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978-0-521-80620-6 - Creep and Fracture of Ice
Erland M. Schulson and Paul Duval
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Introduction

Creep and fracture of ice are significant phenomena with applications in climatology, glaciology, planetology, engineering and materials science. For instance, the flow of glaciers and polar ice sheets is relevant to the global climate system and to the prediction of sea-level change. The ice stored within the Greenland and the Antarctic ice sheets, should it flow into the sea, would raise the level by $\sim$7 m and $\sim$60 m, respectively. The creep of ice sheets, which can impart strains that exceed unity in several thousands of years, is also relevant to paleoclimatology. The determination of the age of ice and the age of greenhouse gases (Chapters 2, 3) entrapped within deep ice cores depends in part upon constitutive laws (Chapters 5, 6) that describe the deformation of the bodies – laws that must incorporate plastic anisotropy (Chapters 5 and 7) and the presence of water near the bottom. Fracture, too, plays a role in ice sheet mechanics. When the bed steepens, the ice flows more rapidly and creep can no longer accommodate the deformation (Chapters 9, 10). Fracture ensues, leading to the formation of glacier icefalls and crevasses. Fracture is of paramount importance in the catastrophic failure of icefalls, and it is a key step in the calving of icebergs and thus in the equilibrium between accumulation and loss of mass from polar ice sheets. Fracture is also fundamental to the integrity of the ice cover that forms on the Arctic Ocean (Chapter 15) and to the attendant release through open cracks or leads of heat and moisture to the atmosphere.

Water ice is abundant in the outer Solar System. Within the icy moons of the outer planets, pressure can reach as high as several GPa and temperature can reach as low as 40 K. As a result, several high-pressure phases exist (Chapter 8). Their behavior, whether ductile or brittle, influences the thermal evolution and tectonic history of the moons. Jupiter's satellite Europa and Neptune's satellite Triton, for instance, are encrusted in ice that, in both cases, overlies a putative ocean. The thickness of the crust is difficult to model owing to uncertainties in the thermal state of the satellite and to incomplete understanding of the creep and fracture of crustal material. The other significant point is that frictional sliding across strike-slip-like faults may generate sufficient heat to locally raise the temperature of the crust tens of degrees above background.

In engineering, creep limits the service life of a floating ice cover when used as a landing for aircraft or as a site for stationary objects. Also, it sets the load produced on an offshore structure by a floating ice cover moving slowly against it. When the cover moves more rapidly, it fractures (Chapter 14), under stresses that exceed the creep strength. In other applications: the fracture of ice is key to polar marine transportation; it plays a role in the removal of atmospheric ice from ships, power-lines and other structures; and it is a factor in the integrity of engineered freeze walls.

Creep and fracture of ice are also relevant to the deformation of other materials. Ice is elastically relatively isotropic (Chapter 4), but is plastically highly anisotropic (Chapter 5). Owing to the latter quality, which arises from the hexagonal crystal structure that the material adopts under terrestrial conditions (Chapter 2), ice is a useful analogue for validating micro-macro polycrystalline models that are used to simulate the behavior of anisotropic materials (Chapter 7). It is proving to be useful also in elucidating the nature of the intermittent and spatially variable plastic flow within materials that possess intrinsically low lattice resistance to slip (Chapters 5, 6). In such cases, deformation is better characterized by power-law distributions and fractal concepts and by the cooperative movement of dislocations than by simple averages and the movement of individual defects. The localization of deformation in slip lines and slip bands with scale-invariant patterns, as shown by X-ray topography in ice crystals (Chapter 5), appears to be an intrinsic feature of crystal plasticity. Through detailed microstructural analysis, ice provides evidence for the role of grain boundaries as sources of dislocations (Chapter 2) and for the importance of dynamic recrystallization in long-term creep (Chapter 6). On fracture, owing to its optical transparency and its relatively coarse grain size (1–10 mm) ice is instructive in revealing the character of primary and secondary cracks and their role in the process of brittle compressive failure (Chapters 11,12). Wing cracks, long postulated as fundamental elements, are important features. So, too, are other secondary features termed comb cracks and their attendant fixed-free microcolumns: under frictional drag across the free ends, the columns appear to bend and then break, thereby triggering a Coulombic fault (Chapter 12). The comb-crack mechanism appears to operate in rocks and minerals as well. Ice has led also to a better understanding of the ductile-to-brittle transition in rocks and minerals, in terms of a competition between creep and fracture (Chapter 13), and it has helped to elucidate the difference between Coulombic or frictional faults and plastic or non-frictional faults and thus between brittle and brittle-like compressive failure (Chapter 12). Ice has also made clear the governing role of friction in post-terminal failure under confinement (Chapter 12). In other words, while the understanding of ice benefits greatly from the understanding of other materials, ice offers something in return.

