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Sintering in a dry snow cover

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The basic shape of bonds in snow is dictated by the geometrical requirements of grain-boundary grooves and is not a simple concave neck as has long been assumed. In fact, all of the earlier work on the theory of sintering in snow was based on an incorrect assumption about the geometry. A theory of the growth of bonds in snow is given here based on observations of their actual shape which is dominated by grain-boundary grooves. The theory describes the growth of the bond by the removal of water molecules from the grain boundary by diffusion due to the stress gradient. Three-dimensional grains are described and the dihedral angle is allowed to increase with time. [S0021-8979(98)08920-8]

I. INTRODUCTION

Ice bonds form between slowly growing, rounded grains in dry snow on the ground. Much attention has been paid to the size, shape, and growth of the grains,[1] but while the bonds are of equal importance to the grains themselves, in recent years relatively little attention has been paid to the bonds. In fact, many observations of the grains have been made, but the bonds have rarely been directly observed. This probably explains why the existing literature describes sintering in snow as if snow were a noncrystalline material with no imposed temperature gradient. Unfortunately, the wrong geometry has been assumed for the grain bond as shown in Fig. 1. The widely held approach to sintering in dry snow could be applied to glass beads held in an adiabatic cell, but not to ice grains in a seasonal snow cover. The actual geometry of grain bonds in snow is described here along with one mechanism for sintering, grain-boundary diffusion. Other mechanisms can also operate and might be important when the snow cover has a temperature change over its depth. Nevertheless, grain-boundary diffusion, which is controlled by the geometry of the grain bond, is one of the basic processes contributing to bond growth and may be the controlling process.

The most studied case of sintering in snow is of well-rounded grains in dry snow where the grains grow slowly while they build intergranular bonds.[2–4] Various indirect methods have been used to infer information about bonds, but these do not provide information about the geometry of the bonds nor about the processes which form them. Even current models describing the mechanics of snow are often based on an incorrect geometry (Fig. 1), a geometry which cannot exist since ice is a crystalline material.

II. OBSERVATIONS

Figure 2 shows a bond in fresh snow where the grain-boundary groove angle is much less than the equilibrium value of 145° because the bonds have just formed. Figure 3 shows three bonds among three grains that have sintered for two months in the laboratory at −3 °C. The grain-boundary grooves and dihedral angles are visible, but the angles are somewhat affected by the irregular geometry of the grains. Figure 4 shows a grain bond in snow stored at a low temperature for several years. The geometry of these bonds is also dictated by grain boundary grooves and dihedral angles in the range of the equilibrium value for ice and water vapor, about (Ref. 5) 145°±2°. These grains are not packed in a regular manner and thus parts of the grain surfaces are still concave, even at this late stage of sintering. A bond of a similar nature is shown by Kuroiwa.[3] Using the ice bond ''b'' in Fig. 8 of Ref. 3, I measured dihedral angles of 138° and 148° on two sides of a bond that had grown for 6 days at −3 °C. Based on this, my own microscopic observations done in the laboratory, and the rapid development of strength in snow, it is clear that the bonds grow rapidly at first and that the growth rate decays rapidly with time. Thus the dihedral angle increases with time of sintering and quickly approaches its equilibrium value.

III. THEORY

Zhang and Schneibel[6] described the sintering of two-dimensional grains joined by grain boundary grooves. They assumed two-dimensional grains with a fixed dihedral angle throughout the process, an assumption which clearly does not apply to snow. In spite of this limitation, the basic ideas of Zhang and Schneibel[6] and other earlier works are applicable to sintering in snow and their approaches are extended here to include three-dimensional grains and a dihedral angle that enlarges as the bond grows. While two spherical grains were used in laboratory observations of sintering, the natural forms of snow, as shown in Figs. 2, 3, and 4, clearly show that the grains in snow are much more irregular than that.

In the theory, two spherical ice grains are joined at the missing spherical segments (Fig. 5) and, as they grow, the original volume of ice in each grain is preserved by growth of the spheres. While Zhang and Schneibel[6] considered simultaneous diffusion along the grain surface to distribute the molecules removed from the grain boundary, in this theory

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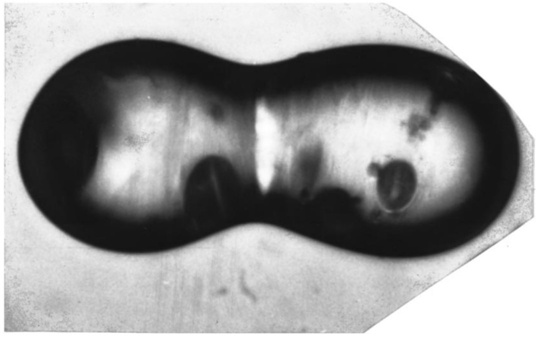

FIG. 1. The geometry that has long been assumed to describe rounded grains with bonds in dry snow. Actually, these grains are glass beads: ice grains form a neck with a grain-boundary groove and, given enough time, an equilibrium grain-boundary groove angle of about 145°.

