THE ROYAL SOCIETY

Ice surfaces: macroscopic effects of microscopic structure

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The balance between ice and water controls the habitability of an important fraction of the globe and influences the majority of the world's population. The freezing of water to form ice is one of the most common phase transformations in the natural environment. However, a complete understanding of its microscopics and their influence on macroscopic phenomena still eludes us. As this millennium comes to a close, we are beginning to understand how the microscopic interfacial structure of ice controls pattern formation during ice-crystal growth, the evolution of the polycrystalline fabrics of the great ice sheets, the dynamics of ground freezing, ozone destruction, and the mechanism of charge transfer that drives thunderstorm electrification. This paper describes our evolving understanding, its implications for the basic principles of melting and freezing, and their environmental consequences.

Keywords: premelting; ice; phase transitions; surfaces; disorder; environment

1. Introduction

More than two-thirds of our planet's surface is covered by water. Our mean distance from the Sun, the geometry of our orbit, and the radiative properties of our atmosphere contrive to make the mean surface temperature *ca.* 15 °C; 25 °C in the large tropical and subtropical belt, and between −20 and −40 °C in the small polar caps. Water becomes ice at just around the middle of that temperature range. Only a small shift in temperature determines whether precipitation will fall as rain or as snow and whether an ocean region will be blue water or white ice. It is no wonder, then, that ice cover is an extremely sensitive geophysical variable, and that ice has innumerable and profound consequences for climate, the hydrological cycle, vegetation and all other elements of the biosphere, land forms, and, hence, all human activities. Many aspects of its microphysics and chemistry have large-scale consequences.

The difficulties associated with observing processes in their natural setting often impede our ability to extract the essential features, and, hence, controlled laboratory experiments play a significant role in the development of our understanding. Our exploration of these phenomena, and the challenges that they offer, begins at a microscopic scale, on the surface of ice, and moves toward larger scales. The challenges encountered are at least as old as science itself.

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2. History

One may argue that the strikingly detailed observations of snow and ice made during the winter of 1635 by Descartes initiated the scientific method. Among other things, his work highlighted the role of ice surfaces in its melting and adhesive behaviour (Frank 1974). Over 200 years later, in 1842, Michael Faraday began a 20 year investigation into the properties of snow and ice. Faraday's publications based on this research (see, for example, Faraday 1860) clearly demonstrate the notion that melting and freezing are influenced by the interfaces that separate solids from liquids.

> Two pieces of thawing ice, if put together, adhere and become one; at a place where liquefaction was proceeding, congelation suddenly occurs... a particle of water, which could retain the liquid state while touching ice only on one side, could not retain the liquid state if it were touched by ice on both sides; but became solid, the general temperature remaining the same.

Although Faraday and Tyndall's (Tyndall 1858) experiments were proof to them that an interfacial film of liquid existed at equilibrium, their powerful contemporaries, James Thomson and his brother Sir William Thomson (who later became Lord Kelvin), countered with an explanation growing out of their work on the influence of pressure on phase changes, arguing that regelation, which is now called sintering, of ice results from the temporary lowering of the melting temperature due to the increase of pressure at the points of contact. Faraday argued that the pressure-melting experiments did not have sufficient resolution to resolve the dispute, and that

> ...experiment might be so applied as to advance the investigation of this beautiful point in molecular philosophy to a further degree than has yet been done; even to the extent of exhausting the power of some of the principles assumed in one or more of the three views adopted, and so render our knowledge a little more defined and exact than it is at present.

Despite Faraday's call for refined study, pressure melting came to be the textbook explanation for the rapid sintering and slipperiness of ice. However, simple calculation shows that pressure melting cannot account for the low friction of ice except at temperatures very close to the normal melting point; for a typical person on a conventional ice skate, the depression of the melting point is less than 0.1 K. At lower temperatures, as was argued by Bowden & Hughes (1939) and as developed further by Evans *et al.* (1976), the low-friction coefficient in ice skating is due to frictional heating. Nonetheless, for an explanation of Faraday's observations we require a more general phenomenon, found in virtually all forms of solid matter.

3. The surface of ice

Imagine moving toward the surface of an ice crystal from deep within its interior. During your transit along a crystallographic axis you encounter molecules with periodic regularity, each molecule being coordinated with its nearest neighbours. However, the coordination becomes distorted as you near the crystal's surface where the

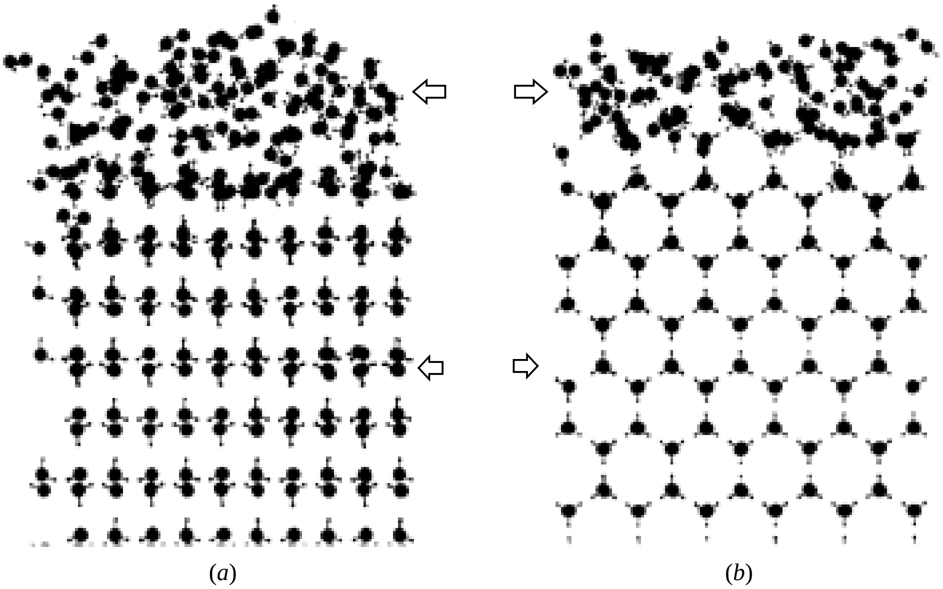

Figure 1. A simulated molecular scale picture of the surface region (the top of the picture) at the primary crystallographic orientations of ice: (*a*) the basal facet and (*b*) the prism facet. The liquid-like disordered structure appears at the surface at temperatures below the bulk melting temperature, and its extent depends on the underlying crystallographic structure and the temperature. The large solid circles are the oxygen atoms and the small dots are the hydrogen atoms averaged over 10 ps at a temperature 8 K below the bulk melting temperature (from the molecular dynamics simulations of Furukawa & Nada (1997)). The upper (lower) arrows indicate the 'quasi-liquid' layer (bulk ice crystal). More accurate intermolecular potentials are being developed (Batista 1999) that will improve such simulations.

molecules are the most poorly bound and, relative to those in the interior, experience the greatest deviation from the crystal's harmonic structure.

At higher temperatures, thermally activated fluctuations cause the greatest vibrations at the surface and, at a sufficiently high temperature but still below the melting point, intermolecular bonds rupture and eventually molecules begin to flow in a film confined to the surface; a kind of quasi-liquid, with some structural characteristics of the solid below, but with the mobility of a fluid (figure 1).