Ice offers some insight into the scale effect in brittle failure. It is now clear that the failure envelope of the arctic sea ice cover has the same shape as the envelope for test specimens harvested from the cover (Chapter 15). Similar, too, is the appearance within the cover of deformation features that resemble the wing cracks, comb cracks and Coulombic shear faults of test specimens. The implication is that, on both spatial scales, brittle compressive failure is governed by similar physical processes.

In discussing the creep and fracture of ice, we focus not on applications per se. Rather, our primary objective in this book is to elucidate physical mechanisms that govern the deformation. That said, we do address the flow of ice of polar ice sheets (Chapter 7) through micro-macro modeling, the nature of ice forces on offshore structures (Chapter 14) and the processes underlying the fracture of the arctic sea ice cover (Chapter 15).

For a discussion of topics beyond the scope of this book, we recommend: Hobbs (1974) and Petrenko and Whitworth (1999) on ice physics; Hutter (1983), Hooke (1998), Lliboutry (2000) and Paterson (2000) on glaciology; Bamber and Payne (2003) on the overall mass balance of the cryosphere and on ice dynamics; Schmitt *et al*. (1998) on extra-terrestrial ice; Lock (1990) on the growth and decay of ice; Wadhams (2000) on ice in the ocean; and Weeks (2009) on sea ice. For a discussion on atmospheric icing, we recommend a series of papers edited by Poots (2000).

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2

Structure of ice

2.1 Introduction

There are 12 crystalline forms of ice.[1] At ordinary pressures the stable phase is termed ice I, terminology that followed Tammann's (1900) discovery of high-pressure phases. There are two closely related low-pressure variants: hexagonal ice, denoted Ih, and cubic ice, Ic. Ice Ih is termed *ordinary ice* whose hexagonal crystal symmetry is reflected in the shape of snow-flakes. Ice Ic is made by depositing water vapor at temperatures lower than about −130 °C. High-pressure ices are of little interest in relation to geophysical processes on Earth, but constitute the primary materials from which many extra-terrestrial bodies are made. We describe their structure and creep properties in Chapter 8.

In addition to the 12 crystalline forms, there are two amorphous forms. One is termed *low-density ice* (940 kg m^{-3} at −196 °C at 1 atmosphere) and the other, *high-density ice* (1170 kg m^{-3}, same conditions). The density of ice Ih is 933 kg m^{-3} at the same temperature and pressure (Hobbs, 1974). Amorphous ices can be made at low temperatures in five ways (see review by Mishima and Stanley, 1998): by condensing vapor below −160 °C; by quenching liquid; by compressing ice Ih at −196 °C; by electron irradiation; and through transformation upon warming from one amorphous state to another. Although once thought to be a nanocrystalline material, amorphous ice is now considered to be truly glassy water. Its mechanical behavior remains to be explored.

In this chapter we address the structure of ice Ih. In relation to creep and fracture, the important elements include crystal structure and defect structure where the latter includes point, line, planar and volumetric features. Dislocations play an essential

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[1] Ice is generally understood to be frozen water. Astrophysicists use the term *water ice* to distinguish frozen water from ices of NH_3, SO_2, CO_2 and CH_4–N_2 when they exist in the solid state either as molecular solids, mixtures of solids, hydrates or clathrate hydrates. Molecular ices represent a large fraction of the mass of the outer Solar System (Schmitt *et al.*, 1998). In this book, ice means frozen water.

