, t) - \eta^2 \kappa t e^{-\eta z} - h(\eta, z, t)/4\nu] d\eta \\ &- \frac{E\alpha a \Delta T}{(1-\nu)} \int_0^\infty J_1(\eta a) [J_0(\eta r) - J_1(\eta r)/\eta r] \\ &\times [f(\eta, z, t) - (2\nu - 1 + \eta z)\eta^2 \kappa t e^{-\eta z} \\ &- (2 - 2\nu - \eta z)g(\eta, z, t)] d\eta \quad (\text{A7}) \end{aligned}$$

$$\begin{aligned} \tau_{\theta\theta}(r, z, t) &= \frac{2E\nu\alpha a \Delta T}{(1-\nu)} \int_0^\infty J_1(\eta a) J_0(\eta r) \\ &\times [g(\eta, z, t) - \eta^2 \kappa t e^{-\eta z} - h(\eta, z, t)/4\nu] d\eta \\ &- \frac{E\alpha a \Delta T}{(1-\nu)} \int_0^\infty \frac{J_1(\eta a) J_1(\eta r)}{\eta r} \\ &\times [f(\eta, z, t) - (2\nu - 1 + \eta z)\eta^2 \kappa t e^{-\eta z} \\ &- (2 - 2\nu - \eta z)g(\eta, z, t)] d\eta. \quad (\text{A8}) \end{aligned}$$

At $t=0$, the only non-zero stresses are $\tau_{\theta\theta}$ and τ_{rr} , having the values, on $z=0$, of

$$\tau_{\theta\theta} = \tau_{rr} = -\frac{E\alpha \Delta T}{(1-\nu)} H(a-r), \quad (\text{A9})$$

where $H(x)$ is the Heaviside step function, which is zero for $x < 0$ and unity for $x \geq 0$. Both stresses are zero for $z > 0$.

At $t=\infty$, $\tau_{\theta\theta}$ are again the only non-zero stresses, and on $z=0$, (A7) and (A8) reduce to

$$\tau_{rr} = -\frac{E\alpha \Delta T}{2} \left[H(a-r) + \frac{a^2}{r^2} H(r-a) \right], \quad (\text{A10})$$

$$\tau_{\theta\theta} = -\frac{E\alpha \Delta T}{2} \left[H(a-r) - \frac{a^2}{r^2} H(r-a) \right]. \quad (\text{A11})$$

It is important to note that $\tau_{\theta\theta}$ has a discontinuity of $E\alpha \Delta T$ on passing through $r=a$.

APPENDIX B

Equilibrium Stresses on the Surface of the Semi-Infinite Model

In Section 5 of the text describing the stresses of the semi-infinite model, it was shown that $\tau_{\theta\theta}$ attains a large tensile value $[2.3 \text{ bars } (^{\circ}\text{C})^{-1}]$ at the edge of the warmed area as the equilibrium state is approached. We show here that this tensile stress is a consequence of the temperature discontinuity in this region and that significant tensile stresses are unlikely to arise in ice crystals in clouds.

Consider the semi-infinite substrate to be warmed by an amount ΔT on the surface $z=0$, $r < a$, but instead of imposing zero temperature difference on $r > a$, allow heat transfer across it according to the usual Newtonian relation

$$\partial T / \partial z = h[T(r, 0) - T_e], \quad z=0, \quad r > a. \quad (\text{B1})$$

FIG. B1. Equilibrium values of $\tau_{\theta\theta}$ on the exterior surface of a semi-infinite solid for different values of the ventilation parameter ah . The dashed line corresponds to the results of Section 5 in which zero temperature difference is maintained outside the warmed region.

Here h is a parameter incorporating the heat transfer due to evaporation as well as conduction. For water vapor in air, it can be described to sufficient accuracy by (Johnson and Hallett, 1968)

$$h = \text{Nu}(k + \beta DL_s)/lK, \quad (\text{B2})$$

where Nu is the experimentally determined Nusselt number associated with the characteristic length l , k and K are the thermal conductivities of air and ice respectively, D is the diffusion coefficient of water vapor in air, L_s the latent heat of sublimation of ice, and β the slope of a linear approximation to the saturated water vapor density vs temperature curve. Using expressions for the Nusselt number for ice crystals as suggested by Jayaweera (1971), it can be shown that even for the largest ice crystals of interest to cloud physics, $h < (5d)^{-1}$, where d is the crystal diameter (plate-like) or width (columnar-type).

The mixed nature of the temperature boundary conditions (i.e., specification of the temperature as well as its gradient on the exposed surface) increases the complexity of the problem to the extent that a complete time-dependent analytic solution has not yet been obtained. For the equilibrium situation of interest to us, however, Mahalanabis (1967) has shown that

$\tau_{\theta\theta}$ is given by

$$\tau_{\theta\theta}(r, z) = E\alpha \left[\int_0^\infty \phi(\eta) J_1(\eta r/a) e^{-\eta z/a} d\eta - \frac{r}{a} \int_0^\infty \eta \phi(\eta) J_0(\eta r/a) e^{-\eta z/a} d\eta \right], \quad (\text{B3})$$

where an obvious correction to the numerical factor preceding the integrals as published in that paper has been made. For the boundary condition outlined above, and to sufficient accuracy for the present purposes,

$$\phi(\eta) = \frac{2\Delta T \sin \eta}{\pi(\eta + ah)\eta} - \frac{2ah\Delta T g(\eta)}{\pi^2(\eta + ah)}, \quad (\text{B4})$$

where

$$g(\eta) = [2\gamma - 2 - \pi ah + 2 \log(2ah) - \text{Si}(2\eta)/\eta] \sin(\eta)/\eta + [\gamma - \pi ah + \log(2\eta) - \text{Ci}(2\eta)] \cos(\eta)/\eta^2 + \pi ah \sin(\eta)/\eta^3, \quad (\text{B5})$$

γ is Euler's constant, and $\text{Si}(x)$ and $\text{Ci}(x)$ are the sine

and cosine integrals:

$$\left. \begin{aligned} \text{Ci}(x) &= - \int_x^\infty \frac{\cos s}{s} ds \\ \text{Si}(x) &= - \int_x^\infty \frac{\sin s}{s} ds \end{aligned} \right\} \quad (\text{B6})$$

For more details on this solution, and the techniques used to obtain it, the reader is referred to the paper by Mahalanabis.

Values of $\tau_{\theta\theta}$ were obtained by integrating (B3) numerically and Fig. B1 shows the variation on the surface $z=0$ for particular values of the parameter ah . Appreciable tensile stresses only arise when $ah > 0.5$; i.e., when ventilation is strong enough to maintain the ice surface close to the environmental temperature, thus generating large temperature gradients near the droplet. Since extreme values of ah for cloud situations are unlikely to exceed 0.1, it is apparent that $\tau_{\theta\theta}$ in ice crystals in clouds will be less than 0.2 bar ($^{\circ}\text{C}$) $^{-1}$, which can be ignored.

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