When one first hears the term 'surface melting' one's natural reaction is to imagine how a solid, as it is heated, melts from its surface inward. This kind of example, first considered by Tammann (1909), is analogous to a lump of solder under a soldering iron, which begins to liquefy at its surface simply because the outside is hotter than the inside; the melting process is limited by the transient flow of heat. Our modern description of surface melting specifically refers to a less obvious effect: the surface of a solid, at a uniform temperature, develops a thin coating of its melt at temperatures below the bulk transition temperature. The layer is a stable and reversible characteristic of the equilibrium state. It is a precursor of the complete melting of the solid, and it is a very general property of nearly all solid matter, influencing crystal growth, adhesion and other behaviour (Wettlaufer 1999*a*). Metals, semiconductors, solid rare gases and molecular solids, including ice, undergo the

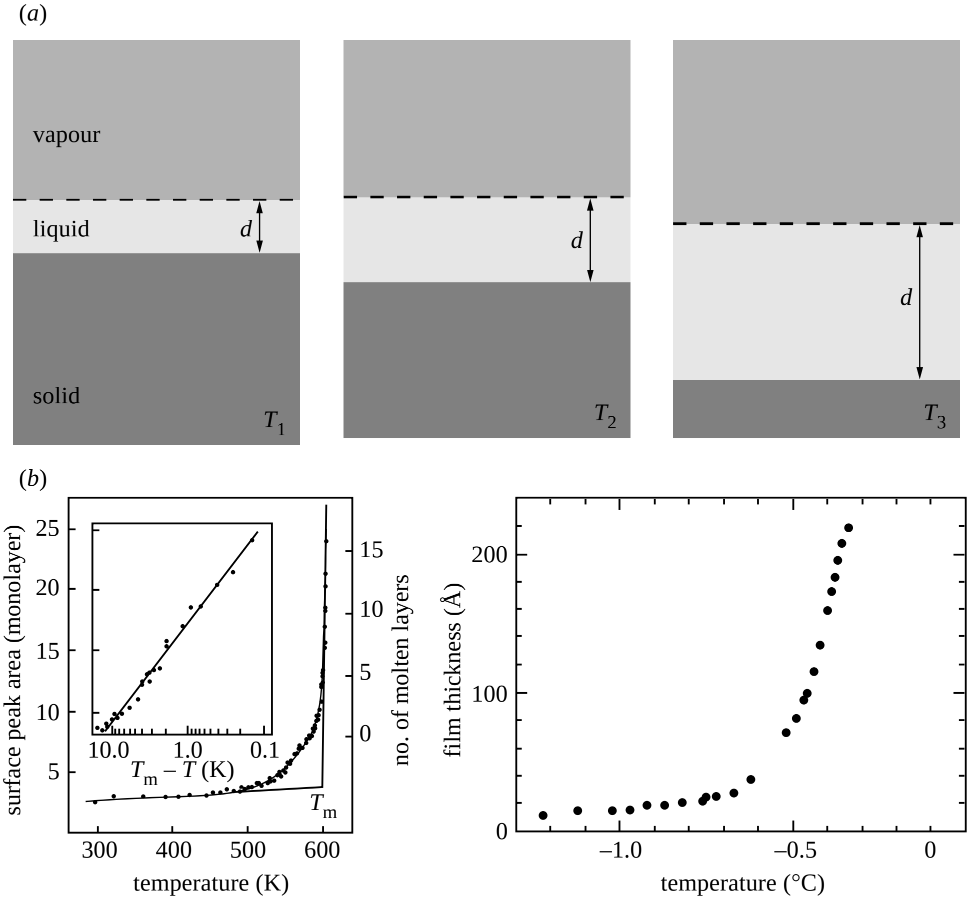

Figure 2. (a) Surface melting is a general phenomenon. It is a special case of wetting, wherein the 'substrate' is the solid phase of the liquid melt. If the cohesive forces in a fluid are stronger than the adhesive forces of attraction between the substrate and the fluid, the latter stands as a droplet with a finite contact angle, rather like water droplets on a freshly waxed car. If the intrafluid forces are weaker than the adhesive forces, the droplet spreads to completely wet the surface. Such is the case for surface melting. As the temperature rises, $T_1 < T_2 < T_3$, the film thickness increases as depicted here, and illustrated in (b) for two different materials. (b) The figure on the left shows the thickness of the surface-melted layer on the (110) face of a lead crystal, measured by Frenken & van der Veen (1985) using the technique of ion backscattering. The right-hand vertical axis is the number of monomolecular layers and the bulk melting temperature is denoted by T_m. On the right, we see the thickness of the surface-melted layer on the basal plane of ice, obtained by Elbaum *et al.* (1993) using the technique of optical reflectometry.

process: it typically begins well below the melting point as a layer a few molecules thick, which gradually thickens with rising temperature, and finally diverges at the melting point. Surface melting was surmised long ago, from the observation that solids are generally wetted by their melts (see figure 2). This evidence of the lowering of the surface energy of a solid by a liquid film led Stranski (1942) to conclude that a liquid film could coat a solid below its melting point. Frenken (1946) argued that it is such preexisting liquid films that explain the asymmetry of the melting transition about the bulk melting temperature: melting, in contrast to freezing, has no nucleation barrier because the liquid phase is already present on the surface. However, to begin freezing, a germ of the solid phase must be created, and this requires a liquid to be cooled below its bulk transition temperature.

The *premelting* of a material, that is, the existence of a liquid in the solid region of the bulk phase diagram, can be caused by a number of mechanisms. An example that is pervasive in nature is the Gibbs–Thomson shift in bulk coexistence due to a combination of the surface energy, γ, and curvature, $\mathcal{K}$, of the solid–liquid interface. For an isotropic solid, the shift in the temperature T from the bulk melting transition T_{m} is $T_{\mathrm{m}} - T = T_{\mathrm{m}}\gamma\mathcal{K}/\rho_{\mathrm{s}}q$, where ρ_{s} is the solid density, q is the latent heat of fusion, and $\mathcal{K}$ is positive for convex interfaces seen from the liquid side. Hence, small convex crystals have lower melting points than larger crystals.

Although *interfacial premelting* is less familiar, it is no less common. Its existence depends on a competition between the attraction of the liquid to the solid (adhesion) and the attraction of the liquid to itself (cohesion). The origin of the competition may be long-range intermolecular dispersive–van der Waals or surface ionization forces, which have unique consequences in ice systems (Elbaum & Schick 1991; Wilen *et al*. 1995). Melting is inhibited by the latent heat associated with the ice to water conversion, and it is driven by the tendency to reduce the interfacial free energy. A thermodynamic description incorporates the bulk and interfacial free energies and the dominant intermolecular interactions in the system (recent reviews are Dash *et al*. 1995; Frenken & van Pinxteren 1994; Petrenko & Whitworth 1999; Oxtoby 1999; Wettlaufer 1999*a*). Other variants of surface melting include *grain-boundary melting*, wherein premelting occurs at junctions between crystals of the same material, and *interfacial melting*, wherein a melt layer appears at the interface between a solid and a rigid wall. Depending on the nature of the substrate, the temperature, and the presence of soluble impurities, system-specific short-ranged screened Coulomb interactions may also be present (Wettlaufer 1999*a*, *b*). *Complete* interfacial or surface melting refers to the continued thickening of the film, without limit, as the melting line is approached from the solid region of the bulk phase diagram. Because the adhesive interactions tending to thicken the film may be attenuated as it grows, the phenomenon of *incomplete* melting, where the film growth halts before the melting point is reached, is possible. The effect has been observed in ice (Elbaum *et al*. 1993) at its interface with vapour.