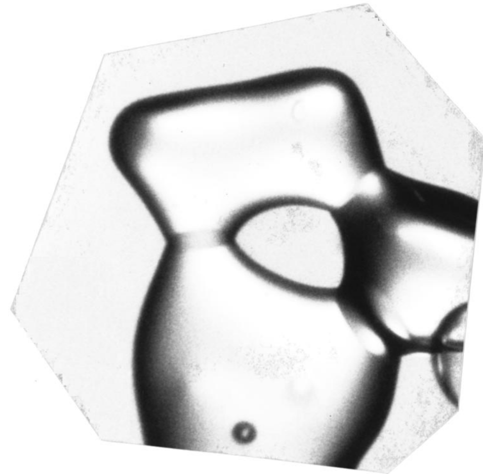

FIG. 3. Rounded grains which have sintered for two months at −3 °C. The dihedral angles are determined in part by the irregular shape of the grains.

that distribution is assumed to occur without restriction since the grains tend to remain spherical during sintering in laboratory experiments. These rounded grains are the ''equilibrium form'' of the ice crystal at common temperatures and all grains in snow eventually approach a well-rounded shape, except at much lower temperatures or high growth rates.[1] The bond grows due to the gradient of normal stresses along the grain boundary and the rate of bond growth is tied directly to the rate at which the dihedral angle enlarges.

The geometry of this simple, two-grain system is characterized by the grain radius (R), dihedral angle (A), and radius of the grain bond (Y). The angle and relative bond size are connected by

$$Y=R\ \sin(A/2). \tag{1}$$

The radius of a grain at any time during sintering is related to its radius at the start of sintering (R_0) by

$$2R^3=4R_0^3-(2R^2+Y^2)\sqrt{R^2-Y^2}, \tag{2}$$

and to the dihedral angle by

$$R^3=\frac{4R_0^3}{2+\cos(A/2)(2+\sin^2(A/2))}. \tag{3}$$

A gradient of normal stress occurs along the grain boundary before the dihedral angle reaches its equilibrium value. The grain boundary grows when water molecules diffuse out of the grain boundary, a flux that arises from the stress gradient along the boundary. This molecular flux (J) is given by

$$J=\frac{\delta D}{kT}\frac{d\sigma}{dy}, \tag{4}$$

where δ is the width of the diffusive layer, D is the coefficient of grain-boundary diffusion, k is Boltzmann's constant, T is absolute temperature, σ is the normal stress acting across the grain boundary, the tensile stress is positive, and y is the radial coordinate along the boundary.

Since the grain boundary remains flat, the plating rate or the rate of growth of the spherical segment, v, varies only with time. Then continuity at any radial position y requires that

$$y\nu=-\Omega J, \tag{5}$$

where Ω is the molecular volume and v is negative when material is removed from the grain boundary. Now we can integrate the stress gradient to give

$$\sigma=\sigma_0-\frac{kT\nu}{2\Omega D\delta}y^2 \tag{6}$$

where σ_0 is the stress at the center of the bond.

The sum of the forces across the entire grain boundary is zero when

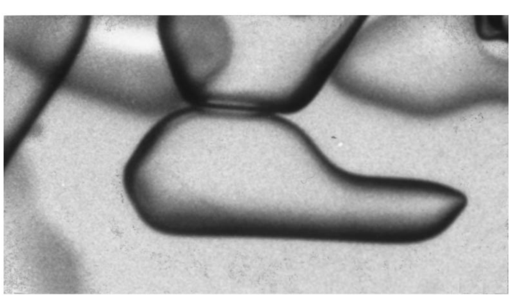

FIG. 2. Fresh, dry snow with newly formed bonds showing a grain boundary with a small angle in the grain-boundary groove.