Cambridge University Press
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role in creep and in the formation of micro-cracks and also in the evolution of the microstructure. We consider the elements in turn.

2.2 Crystal structure of ice Ih

2.2.1 Unit cell and molecular stacking

The crystal structure of ice Ih is well established (Pauling, 1935). It is illustrated by the ball and stick model shown in Figure 2.1. The oxygen and hydrogen atoms are represented by large and small spheres, respectively, and the oxygens are numbered for reference. Hexagonal symmetry can be seen by connecting oxygen atoms. The unit cell, also shown in the image and defined in the caption, contains four molecules – one for each of the eight corner sites (occupied by atoms numbered 1, 2, 3, 7, 21, 22, 23, 27), which are shared eight times, one for each of the four edge sites (14, 15, 16, 20), which are shared four times, plus two for the two body sites (8, 11). Each oxygen atom has four oxygens as nearest neighbors that are situated near the vertices of a regular tetrahedron, which is centered about the atom of interest. The tetrahedron around oxygen 8, for instance, is made from oxygens 1, 2, 7 and 11; and the tetrahedron around oxygen 11 is made from oxygens 8, 14, 15 and 20. All other crystalline forms of ice are also built from tetrahedral units of this kind, a consequence of the fact that the free H_2O molecule is bent through an H–O–H angle of 104.52°. The actual tetrahedral O–O–O angle of ice Ih is 109.47°.

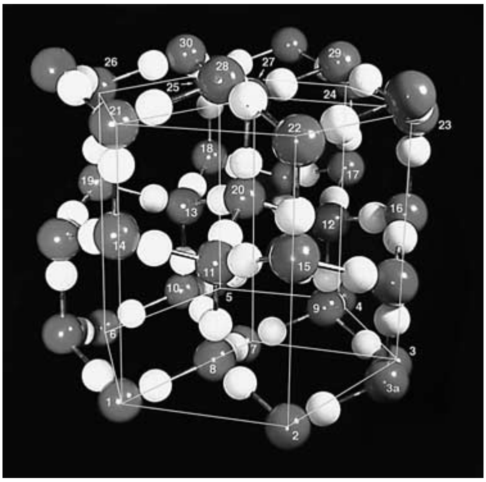

Figure 2.1. Photograph of a ball and stick model of the crystal structure of ice Ih. The larger balls represent oxygen and the smaller balls, hydrogen. The sticks represent hydrogen bonds between H_2O molecules. The corners of the Ih unit cell are delineated by oxygen atoms 1, 2, 3, 7, 21, 22, 23, 27.

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The O–O distance is 0.276 nm and the O–H distance is 0.0985 nm at temperatures of terrestrial interest (Hobbs, 1974). Strong covalent bonds join the oxygen atom of each molecule to two hydrogen atoms, while weak hydrogen bonds link the molecules to each other. The weak bonds account for the relatively low melting temperature of ice.

The sequence of molecular stacking, when projected onto the basal plane (which in Figure 2.1 is defined by the hexagonal ring of atoms 1, 2, 3, 4, 5, 6, 7) is … ABBAABBA … Six layers are shown: atoms 1 through 7 define layer-A; 8–10 layer-B; 11–13 another layer-B; 14–20 another layer-A; 21–27 layer-A; and 28–30 layer-B. Alternatively, the sequence may be viewed as … A′B′A′B′A′B′ … where the prime denotes pairs of molecules joined in a dumb-bell manner along the *c*-axis. In the latter scheme dumb-bells from atoms 8 and 11, from 9 and 12, and from 10 and 13 constitute a B′ layer; and from 14 and 21, 15 and 22, 16 and 23, 17 and 24, 18 and 25, 19 and 26, and 20 and 27 constitute an A′ layer. The alternate scheme is reminiscent of atomic stacking within closely packed hexagonal metals. However, contrary to comments one occasionally reads, ice Ih does *not* possess the closely packed crystal structure of hexagonal metals. Instead, its structure is rather open (more below).