Two important results obtain from the mean-field description of the processes involved in surface melting (see figure 2). The first is that for materials controlled by long-range intermolecular forces, the film thickness d is proportional to the excursion of the temperature from its bulk melting value as

$$d = \lambda(T_{\mathrm{m}} - T)^{-1/\nu}. \tag{3.1}$$

The fall-off of the intermolecular forces is characterized by a positive exponent ν; electrostatic ($\nu = 2$) or dispersive–van der Waals ($\nu = 3$) interactions are important. Equation (3.1) shows that

(i) there is a film of liquid at the interface at subfreezing temperatures; and

(ii) the film thickness becomes arbitrarily large as the temperature rises toward the bulk melting temperature.

Therefore, a crystal will melt inward from its surface.

The other important result is that there is, in common with wetting phenomena (see, for example, Leger & Joanny 1992), a disjoining pressure between the solid and the liquid due to the fact that at a surface-melted interface, the adhesion of the fluid to the underlying solid is stronger than the fluid's own cohesion. Hence, the liquid–vapour interface is effectively repelled by the solid–liquid interface:

$$P_{\mathrm{l}} - P_{\mathrm{s}} \propto d^{-\nu}. \tag{3.2}$$

In the specific case of complete surface melting driven by van der Waals interactions, the constant of proportionality is the Hamaker constant.

As the temperature rises and the films thicken, their very nature changes: from a disordered solid on an angstrom scale to a partly structured quasi-liquid and, finally, to a fluid. Hence, direct observations are difficult, and convincing evidence has come only within the last few decades. Frenken & van der Veen (1985) observed the surface melting of lead using experiments that detect the manner in which the surface disorder influences the scattering of ions, and Zhu & Dash (1986) observed the surface melting of argon films using sensitive calorimetric techniques. These early, and qualitatively different, measurements set the stage for further studies, and, during the intervening time, many laboratories, using various experimental techniques, have shown that virtually all solids undergo surface melting along at least one crystallographic plane.

Although the existence of surface melting in ice is well documented, the results are extremely variable.† The variability lies both in the great sensitivity to the atmosphere and conditions of preparation, and in the inherent differences in measurement technique. Sample preparation is a primary difficulty due to the delicate equilibrium of such a high vapour pressure material. Therefore, the question of whether a sample is growing or evaporating is often left unaddressed. An additional factor is the great sensitivity of the film to dissolved impurities. Recent theoretical work (Wettlaufer 1999*b*) shows that the presence of impurities both enhances surface melting and strongly influences the film-thickness–temperature behaviour (figure 3). The fact that the techniques themselves are designed to measure different structural aspects of the surface, and that it is extremely difficult to quantify the presence of unwanted impurity contamination, leaves active debate in the community regarding the interpretation of the various results throughout the entire temperature range. Therefore, studies continue to be pursued with greater temperature control and refined methods (optical and X-ray techniques) that capture the extremes of the surface structure. Optical methods have the advantage of measuring the phase of the material, and X-ray methods probe the local molecular structure. Both are necessary to complete our understanding.

In the future, refinement of technique should facilitate a convergence of interpretation and understanding of the data gleaned from optical and X-ray methods. Yoshinori Furukawa and Minoru Maruyama plan to construct an apparatus that will bring to bear both optical ellipsometry and X-ray scattering on the same sample. Hence, within the next few years we should see data coming out of this effort. Moreover, the number of groups now active in the field leads one to expect that either entirely new methods, or significant modifications of existing approaches, will make

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† Evidence comes from studies using many techniques reviewed in Dash *et al.* (1995) and Wettlaufer (1999*a*). Length restrictions do not allow a complete listing of all the original studies.

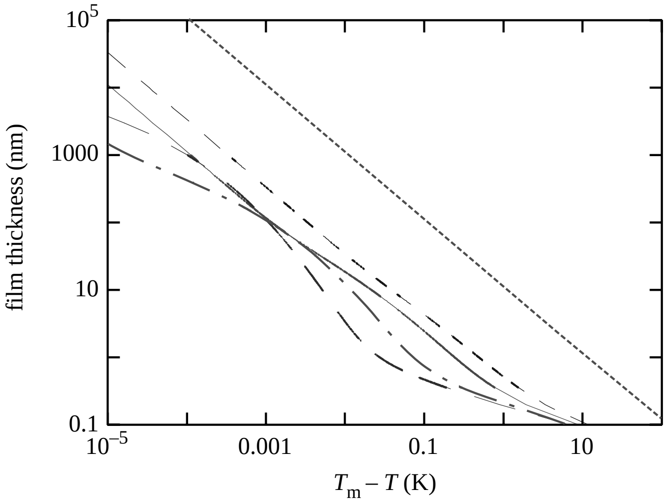

Figure 3. Film thickness versus undercooling at the interface between ice and water vapour. $N_i = 6 \times 10^{-4}$ (long dashed line), 6×10^{-3} (dash–dot line), 0.06 (solid line), 0.18 (small dashed line), and 6 (dotted line) μM m^{-2} NaCl (Wettlaufer 1999*b*). For simplicity, NaCl is assumed to be non-volatile; the purpose of the plot is to show the sensitivity to impurities. The Hamaker constant, A_H, which describes the strength of the van der Waal's interaction, can be related to the interfacial coefficient in equation (3.1) λ, namely $6\pi\rho_s q_m \lambda^3 = A_H$. Hamaker constants can be calculated using the complete theory of dispersion forces (Elbaum & Schick 1991; Wilen *et al.* 1995), which requires as input spectral data for the dielectric functions of ice, water and the substrate of interest, or they can be taken from experimental measurements. In the former case, the results are often sensitive to the dataset and fitting model used to incorporate them into dispersion force theory. Elbaum & Schick (1991) used two datasets to calculate film thickness versus temperature, and here the data that produced the largest Hamaker constant (Daniels 1971) for the vapour interface was used, giving $|A_H| = 3.07 \times 10^{-22}$ J. As its temperature increases, the lowest concentrations change slope twice (in this range), and above *ca.* 1 mK, the *lower* dopant level yields a *thicker* film. As the temperature increases further, there is another crossover (not seen on this scale). Clearly, the thickness is sensitive to small amounts of impurities, and, hence, it is quite dependent on factors that are extremely difficult to control in an experimental apparatus.

their appearance during the next several 'student generations'. Both the predicted sensitivity of surface melting to soluble impurities, and the importance of surface melting in environmental phenomena, strongly indicate the need for experiments wherein samples are systematically doped with impurities.

We can expect advances using X-ray techniques to provide deeper insight on the spatial variation in the density moving from the bulk solid into the bulk liquid of a surface-melted crystal. At temperatures very near the bulk transition, the liquid layer is larger than the correlation length of the bulk liquid. However, the fact that the nucleation barrier in two dimensions is substantially lower than that in three dimensions indicates that the monolayer of water adjacent to a primary facet of ice is structured with solid-like ordering. Evidence of the shift in the nucleation barrier derives from studies of very near equilibrium crystal growth (Wilen & Dash 1995*a*; Dash *et al.* 1999), but a direct measurement of the requisite fall-off in the molecular order has yet to be made. The implications for crystal growth are important because the anisotropy of surface melting is intimately wed to the anisotropy in the growth kinetics. The issue is also basic to the role of dimensionality—between two and three dimensions—in the nature of the melting transition (Dash 1999).

Interfacial melting has been less well studied experimentally because the interface must be accessed through either the solid ice crystal or the material against which the ice rests. Moreover, interfacial ionization and roughness may be present and create new forces that modify the melting behaviour. Direct and indirect studies have been made by Gilpin (1980), Furukawa & Ishikawa (1993), Churaev *et al.* (1993), Beaglehole & Wilson (1994), Wilen & Dash (1995*b*), Döppenschmidt *et al.* (1998) and Pittenger *et al.* (1998). Presently, we are focusing on several of the many environmental phenomena influenced by the surface of ice.