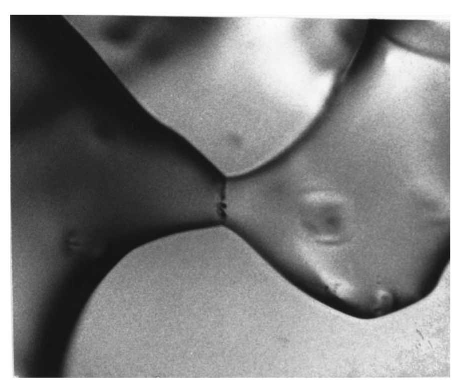

FIG. 4. Snow grains stored at −24 °F for several years showing distinct grain-boundary grooves at the bonds. These bonds have dihedral angles in the range of 145° even though the grains are still irregular.

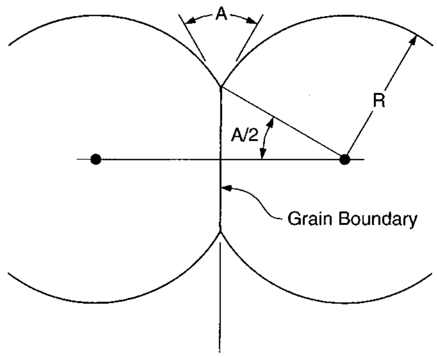

FIG. 5. The idealized form of two grains of ice with a grain-boundary groove. The angle will grow until it reaches 145°.

$$\int_0^Y \sigma y \; dy + Y\gamma \sin(A/2) = 0, \tag{7}$$

where $\sin(A/2)$ equals Y/R. Then integrating and taking v as zero when R equals its maximum value R_m, it follows that σ_0 equals $-2\gamma/R_m$. The grain-boundary stress is thus given by

$$\sigma = 4\gamma\left(\frac{1}{R} - \frac{1}{R_m}\right)\left(\frac{y}{Y}\right)^2 - \frac{2\gamma}{R_m}. \tag{8}$$

While σ_0 equals $-2\gamma/R_m$, at the circumference of the bond

$$\sigma(Y) = \frac{4\gamma}{R} - \frac{6\gamma}{R_m}. \tag{9}$$

This derived value is not the same as the value which is usually assumed for the end condition because that assumption is only valid when the growth stops and the stress gradients disappear. After the growth stops, R equals R_m and $\sigma(Y_m)$ equals $-2\gamma/R_m$. In fact, at equilibrium the ice grains would experience a pressure equal to $-2\gamma/R_m$ everywhere because all stress gradients would disappear.

The growth rate of the spherical cap, which is the negative of v, as derived from Eqs. (4), (5), and (8), is given by

$$\frac{dh}{dt} = 8\frac{D\delta\Omega\gamma}{kT}\left(\frac{1}{R} - \frac{1}{R_m}\right)\frac{1}{Y^2}, \tag{10}$$

which goes to zero when R equals R_m. Converting to dimensionless variables using $\tilde{R}$ as R/R_m, $\tilde{y}$ as y/Y, $\tilde{\sigma}$ as $\sigma R_m/2\gamma$, and $\tilde{t}$ as $2^{1/3}D\delta\gamma\Omega t/kTR_0^4$, dimensionless stress is given by

$$\tilde{\sigma} = 2\left(\frac{1}{\tilde{R}} - 1\right)\tilde{y}^2 - 1. \tag{11}$$

This is compressive and is a maximum at the center of the bond. For $\tilde{R}$ of 1.0 where bond growth is complete, the stress is constant. Figure 6 shows how the compressive stress in the grain boundary decreases radially to a minimum at the edge of the bond. For an A_m of 145°, $\tilde{R}$ is equal to or greater than 0.896 and $\tilde{\sigma}$ ranges from -1.0 at the center to -0.77 at the groove.

Solving for one dependent variable only, the dihedral angle increases in time according to the solution of

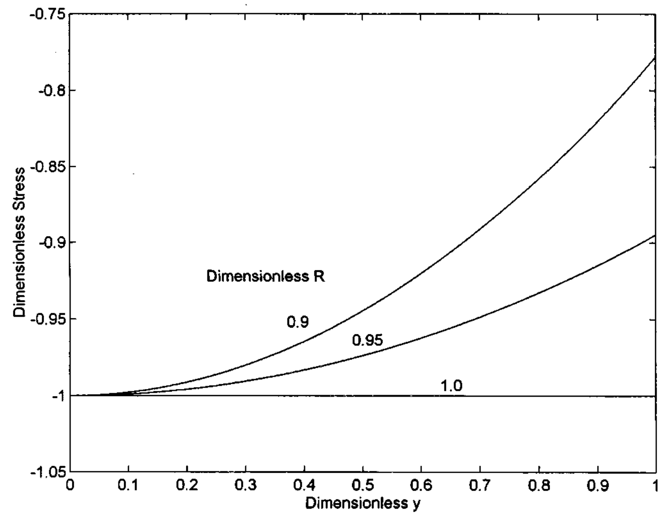

FIG. 6. Dimensionless stress vs dimensionless radial distance from the center of the bond with dimensionless grain size as a parameter.

$$\tilde{t} = \frac{1}{2}\int_0^{A/2} \frac{\sin^3(A/2)[2 + 2\cos(A/2) + \sin^2(A/2)]}{\Delta^{1/3} - \Delta_m^{1/3}}\Delta^{-2} dA, \tag{12}$$

where Δ is given by

$$\Delta = 2 + \cos(A/2)[2 + \sin(A/2)]. \tag{13}$$

The growth of the dihedral angle with time is shown in Fig. 7 as it approaches a maximum value of 145°, or 2.53 rad. The growth occurs quickly at first but the rate slows markedly as the bond develops. This pattern of the growth explains why snow develops some strength quickly since the size of the bond increases as $\sin(A/2)$ and its area as $\sin^2(A/2)$.

The computed result is also shown on a log–log scale in Fig. 8 where it can be seen that $\sin(A/2)$, or Y/R, increases as $t^{0.25}$ during the initial phase of sintering. This is the highest value of the exponents found by Kuroiwa[3] in his experiments with sintering in snow, suggesting that this theory predicts a dependence on time which is slightly too high. The

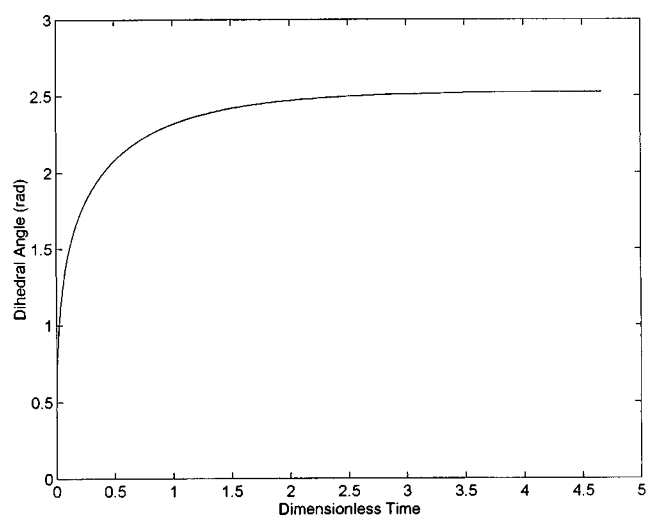

FIG. 7. Dihedral angle vs dimensionless time.

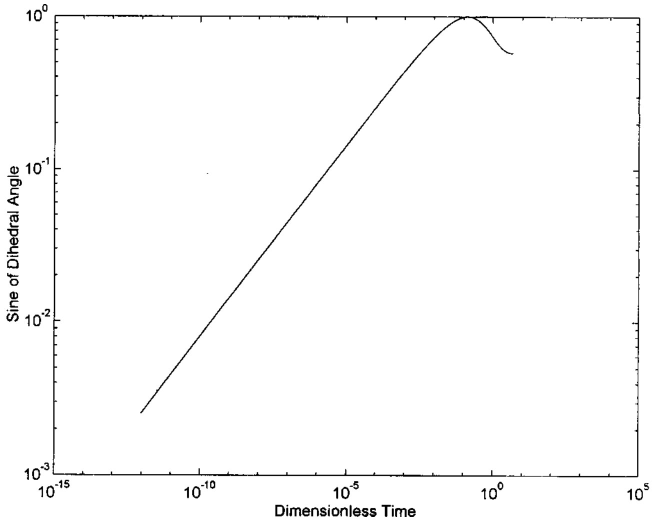

FIG. 8. Log of sin(A/2) vs log of dimensionless time; sin(A/2), or Y/R, increases as $\tilde{t}^{0.25}$ over the straight portion of the curve.

theory may also over predict the dependence on grain size, suggesting that time to reach a certain A increases as R_0^4. Kuroiwa's data[3] suggest that the dependence is weaker than R_0^2 while Kingery's[2] data supported the fourth power dependence. The theory does show that some bond strength will develop quickly since Y/R reaches 0.10 when $\tilde{t}$ reaches 2E -6. While it is not possible to put an absolute value to this time without having reliable values for D and δ, the suggestion that the next gain of 0.10 takes about 16 times as long seems reasonable based on both sintering observations and common experience with snow. It is also a common experience that smaller grains, such as those in wind crust, sinter more quickly than large grains.

IV. DISCUSSION

Strong bonds form among rounded, slowly growing grains in snow. Their growth processes and geometry have probably been misunderstood, even though sintering in snow was widely studied some years ago. The bonds are usually described as necks with a concave geometry as in studies of sintering of other materials. However, this geometry would not seem possible for a crystalline material because the equilibrium form of the crystal requires the presence of a grain-boundary groove at the crystalline boundary. Perhaps the geometry is different at very high growth rates where the grains are faceted.[1]

In the past it has been assumed that the reverse geometry causes the migration of water molecules to the neck by one of several possible processes and the dominant mechanisms were identified by the observed dependence on time. Kingery,[2] who first applied this approach to ice grains, concluded that the bonding was due to surface diffusion. However, the coefficient of surface diffusion required was very high, and while this might be explained by a highly mobile, surface transition layer, this idea remains to be convincingly demonstrated. Kuroiwa[3] concluded that volume diffusion was the dominant process, but Hobbs and Mason[4] believed that sublimation, transfer through the vapor phase, had to be the dominant mechanism. The vapor transfer mechanism, which depends on the assumption of the reverse geometry of the neck, has since received wide acceptance and was supported by the strength tests of Ramseier and Keeler.[7] In fact, various mechanisms may dominate under different conditions or during different stages of sintering. However, the classical concepts based on a concave neck cannot dominate after the grain boundary groove is established, which appears to happen the instant that contact is made. The grain boundary groove angle in the bond at equilibrium is about 145° but, in fresh snow the angle is much smaller because the bonds have just formed.

Keeler[8] found a higher rate of bond growth in natural snow than expected from laboratory experiments. This is almost certainly due to the macroscopic temperature gradients that occur in nature, but were absent in the laboratory experiments. These gradients cause vapor movement at a much greater rate than could occur just due to gradients in curvature or stress. Since the rate limiting factor in mass flow in snow is probably the vapor density gradient, which is controlled by the temperature gradient, the temperature gradient may play a role in the rate of growth of the bonds, as it does in the rate of growth of the grains. Hosler, Jensen, and Goldshak[9] observed that humidity also affects the rate at which strength develops, at least initially.

Quantitative results from the theory of grain boundary diffusion given here depend on the product $D\delta$ for which few estimates exist. Using a measured rate of bond growth from Kuroiwa[3] and taking $\tilde{t}^{0.25}$ as proportional to Y/R as discussed above, $D\delta$ must equal 536 μm^3/s. Kingery's[2] theory required a very large value for the coefficient of surface diffusion, and even if the grain boundary thickness is 1 μm, Kingery's estimated value of the coefficient of surface diffusion is orders of magnitude greater than 536 μm^3/s while Wilkinson's[10] estimated value of $D\delta$ is significantly less. Thus while the theory given here is an important extension of earlier work on sintering by grain-boundary diffusion, its quantitative application depends on obtaining more reliable values of $D\delta$.

V. CONCLUSIONS

Earlier theories of sintering in snow were based on an incorrect assumption about the geometry of the bond. The bond was assumed to have the reverse, or concave, curvature of liquid bridges between solids. However, since ice is a crystalline material, the neck must have a grain boundary groove which is the dominate feature of its geometry. The growth of necks between ice grains is modeled by the diffusion of water molecules out of the neck under a stress gradient. The grains are assumed to be spherical while the dihedral angle grows out to an equilibrium value of 145°. The growth is rapid at first so snow quickly develops some strength.

The growth rate is predicted to vary as the one-fourth power of time, a dependence which is a little stronger than observed. The time to sinter to a certain neck size is predicted to vary as the fourth power of the grain size, a dependence which is too strong according to the data of Kuroiwa[3] but just right according to the data of Kingery.[2] The required value for $D\delta$ seems too high unless the grain boundary is quite thick with a high degree of self-diffusion. Better values of $D\delta$ are needed to test the theory and other mechanisms may have to be added to account for the effects of a macroscopic temperature gradient in the snow.

ACKNOWLEDGMENT

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