In crystallography, the lattice of oxygen atoms in the Ih structure is described by the space group P6_3/mmc. The letter P means that the space lattice is primitive; 6_3 means that the principal axis of symmetry (i.e., the *c*-axis) is a hexagonal screw axis that passes through the center of horizontally oriented, hexagonal puckered rings of atoms (e.g., atoms 2, 3a, 3, 9, 7, 8 of Figure 2.1). When a ring group is translated along the *c*-axis and simultaneously rotated about that axis, the atoms in the group coincide with atomic positions in the crystal when the group has translated a distance of $3c/6$ and rotated by $2\pi/6$. Of the letters mmc, the first means that there are planes normal to the principal axis of symmetry that mirror atomic positions. The remaining m and c mean that there are two sets of symmetry planes parallel to the *c*-axis and that one of these defines another set of mirror planes and the other defines a set of glide planes. Within this context a "glide plane" is not one on which dislocations slip (Section 2.4), but one in which, upon displacement of $c/2$ along the *c*-axis, a mirror image of an oxygen atom corresponds to an atomic position in the crystal.

2.2.2 Lattice parameters, thermal expansion and density

The lattice parameters of ice Ih vs. temperature under atmospheric pressure were measured by Röttger *et al*. (1994) through diffraction measurements using synchrotron radiation, Table 2.1. At −20 °C the values commonly taken are $a = 0.4510$ nm and $c = 0.7357$ nm. The c/a ratio shows no significant variation with temperature

Table 2.1. *Lattice parameters of ice Ih vs. temperature at atmospheric pressure*

T (°C)	−263	−233	−203	−173	−143	−113	−83	−53	−23	−8
a (nm)	0.449 69	0.449 67	0.449 59	0.449 66	0.449 88	0.450 21	0.450 63	0.451 17	0.451 81	0.452 14
c (nm)	0.732 11	0.732 05	0.731 98	0.732 04	0.732 40	0.732 96	0.733 72	0.734 47	0.735 61	0.736 16

From Röttger *et al.* (1994)

Table 2.2. *Density of ice Ih vs. temperature under atmospheric pressure*

T (°C)	−260	−220	−200	−160	−138	−80	−60	0
Density (kg m^{-3})	933.3	933.0	932.8	931.9	929.6	924.5	922.7	916.4

From Hobbs (1974)

and has the value $c/a = 1.628$. This is very near the ideal value 1.633 for hard spheres that are closely packed, even though, as already noted, the crystal structure of ice Ih is not closely packed.

The fact that the c/a ratio is essentially independent of temperature implies that thermal expansion occurs isotropically. The coefficient of linear expansion has the value $\alpha = 5.3 \times 10^{-5}$/°C at −20 °C. At lower temperatures the coefficient is lower, reaching 1.0×10^{-5}/°C at −173 °C. At still lower temperatures, the coefficient reaches zero (at ~−200 °C) and then becomes negative before approaching again the value zero at absolute zero. Petrenko and Whitworth (1999) discuss the nature of this property.

Incidentally, the thermal expansion coefficient near the melting point is relatively high. When coupled with a low Young's modulus of $E \sim 10$ GPa (Chapter 4) and with a relatively low tensile strength of $\sigma_t \sim 1$ MPa (Chapter 10), this translates to a *low thermal shock resistance* of $\Delta T \sim \sigma_t / E\alpha \sim 2$ °C. For concrete and diamond $\Delta T \sim 10$ °C and ~1000 °C, respectively (Ashby, 1989).

The density of ice can be deduced from the lattice parameters and from the fact that there are four molecules per unit cell. Table 2.2 lists values under atmospheric pressure. At the melting point the expected density is 916.4 kg m^{-3}, in agreement with the value obtained using the hydrostatic weighing method on glacier ice single crystals (Bader, 1964). The density ρ is higher under higher pressure. At −35 °C, for instance, $\rho = 942.6$ kg m^{-3} under a pressure of 200 MPa (Gagnon *et al.*, 1988). At this pressure and temperature, ice Ih and ice Ic are almost in thermodynamic equilibrium with each other.