4. Ice in the atmosphere

The distribution of clouds influences the global radiation balance and, hence, the Earth's climate. The radiative, hydrologic and chemical fluxes in the troposphere are modulated by the distribution and types of ice particles (Baker 1999). Their surface properties are important for the efficiency of chemical uptake of natural and anthropogenic impurities. In this section, two active areas of research are described.

(*a*) *Thunderstorm electrification*

One of the most spectacular and mysterious phenomena in our common experience is thunderstorm lightning. Its causes have been ascribed to everything from divine intervention to the origin of electricity. Field and laboratory simulations have led us to the common understanding that lightning is associated with ice, and have discerned the following primary features. Lightning is typically discharged from regions in a cloud where cooling due to updraughts produces subzero temperatures and ice is formed from cloud moisture. The charging occurs mainly at collisions between small ice particles carried in updraughts and large aggregates, known as soft hail or graupel, which are falling. As the small particles bounce away from the collisions, they tend to be positively charged, leaving an equal and opposite charge on the hail. What is sought is the underlying cause of this charge transfer. Numerous laboratory studies have provided detailed measurements of the dependence of the charging on temperature, humidity and growth rate. Several theories have been advanced, including frictional charging, induction, thermoelectricity and contact electrification. But none can account for the amount, and in some cases even the sign, of the effects. Based on the temperature range of the active cloud region, Turner & Stow (1984) proposed that the charging mechanism might involve surface melting on ice particles. Baker & Dash (1989) advanced a theory of the collisions that argued that the charge could be carried by small amounts of liquid film transferred during the collisions. Their theory was recently put to an experimental test by Mason (1998), who used a quartz crystal microbalance to detect whether mass transfer is associated with charge transfer in ice collisions. Very thin quartz crystals, whose natural resonance frequency may be several million cycles per second (MHz), are the basic timing devices in quartz watches. Their resonant frequency decreases due to the added mass, and the technique can detect changes of the order of tenths of nanograms (or tens of equivalent monolayers). Mason deposited layers of ice on each of two crystals facing

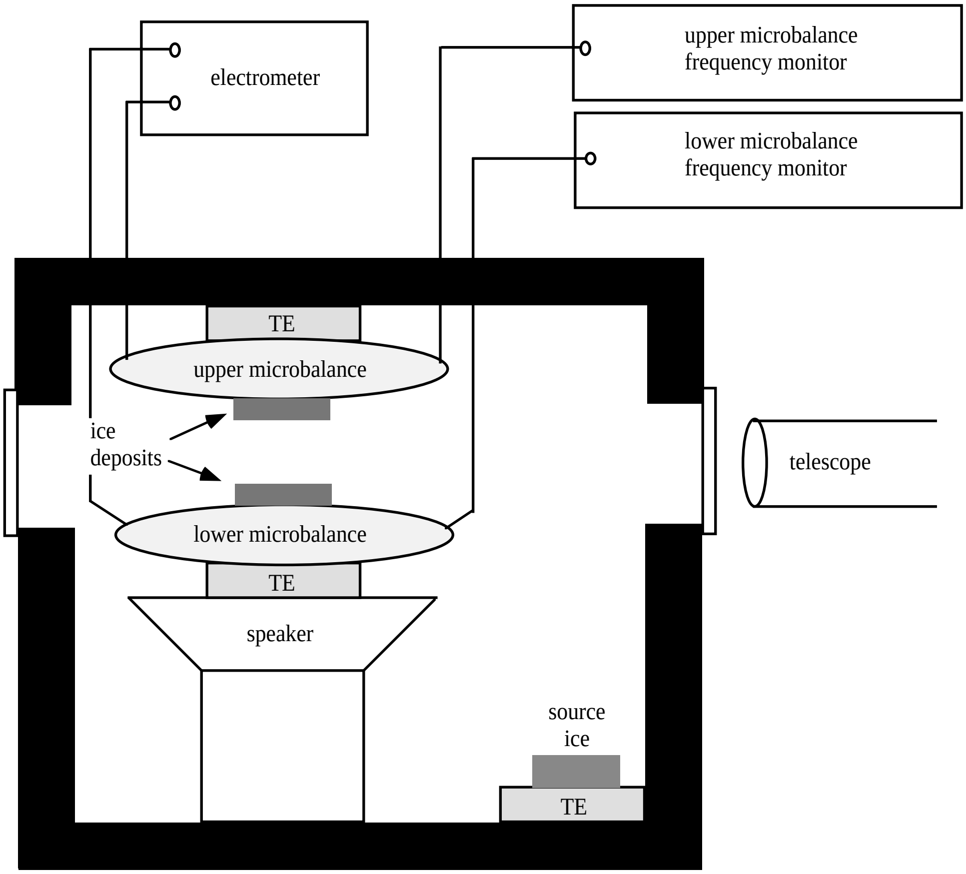

Figure 4. Experiment designed by B. Mason and J. G. Dash to measure the exchange of mass and charge between two colliding ice surfaces. Ice is deposited on each of two high-frequency quartz crystal microbalances, whose temperatures are independently controlled by thermoelectric coolers (TEs). The humidity is set by the temperature of the vapour source seen in the lower right-hand corner of the cell. When a collision is produced by pulsing the speaker, the momentary charge transfer is detected by the electrometer. The frequencies of the microbalances, measured before and after the collision, indicate how much mass is exchanged. The experiment found that growing ice gained mass and lost negative charge after a collision, both of which increased with growth rate; typical transfers at moderate growth rates were of the order of picocoulombs of charge and hundreds of monolayers of mass. The charge transfers were in qualitative agreement with earlier studies, but no previous work had detected mass. (Adapted from Mason (1998) and Wettlaufer & Dash (2000).)

each other (figure 4). With one crystal mounted on a small loudspeaker, collisions could be initiated between the two ice surfaces. By monitoring the frequencies of the quartz crystals before and after the collisions, it was found that growing ice gained mass after a collision. By monitoring the momentary currents flowing during the collisions, it was found that growing ice was positively charged after a collision. Negative charge flows from the growing surface rather than, for example, the subliming surface losing positive charges. Mason's findings of the dependencies of these results on temperature, growth rate, and collision impact seem to offer the most detailed description yet of the charging process. In order to complete the picture of mass and charge transfer and to guide future experiments we have developed a theory that involves a combination of two new types of surface melting, dislocation and impurity induced surface melting, and the differential mobility of charge carriers in ice and water.

(*b*) *Polar stratospheric clouds*

Higher in the atmosphere, a layer of ozone in the stratosphere protects life on the surface of Earth because of its efficient shielding of ultraviolet radiation. The present destruction of ozone owes itself, in large part, to the production of chemicals by humanity. Particles in polar stratospheric clouds (PSCs) are known to act as substrates for important chemical reactions that determine the fate of ozone (Peter 1999). In particular, the reaction

$$\mathrm{HCl} + \mathrm{ClONO_2} \longrightarrow \mathrm{Cl_2} + \mathrm{HNO_3} \tag{4.1}$$

is regarded by atmospheric chemists to be the most important heterogeneous chlorine activation reaction. The reaction can convert a rather inert species of chlorine, in HCl and $ClONO_2$, into highly reactive ozone-destroying species Cl_2 within hours under the right PSC formation conditions. The cloud particles facilitate chemical reactions because they serve as reservoirs for the various reagents, and an important aspect of the reaction efficiency concerns the mechanism by which species can be accommodated on the particle surfaces. Much of the present understanding is gleaned from laboratory experiments in which PSC formation conditions are simulated (see, for example, Molina 1994; Abbatt 1995; Peter 1999).

The three thermodynamically stable solid phases found in PSCs (ice, nitric acid trihydrate ($HNO_3{\cdot}3H_2O$, NAT) and sulphuric acid tetrahydrate ($H_2SO_4{\cdot}4H_2O$, SAT)) have well-understood equilibria (Peter 1999). However, depending on the local thermodynamic conditions during cloud formation, and the presence of intermediate metastable states, the evolution of these particles can take substantially different paths. In one path, a particle consists of a core of SAT and NAT surrounded by a shell of ice, whereas in the other path, the core consists of ice and the shell can be either liquid or solid acid. Hence, in one case, further chemical uptake must occur on (doped) ice surfaces, whereas in the other, the uptake may occur on a liquid. An outstanding question concerns whether impurity-induced surface melting (figure 3) can produce a sufficient amount of liquid so that, from the perspective of further chemisorption, path one is quantitatively similar to path two when the acids are in the liquid phase. The question is much more than academic. Carslaw & Peter (1997) have analysed recent experiments involving the reaction shown in (4.1) and found a discrepancy in the reaction rates of up to two orders of magnitude. Therefore, the most crucial mechanism driving stratospheric ozone destruction is not known to a sufficient accuracy to provide reliable input to global models that predict ozone losses, and, hence, comparison with observations is presently out of reach.

5. Ice on and in the ground

Ice covers a substantial fraction of the Earth and that which we find in the great ice sheets and in permafrost regions constitutes one of the best records of past climates

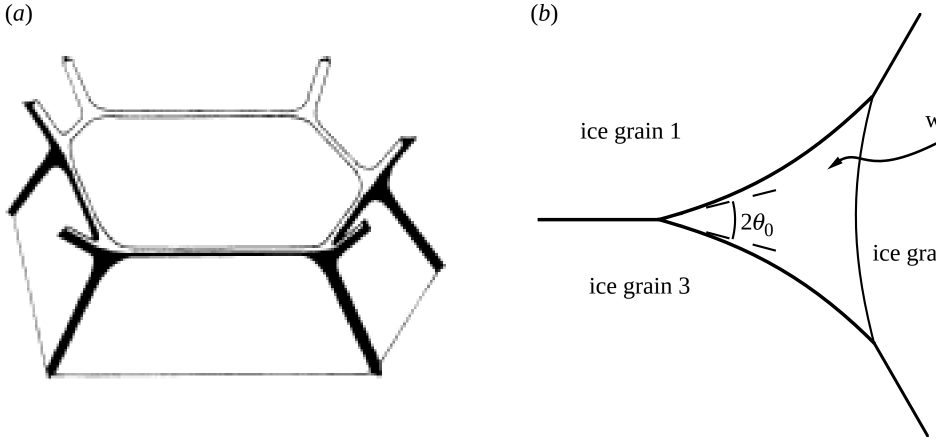

Figure 5. A schematic of the *vein–node* system in polycrystalline ice (modified from Nye (1991)). (*a*) depicts the *veins* at a triple-grain junction, and the *nodes* where four veins, and, hence, four grains, intersect. (*b*) is a cross-section of a vein showing the dihedral angle. The node shape and vein cross-section depend only on a ratio of grain-boundary (γ_{ss}) and solid–liquid (γ_{sl}) interfacial energies, and water enters the grain-boundary groove at an angle $2\theta_0$. For a given dihedral angle, the nodes have a regular tetrahedral symmetry and the veins have a three-fold symmetric cross-section. For ice near the melting point, such a network can be responsible for the communication of liquid throughout the volume of the sample.

(Johnsen *et al*. 1999). However, the chemical and isotopic proxies that form the basis of our understanding evolve according to microscopic processes, largely at interfaces between grains, that are just now being explored quantitatively (Nye 1999).

(*a*) *Glaciers and ice sheets*

When snow is deposited it records the chemical and, hence, thermal environment that existed between ice crystals during their formation and growth. Therefore, the growth and decay of glacier ice, and the distribution of isotopes and atmospheric chemicals in deep ice cores constitute two central issues in climate-change research. Intraglacial liquid can be caused by the presence of impurities (Raoult's law), interfacial curvature (Gibbs–Thomson) effects, non-hydrostatic stresses, radiatively induced internal melt figures (called Tyndall figures), and surface melting at interior interfaces associated with air and or water-vapour bubbles. Raymond & Harrison (1975) observed these features in temperate† glaciers.

Where, within the polycrystalline network, liquid water resides is directly relevant to both the growth and decay of a glacier and the mechanisms through which chemicals are redistributed through an ice sheet. Nye (1991) derived a theory that describes the thermal evolution of temperate polycrystalline ice based on curvature and impurity effects, which create water at tri-grain junctions in microscopic channels (10–100µm) called *veins* and at *nodes* separating four grains (figure 5). This water allows a polycrystalline sample to communicate via a liquid network distributed throughout its volume. Upon balancing the interfacial coefficients, the dihedral angle $2\theta_0$

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† Polycrystalline ice at temperatures very near the bulk melting temperature, $T \approx T_{\mathrm{m}}$, containing a finite liquid volume fraction.

is determined by the ratio $2\cos\theta_0 = \gamma_{\mathrm{ss}}/\gamma_{\mathrm{sl}}$, where γ_{ss} (γ_{sl}) is the grain-boundary (solid–liquid) interfacial energy. There remains a basic issue of the stability of the boundary, for, as Cahn (1991) has shown, in two dimensions, two-phase trijunction angles are determined by the ratio above, and grain boundaries can become unstable to wetting and be replaced by two interfaces. Such an instability could be induced, for example, by increasing the amount of a dopant.

(i) *Grain-boundary melting*

The question of whether or not grain-boundary melting occurs is an outstanding and important one. There are two principal ways in which grain-boundary melting can be observed. One is to examine the dihedral angle subtended by a grain-boundary groove, and the second is to measure the liquid film thickness at the boundary directly as a function of temperature. In the former method, complete grain-boundary melting is indicated by a value of zero for the dihedral angle. In the latter method, one would observe either a divergence (complete melting) or saturation (incomplete melting) of the film thickness as the bulk melting temperature is approached, just as described earlier for interfacial melting.

Using an optical microscope, Mader (1992) observed dihedral angles typically ranging between 30° and 40°. Of course, this implies that the grain boundary is not *completely* wetted by liquid water, but to a degree that is much greater than expected. Long-range dispersion forces across a grain boundary are always attractive; they *preclude* the possibility of *complete* melting (Wilen *et al*. 1995). The theory of these forces predicts that the temperature at which the film thickness saturates is extremely close to T_{m}. Only an experiment with very fine resolution (in measuring angles or temperature) could determine the precise nature of the melting behaviour.† Refined experiments with finer resolution than that of optical microscopy may be up to the task and are presently being designed in Larry Wilen's laboratory at Ohio University and Yoshinori Furukawa's laboratory at Hokkaido University. Finally, an interesting and relatively unexplored connection between the effective behaviour of ice and that of the Earth's mantle was noted by Nye. The mantle has a geometrically similar two-phase network (Frank 1968; McKenzie 1984), and, hence, transport of the liquid phase of mantle material due to macroscopic and microscopic driving forces controls the detailed deformation of rock.

(*b*) *Frost heave*

'Frost heave', the deformation of wet soil during freezing, dramatically alters landscapes, destroys roads, runways and pipelines, and redistributes methane in permafrost regions. The existence of water in soils, below the bulk freezing point, has been associated with frost heave for decades, but the basic causes have only recently been addressed within the context of the modern theories of interfacial premelting. During frost heaving, the soil is cooled by the air, which causes some of the soil water near the surface to freeze. Warmer water from deeper regions is drawn toward the lower temperature, tending to fill the pores, and continues to invade the colder

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† This question of spatial resolution is similar to that encountered in wetting dynamics, wherein the spreading of a completely wetting fluid exhibits a 'macroscopic' or 'apparent' contact angle, but nonetheless joins a microscopic precursor film with zero contact angle (Leger & Joanny 1992).

Figure 6. The general phenomenon of frost heave is the uplifting of moist soil during a cold spell. The phenomenon has dramatic consequences because the plethora of interfaces in a soil (see figure 8) allows a much greater flow of unfrozen water than can flow on a single surface (see figure 7). Thermomolecular and capillary pressure draw unfrozen water toward the lower temperatures where it feeds interfacial films and eventually solidifies in lenses to heave the soil. Although the process has deleterious effects on engineered structures, it can also create beautiful geomorphological patterns such as these circles of stone observed and studied by Bernard Hallet (Seattle) on the Arctic Island of West Spitsbergen. (Photograph by Hallet; adapted from Wettlaufer & Dash 2000.)

region until the build-up of pressure can counteract the flow (figures 6–8). This maximum frost-heave pressure is extremely large: *ca.* $160\,\mathrm{lb\,in^{-2}}$ (*ca.* 11 atm) for every degree below 0 °C. This pressure is about 10 times that required for a hydraulic lift to raise a 3000 lb car. Normally, long before the maximum frost-heave pressure is reached, the soil breaks open. Water then flows into the rupture where it freezes into a solid 'lens' of ice. As water continues to flow upward, the lens grows, forcing the soil further apart, and the surface of the ground heaves.

A very general physical principle underlies the phenomenon: the tendency of all systems to reach a state of lowest free energy. Frost heave is the response of the mobile part of the system—the unfrozen water—to move toward a region of lower free energy, driven by an effective pressure, the *thermomolecular pressure*. Whereas equations (3.1) and (3.2) depend on the nature of the dominant interactions in the system, the relationship between the pressure in the liquid and the temperature is

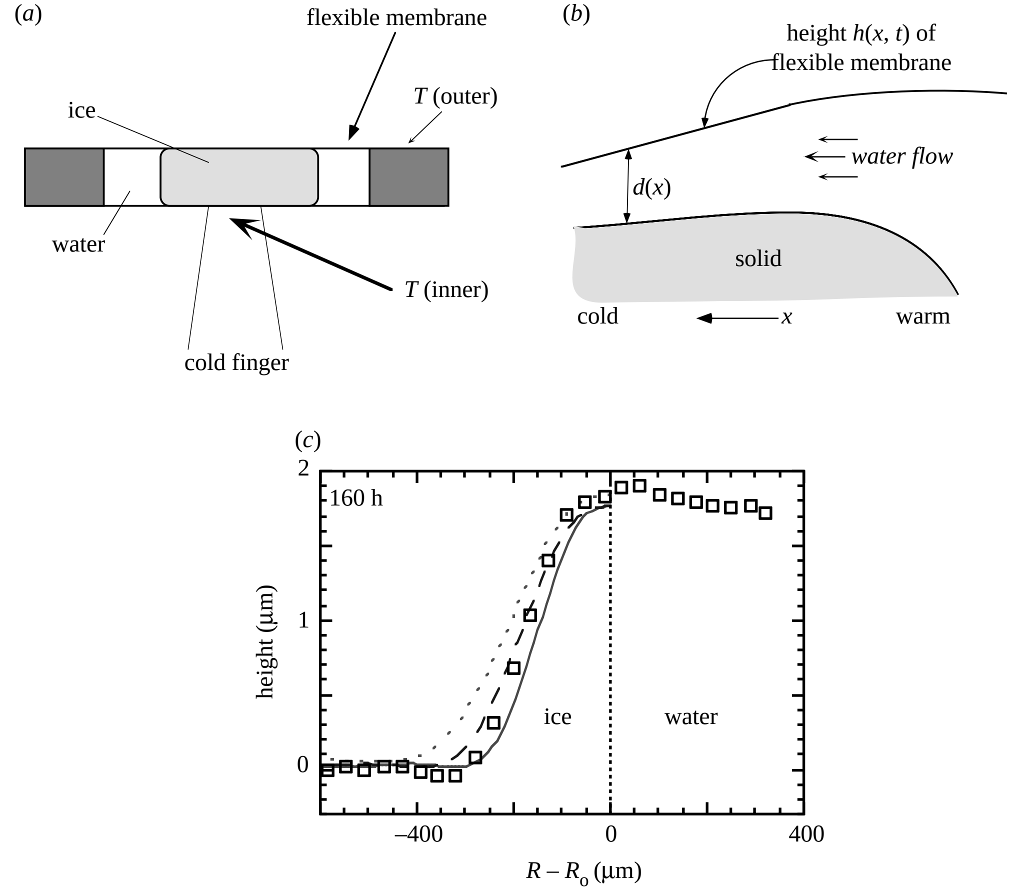

Figure 7. (*a*) Cross-section of the Wilen & Dash (1995*a*, *b*) experimental cell. The temperatures at the cold finger, $T_{(\mathrm{inner})}$, and at the outer rim, $T_{(\mathrm{outer})}$, are controlled to place the position of the ice–water interface about midway across the cell radius. (*b*) The local cell configuration. The membrane is under tension and exerts a restoring force proportional to its curvature. The temperature gradient is constant and, because the viscous flow driven by the thermomolecular pressure gradient is slow, the film thickness d can relax to the local thermal equilibrium value and, hence, depends only on x. The flow and continual solidification drives the evolution of the membrane height $h(x,t)$ relative to an initial reference height $h(x,t_0)$. (*c*) Comparison of the theoretical predictions made by Wettlaufer *et al.* (1996), and the experimental values for the membrane height $h(x,t)$ at 160 h. $R - R_0$ is the experimental x-coordinate. At the bulk ice–water interface, $R = R_0$. The predictions for the surface melting driven by short- and long-range electrostatic, and non-retarded, van der Waals intermolecular interactions are shown by the solid, dashed and dotted lines, respectively. The labels ‘ice’ ($R - R_0 < 0$) and ‘water’ ($R - R_0 > 0$) refer to regions where the bulk phases are stable. For $R - R_0 < 0$, an interfacial water film coexists between the membrane and bulk ice.

independent of these interactions (Dash *et al.* 1995; Wettlaufer 1999*a*):

$$P_{\mathrm{l}} = P_{\mathrm{s}} - \frac{\rho_{\mathrm{s}} q_{\mathrm{m}}}{T_{\mathrm{m}}}(T_{\mathrm{m}} - T). \tag{5.1}$$

The thermomolecular pressure coefficient, $\rho_{\mathrm{s}} q_{\mathrm{m}}/T_{\mathrm{m}}$, is a basic property of the mate-

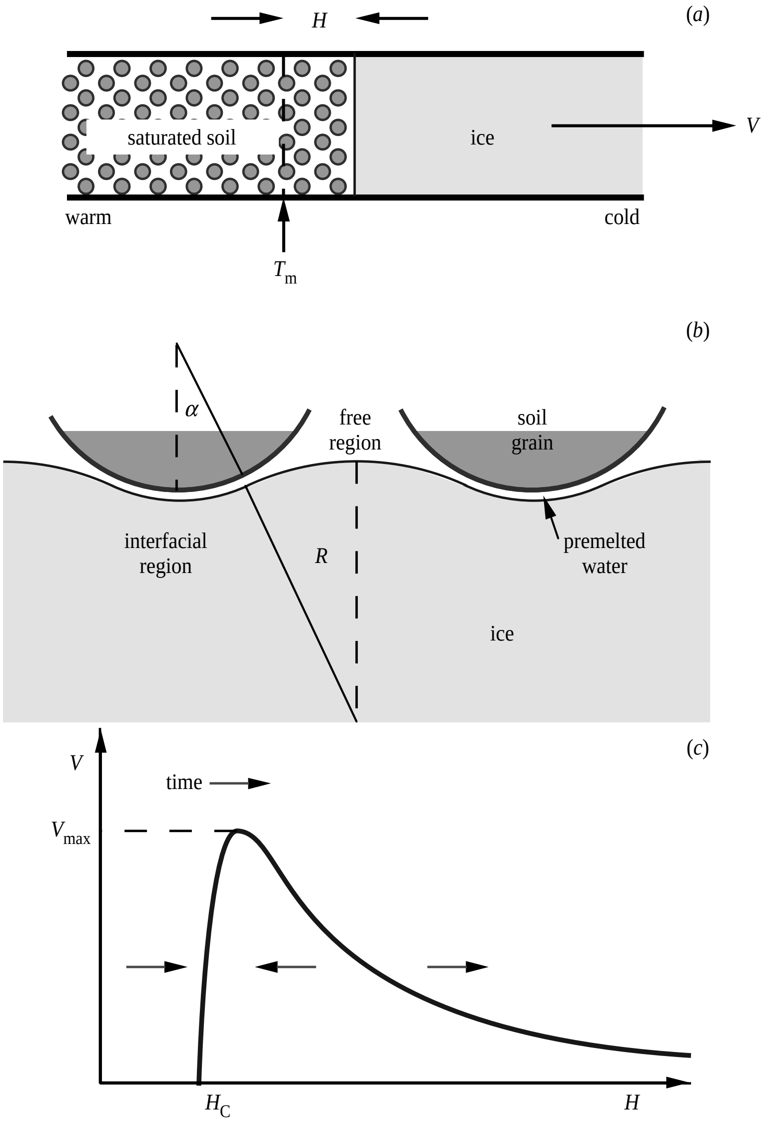

Figure 8. (*a*) Plan view of an experiment in which liquid-saturated soil, placed between two microscope slides, is pulled at constant speed V through a temperature gradient G. (Such experiments have been performed with water and with argon.) If the pulling speed is sufficiently slow, then a steady state can be achieved in which a single ice lens rejects all the soil in advance of it. The ice-lens front lags behind the T_{m} isotherm by a distance H. (*b*) A magnified sketch of the ice-lens front showing soil grains being pushed ahead of the solid by the intermolecular forces in the interfacial region. The ice–water meniscus adopts a constant curvature in the free regions between soil grains. (*c*) A graph of the possible steady states of single-ice-lens growth showing the undercooling of the ice-lens front $\Delta = GH$ corresponding to a given pulling speed V. The arrows show the directions in which the front migrates; the left-hand branch of solutions is stable, while the right-hand branch is unstable. If the pulling speed is too great, then no steady state exists and the planar front recedes to positions of greater undercooling. (Adapted from Worster & Wettlaufer 1999.)

rial. If the pressure in the solid is uniform, the pressure in the liquid film will increase with temperature, and, by imposing a temperature gradient parallel to the interface, the resulting thermomolecular pressure gradient will drive premelted liquid from high to low temperature. The concept provides yet another situation in which microscopic effects produce macroscopic behaviour and motivated a study of frost heave in its most basic elements: at the interface of a single crystal of ice. Wilen & Dash (1995*a*, *b*) constructed an elegant apparatus, pictured in figure 7, that allowed direct measurement of the effect. A plastic membrane is stretched over an ice crystal. A temperature gradient is imposed along the surface, which drives a thermomolecular pressure gradient along the interfacially melted liquid. To maintain its stable thickness, the liquid layer thins, by depositing ice, as it flows toward lower temperatures. The ice build-up required to maintain the equilibrium film thickness lifts the plastic membrane, and this progress is observed by interference microscopy. A theory was then developed to analyse the data, to relate the intermolecular forces within the liquid layer to the growth of the ice (Wettlaufer *et al.* 1996). We were able to show that the existence and mobility of interfacially melted water can be due to several types of surface interactions, each coming into dominance at a different temperature. All of these interactions are combined in typical soils, so that the evolution of frost heave in the environment is quite complicated (figure 6), but progress requires a basic understanding of the component processes.

Because of the increase in the surface area of premelting liquid, frost heave in fine soils can move the ground at rates of millimetres per day. Studies that idealize a natural soil have recently reproduced the robust features of frost heave in porous media. Theory is motivated by experiments being done here in Seattle and by Takeshi Ishizaki (see, for example, Mutou *et al.* 1998) who is now in Tokyo, in a type of Hele–Shaw cell, in which the particle size is much smaller than the gap width (figure 8). The ice lenses in nature form periodically in the direction normal to the heat flux vector. A basic question, involving several competing processes, centres on the stability of a given lens during its growth into a saturated, but unfrozen, porous medium. At the lens–porous medium interface, interfacial melting balances the repulsive interaction responsible for the existence of the film against the lubrication pressure associated with the flow of premelting liquid around the particle and the overburden pressure of the mass of material above the lens. In their steady-state analysis, Worster & Wettlaufer (1999) found that the distance between the zero degree isotherm and the lens–porous medium interface (the undercooling), increases with the rate of growth until a maximum is reached, above which the thermomolecular pressure can no longer supply a sufficient rate of flow to allow this mode of growth to persist. Thus, the lens breaks down and another must form. This has recently been observed in a series of experiments involving solid argon lenses growing into silica powder saturated with liquid argon (Zhu *et al.* 2000). Clearly, if there is pore solid in the region ahead of the advancing interface, the rate of growth of a lens will be substantially impeded. This so-called ‘frozen fringe’ is a canonical feature of most frost-heave models, yet we are just beginning to make convincing local scale measurements that relate the dynamics of lens growth to the presence and evolution of pore solid. Theoretical predictions (Cahn *et al.* 1992) of the volume fraction of pore solid due to the curvature and interfacial melting contributions compare favourably with data from static, isothermal media, but their applicability to dynamical conditions awaits quantitative testing.

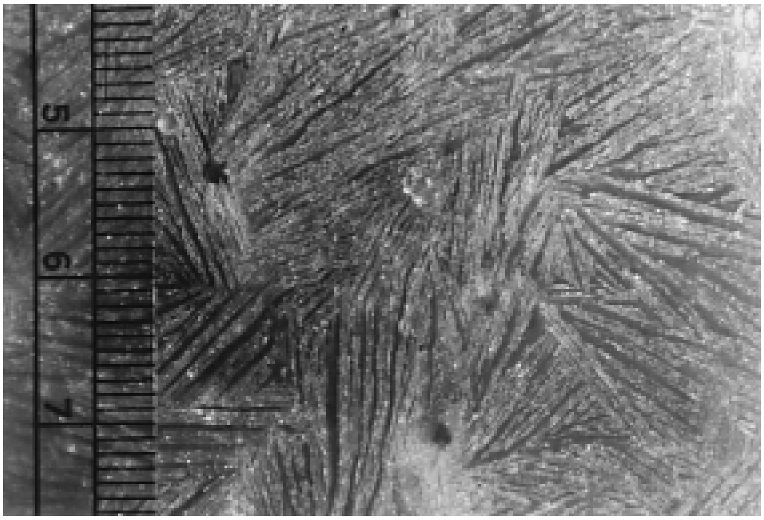

Figure 9. The underside of the laboratory-grown sea ice showing the cellular solid–liquid structure of the interface and two clear brine-drainage channels. The *c*-axes of the ice crystals are oriented principally horizontally, displaying the columnar structure and permeability of natural sea ice. (Adapted from Wettlaufer *et al.* 1997*a*, *b*.)

Finally, on a more speculative note, a glaciological problem in which interfacial melting and the bulk properties of polycrystalline ice may be important is in the mechanics of glacial basal sliding. Among other things, it depends on the bulk water permeability in the subglacial till, and melting between basal rock and ice (see, for example, Alley 1993; Cuffey *et al.* 1999). The volume fraction of ice in the till has a strong influence on the motion of an ice stream, and, hence, a basic understanding of pore ice dynamics and thermodynamics is of importance to a major area of dynamical glaciology.

6. Ice on the ocean

During every day of the year, one of the polar oceans is freezing to form sea ice, which reflects radiation and insulates the ocean below. The ice is exported into the North Atlantic Ocean, where it melts and influences the stability of the water column and large-scale ocean circulation, making oceanic solidification the primary distillation process in the high latitudes (Aagaard & Carmack 1994). Will we always have ice in the polar oceans? Will the ice cover extend out of the polar regions? To what extent are the pollutants that infest freezing waters trapped in the ice and transported? A plethora of basic questions concerning the growth and decay of sea ice bears strongly on a wide variety of environmental problems. One such challenge is to understand how cracks in the perennial ice cover, known as leads, influence the large-scale heat and mass balance in the Arctic. Although leads occupy less than 10% of the surface area, they can account for roughly half of the total oceanic heat loss and may be central to the establishment of the large-scale water mass characteristics in the Arctic Ocean. The important features of leads can be modelled in laboratory experiments. The advantage of this approach is that one can close the mass balance, rarely possible in the field, and control the thermodynamic driving force; always dictated by the uncontrollable meteorological conditions.

The efficient rejection of salt by the ice lattice results in the build up of a solute-enriched boundary layer adjacent to a solidification front (see, for example, Nagashima & Furukawa 1997). Because of the local interfacial depression of the freezing point caused by this build-up, the boundary layer becomes supercooled; the actual temperature is less than the solute-determined freezing point. This allows interfacial corrugations to grow and create a cellular interface (figure 9). The conditions of natural growth are always such that this instability is operative and, hence, sea ice will grow as a two-phase, two-component material, making it among the most dynamic effective media of all terrestrial ice forms (recent reviews include Weeks (1998) and Wettlaufer (1998)). Such materials are generally referred to as *mushy layers* and they occur during directional solidification in many binary systems ranging from metallurgical to geological (Worster 1997).

The length-scale of the cellular substructure is dictated by interfacial energy, which controls the local freezing point at the surface through the Gibbs–Thomson effect. Moreover, the intrinsic anisotropy which characterizes the fabric of the matrix is produced by the sensitive dependence on crystallographic orientation of the attachment of water molecules (Wilen & Dash 1995*a*; Dash *et al.* 1999). Because the substructure is grown into sea ice, its bulk thermal and transport properties owe their origin to the influence of these microscopic effects arising out of interfacial energy. One such macroscopic property is the *permeability*, which describes the resistance to flow of brine through the porous sea ice matrix. The importance of the permeability is great; it underlies the competition that determines the rate at which dense brine is delivered to the surface of the polar oceans. The essence of the competition is as follows. The ice grows because it is colder at its surface than at its base. In order to maintain local thermodynamic equilibrium throughout a growing layer, the salinity of the brine within the ice substructure increases toward the surface. However, because the density of salt water increases with salinity, buoyancy forces will tend to drive the fluid out of the matrix. If the crystals are sufficiently close to one another, the permeability of the layer is decreased and the matrix resists the buoyancy forces. As the layer grows, the buoyancy forces and permeability evolve and ultimately the buoyancy forces win out and the brine trapped within sea ice is released abruptly into the ocean below. Therefore, the microstructure, which controls the permeability, has a direct influence on the evolution of the oceanographic mixed layer and, hence, the large-scale hydrography of the Arctic Ocean. The principal features of this interplay are described using a mathematical model and are borne out by laboratory and field experiments (Wettlaufer *et al.* 1997*a*, *b*, 2000; Worster & Wettlaufer 1997).

7. Concluding remarks

Our examination of ice from its microscopic surface structure to its largest manifestations on Earth, in the oceans and throughout the atmosphere, reveals many large-scale influences of small-scale phenomena. An important duality is that ice acts as a testing ground for basic aspects of the phase behaviour of materials, and that this behaviour is relevant to a myriad of important environmental problems. The remaining challenges are substantial, for although we are beginning to understand several important features, many remain mysterious. A pressing problem concerns the formation of an ice surface during nucleation; the classical theory fails for most materials (Oxtoby 1999) and experimental tests continue (Seeley *et al*. 1999). The abruptness of the solid–liquid interface and its effect on the state of the adjacent liquid are among some of the controlling, but poorly understood, properties. Even though the natural environment is riddled with what in the laboratory are referred to as impurities, the detailed nature of how they influence surface melting is just beginning to be explored. Finally, an area of lively current work is the application of our new understanding of the molecular physics of melting to crystal growth. Future studies may, ultimately, answer the question that moved Descartes: how does nature shape snowflakes?

It is amusing to think that as we look forward to the beginning of a new century, Hermann von Helmholtz's 1865 lecture (von Helmholtz 1910), at Frankfort-am-Main, on 'Ice and Glaciers' still captures the essence of the intrigue of our subject:

> . . . the delight and interest in the magnificence of those scenes will make you the more inclined to lend a willing ear to the remarkable results of modern investigations on the more prominent phenomena of the glacial world. There we see that minute peculiarities of ice, the mere mention of which might at other times be regarded as a scientific subtlety, are the causes of the most dramatic changes in glaciers; shapeless masses of rock begin to relate their histories to the attentive observer, histories which often stretch far beyond the past of the human race into the obscurity of the primeval world. . .

It is a pleasure to participate in the activities of a community so actively engaged in a wide spectrum of important ice science problems. I am particularly indebted to J. W. Cahn, J. G. Dash, H. Dosch, M. Elbaum, S. C. Fain, J. W. M. Frenken, Y. Furukawa, H. E. Huppert, T. Ishizaki, M. Maruyama, J. F. Nye, M. Schick, L. Wilen, D. Winebrenner, M. G. Worster and E. Yokoyama, whose steady stream of new ideas, and criticisms of existing ones, have directly and indirectly influenced this overview. I thank J. G. Dash and M. G. Worster in particular for their comments on the manuscript. N. Untersteiner, A. S. Thorndike and C. F. Raymond nucleated my interest in the field over ten years ago and they have suffered the consequences of my initiation, not the least of which is enduring long descriptions of the latest line of research. My research has been generously supported by the US National Science Foundation and the Office of Naval Research, and the British Natural Environment Research Council.

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