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2.2.3 Bernal–Fowler rules

Pauling (1935) recognized that under ordinary conditions the orientation of the H_2O molecules does not exhibit long-range ordering. That is, of the six possible configurations that a pair of hydrogen atoms may adopt within the tetrahedrally coordinated arrangement of oxygen atoms, none dominates throughout the crystal. The hydrogen atoms, in other words, impose a limited degree of disorder within the crystallographically ordered arrangement of the oxygen atoms. Disordered though it is, the arrangement is constrained by two rules, known as the Bernal–Fowler ice rules (1933):

- two hydrogen atoms must be located near each oxygen atom; and
- only one hydrogen must lie on each O–O bond.

Disobedience leads to point defects (described below), at least at higher temperatures where the atoms are dynamic. At lower temperatures, the hydrogen atoms effectively freeze into a disordered configuration, owing to the extraordinarily slow reorientation of the H_2O molecule in pure ice (estimated to be more than 100 years at liquid nitrogen temperature). This metastable state leads to a large amount ($3.41\ \mathrm{J\ °C^{-1}\ mol^{-1}}$) of zero-point entropy (Pauling, 1935).

2.2.4 Physical characteristics

The Ih crystal structure accounts for several physical characteristics of ordinary ice. The spacing between the oxygen atoms is large relative to the size of the atoms themselves (0.276 nm vs. 0.12 nm in diameter). Consequently, even when the hydrogen atoms are taken into account there is a large amount of open space within the lattice. This translates to an atomic packing factor of 0.34, compared with a packing factor of 0.74 for closely packed hexagonal metals of ideal c/a ratio. This openness accounts for ordinary ice being less dense than water. It accounts also for the pressure-induced reduction of the melting point of 0.074 °C per MPa at elevated temperatures (Chapter 12).

Another characteristic is radial isotropy. The Ih lattice has only one major axis of symmetry; namely, the c-axis. This accounts for the fact that the physical properties (thermal conductivity, elastic stiffness and atomic diffusivity) are isotropic in all directions perpendicular to the c-axis. There is some anisotropy, however, between properties measured in directions parallel to and perpendicular to the c-axis (see Chapter 4 for a detailed discussion of elastic moduli).

The other characteristic stemming from the Ih structure is that the H_2O molecules are concentrated close to the basal planes (defined in Figure 2.1 by atoms 1 through 7, for instance, or by atoms 21 through 27). This, plus the fact that crystal dislocations (described below) are highly mobile on basal planes, allows for easy slip (Chapter 5).

2.3 Point defects

Point defects are atomic-sized features that form within the ice lattice: vacancies, interstitials, solutes, ionic and Bjerrum defects. The first three are similar to point defects within crystals of metals and compounds. The other two are unique to ice and are often termed *protonic defects*. Each plays a role in inelastic behavior, particularly in creep.

2.3.1 Vacancies

A vacancy is defined as an empty molecular site. The defect exists in thermal equilibrium at all temperatures above absolute zero and is stabilized by an increase in entropy that more than compensates for an increase in internal energy. The equilibrium vacancy concentration C_v is given by the Boltzmann relationship (e.g., see Swalin, 1962, or any other book on defects in solids):

$$C_v = \exp(S_v/k_B)\exp(-E_v^f/k_B T) \tag{2.1}$$

where S_v denotes the extra entropy associated with each vacancy, E_v^f the internal energy that must be added to remove a molecule from the interior of a crystal and place it on the surface, k_B Boltzmann's constant and T absolute temperature. Fletcher (1970) estimated that $E_v^f \sim 0.5$ eV, based upon the sublimation energy of ice. This implies an equilibrium molecular fraction at the melting point of around 10^{-10}, assuming $S_v \sim 0$. Although relatively low compared with melting-point concentrations of 10^{-3} to 10^{-4} for vacancies in metals and alloys, the concentration is large enough to account for the formation of vacancy-type prismatic dislocation loops (as well as interstitial loops, more below) upon rapid cooling from −20 °C to −60 °C (Liu and Baker, 1995).

2.3.2 Interstitials

An interstitial is formed when a molecule becomes situated somewhere within the open space of the Ih crystal lattice. It, too, is thermodynamically stable at all temperatures above absolute zero, for the same reason. Interstitials are created at free surfaces and interfaces, but independently from vacancies that are also created there. The equilibrium interstitial concentration C_i may be approximated by the expression: