increases the mass input, and melting has little effect. Below the equilibrium line, increases in precipitation reduce the net summer ablation and partially offset increases in melting. Although the altitude of the equilibrium line increases with increased temperature, it decreases with increased precipitation and with increased cloudiness (27). Therefore, changes in position of the equilibrium line might be small as temperature and precipitation increase together. Because nearly 100% of the Antarctic ice sheet and 85% of the Greenland ice sheet are above the present equilibrium line, the dominant short-term effect is likely to be ice-sheet growth. An increase in precipitation and temperature should cause an immediate positive change in the mass balance and a gradual steepening of an ice sheet, which would continue for many years as the ice flow responded to the driving stresses.

In conclusion, Greenland ice-sheet growth is consistent with the generally warmer temperatures (28) experienced in this century. If climate continues to warm, enhanced precipitation in polar regions may offset increases in melting. Although the Antarctic ice sheet is a likely source of water for current sea-level rise, its mass balance is uncertain. Over much of Antarctica, which contains 91% of the earth's ice, the annual mass input is only 10% of the Greenland values, so that significant elevation changes may be ten times as small. Laser altimetry measurements (29) are needed there, because of its better range precision and ability to cover the critical ablation zones where radar altimeters do not adequately follow the more irregular ice surfaces.

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Thermomolecular Pressure in Surface Melting: Motivation for Frost Heave

J. G. Dash

A thermomolecular pressure is associated with surface melting, and it can drive mass flow along an interface under a lateral temperature gradient. The pressure is a universal thermodynamic function in the limit of thick films. It may be responsible for frost heave in frozen ground.

S URFACE MELTING CONTINUES TO ATtract considerable experimental and theoretical interest, as it involves fundamental questions in surface science and condensed matter physics and practical applications in materials processing (1-5). Although the phenomenon has been explored in a limited number of materials, it is believed to be a general characteristic of most classes of solid materials. The motivating force for the effect is the lowering of the interfacial free energy of a solid surface by a layer of the melted material, which occurs for all solid interfaces that are wetted by the melt liquid. Such a reduction of the free energy allows a macroscopically thick film of the liquid to be stabilized at a temperature below the normal melting point. The surface free energy of the film varies with its thickness and asymptotically approaches the value for semi-infinite liquid. This variation

Department of Physics, FM-15, University of Washington, Seattle, WA 98195.

with thickness introduces an effective interaction between the interfaces, equivalent to a negative thermomolecular pressure. In this report I show that this negative pressure is readily derived from the thermodynamics of surface melting and that it has a simple and universal expression in thick films. Although the pressure is not readily detected in the usual arrangements of surface melting experiments, it can be seen under certain dynamic and steady-state conditions. The pressures that can be generated in ice by quite modest temperature differences may be large enough to have important practical consequences. The effect may be responsible for frost heave in frozen ground.

Consider a solid in equilibrium with vapor or a wall at temperature T and pressure P. If the interface is wetted by a macroscopic layer of the melt (m) liquid the free energy of the layer is composed of bulk and surface terms

$$G_{\rm m}(T,P,d) = [\rho_{\rm l}\mu_{\rm l}(T,P)]d + \Delta\gamma f(d) + \gamma_{\rm s}$$

where *d* is the thickness, ρ_l and μ_l are the density and chemical potential of the bulk liquid (l), γ_s is the interfacial coefficient of the unwetted solid (s), $\Delta \gamma$ is the difference between the coefficients of the dry and wetted interface, and f(d) is the thickness dependence of the coefficients. In general, f(d) is a positive monotonic function tending to unity at infinite thickness. For example, in simple van der Waals materials with unretarded potentials, $f(d) = (1 - \sigma^2/d^2)$, where σ is a constant on the order of a molecular diameter.

In thermodynamic equilibrium, the chemical potential of the melted layer is equal to that of the solid. Differentiating Eq. 1

$$\mu_{\rm m}(T,P,d) = \frac{1}{\rho_{\rm l}} \left(\frac{\partial G_{\rm m}}{\partial d}\right)_{T,P}$$
$$= \mu_{\rm l}(T,P) + \left(\frac{\Delta\gamma}{\rho_{\rm l}}\right)\frac{\partial f}{\partial d} = \mu_{\rm s}(T,P) \quad (2)$$

The interfacial energy term in μ_m introduces an effective pressure δP_m acting on the melted layer. This can be seen from the general thermodynamic effect on the chemical potential of a system by a change in its external environment (6). If the unperturbed chemical potential of a system is $\mu(T,P)$ and the field energy per molecule is u, the chemical potential is changed to

$$\mu'(T,P,u) = \mu(T,P) + u$$
$$= \mu(T,P) + \delta P/\rho$$
(3)

Hence the interfacial energy term introduces an added pressure

$$\delta P_{\rm m} = \Delta \gamma (\partial f \partial d) = \rho_{\rm l} [\mu_{\rm s}(T,P) - \mu_{\rm l}(T,P)]$$
(4)



Fig. 1. Diagram of the thermomolecular pressure and flow in surface melting of a simple unconfined interface. (A) Initial conditions at a plane interface; (B) the profile, as modified by flow, after an interval. Temperature and pressure increase to the right.

At the bulk transition temperature T_0 , $\mu_s = \mu_l$ hence δP_m vanishes at T_0 . However, the chemical potentials differ at $T < T_0$. Expanding $\Delta \mu \equiv (\mu_s - \mu_l)$ to first order in the temperature difference

$$\Delta \mu(T) = \left[\frac{\partial \Delta \mu}{\partial T} \right]_{T=T_0} (T - T_0)$$
$$= \frac{q_{\rm m}}{T_0} (T - T_0) \tag{5}$$

where q_m is the latent heat of melting per molecule. Combining Eqs. 2 and 5 yields a functional relation for the temperature dependence of *d* that depends on the nature of the intermolecular forces. For example, in the case of van der Waals forces, with substitution of the specific form of f(d) given earlier, the result is a power law in the difference between *T* and T_0

$$d = \left(-2\sigma^2 \frac{\Delta\gamma}{\rho_{\rm l}q_{\rm m}}\right)^{1/3} t^{-1/3} \tag{6}$$

where $t = (T_0 - T)/T_0$ is the reduced temperature. In the case of short range forces, where $\partial f/\partial d \propto \exp(-cd)$, where *c* is a constant, the result is a logarithmic temperature dependence, $d \propto ||nt||$. Other types of interactions, such as dipolar forces, can produce other, similarly specific temperature dependences.

In contrast to the specificity of d(T), the thermomolecular pressure is a universal thermodynamic function. From Eqs. 3 and 5

$$\delta P_{\rm m} = -\rho_{\rm l} q_{\rm m} t \tag{7}$$

The negative sign indicates that the interfacial free energy is lowered by surface melting, so that $\Delta \gamma < 0$. It may appear that the interfaces are mechanically unstable under the influence of a negative pressure acting on the liquid and tending to pull the interfaces apart. However, such thickening of the liquid layer would require the conversion of a quantity of solid to liquid, which would raise the free energy of the system above its equilibrium value. Conversely, the stability of a liquid layer at temperatures below the normal melting point necessitates a negative thermomolecular pressure, that is, a suction.

The presence of a thermomolecular pressure can be detected if a temperature gradient is imposed along the surface. The resulting pressure gradient will cause mass transport in the liquid layer, toward lower temperatures (Fig. 1). Thus, mass transport and heat transport are coupled in the film, analogous to the simultaneous flow of current and heat in a thermocouple. If the temperature difference is maintained, the mass flow can be halted only by application of a hydrostatic pressure, equal and opposite to the thermomolecular pressure. If the interface is a single, low area surface this transport may be slow and difficult to detect, but it could be much more readily observed in a porous medium with large interfacial area.

An important practical manifestation of the effect may be the phenomenon of frost heave, which occurs in water-saturated soils below 0°C. Field observations (7) and laboratory studies (8) have shown the persistence of unfrozen water in porous media when cooled to temperatures as low as -30° C. This fluid tends to migrate along temperature gradients, toward lower temperature, where it deposits in segregated bulk ice "lenses." The process continues as long as the temperature difference is maintained, or until sufficient pressure is applied. Experiments have shown that the pressure is proportional to the temperature difference and can amount to greater than 11 atm/°C (8). The observed pressures are described by an empirical relation that is identical with Eq. 7. A description of frost heave and its serious consequences are given in a report by The National Research Council (9)

Nearly everyone living in the northern and southern temperate zones has experienced the effects of ice segregation and frost heaving through the destruction of roads and highways, the displacement of foundations, the jamming of doors, the misalignment of gates, and the cracking of masonry. Many people often have simply and mistakenly assumed that these effects result solely from the expansion of pore water on freezing. When confined, water can rupture pipes, break bottles, and crack rocks as it freezes. However, most of the destructive effects of frost heaving are caused by "ice segregation," a complex process that results from the peculiar behavior of water and other liquids as they freeze within porous materials. In particular, water is drawn to the freezing site from elsewhere by the freezing process itself. When this water accumulates as ice, it forces the soil apart, producing expansion of the external soil boundaries, as well as internal consolidation. The dynamic process of ice segregation and the expansion resulting from freezing of the in situ pore water, together, cause frost heaving.

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Frost heave has been suggested as the driving mechanism for the development of patterned ground in permafrost terrains and alpine areas, where the seasonal motion of pore water and ice produce sorting and profiling of the ground surface in regular geometric patterns (10).

The physical basis for the persistence of unfrozen water below the normal melting point has been attributed to various mechanisms, including dipolar forces, density variations, and the pressure melting of ice (11). However, the National Research Council reports that there has been no consensus on the fundamental causes

The limitations of all current models may be characterized collectively by simply stating that at present no model enjoys universal or general acceptance. . . . It is not certain that a deterministic formulation adequate for either the scientific or the engineering needs can be developed.

The present theory explains the ice phenomena as consequences of surface melting, and it predicts that similar effects should occur in other materials. However, although Eq. 7 is completely independent of the nature of the interactions, its universality rests on the assumption that the melt liquid is identical with the bulk. This is an approximation because a liquid is modified in the proximity of its boundaries, where it is more ordered (12). The range of the ordering depends on the nature of the liquid and the wall. Therefore the equation is strictly valid only in the limit $T \rightarrow T_0$, where d diverges. As T decreases, the layer thins and the proximity effect becomes more important; as a result, the pressure falls below the asymptotic relation in a nonuniversal manner.

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Air Ventilation by Recoil Aspiration in **Polypterid Fishes**

ELIZABETH L. BRAINERD, KAREL F. LIEM, CRISTIAN T. SAMPER

High-speed x-ray cine films synchronized with intra-pleuroperitoneal pressure measurements show that polypterid fishes aspiration breathe by the deformation and recoil of their bony-scaled integument. Paleozoic amphibians arose from ancient airbreathing fishes and retained piscine bony scales in V-shaped rows along the belly. These scales resemble those of modern polypterid fishes and may have contributed to inhalation by elastic recoil. The discovery that polypterid fishes breathe by recoil aspiration is the first evidence for aspiration breathing in any lower vertebrate. The use of recoil aspiration by polypterids shows that elastic storage in a stiff body wall can contribute to inhalation in animals with limited capacity for active aspiration.

OST AIR-BREATHING FISHES, LACKing the diaphragm or movable L ribs thought necessary for aspiration breathing, use a buccal pulse pump to fill their respiratory gas bladders (1). Aspiration has never been demonstrated in airbreathing fishes or amphibians, although its use has been suggested (2) and refuted (3)for the Amazonian fish Arapaima, and estivating lungfish may ventilate tiny amounts (<0.3 ml) of air by aspiration (4). We show that polypterid fishes ventilate their lungs by aspiration and that this is accomplished by the deformation and recoil of their bonyscaled integument. We call this novel ventilatory mechanism "recoil aspiration." The discovery that polypterid fishes breathe by recoil aspiration may affect our understanding both of early tetrapod breathing mechanics and of the role of elastic storage in ventilation.

The fundamental difference between pulse pump and aspiration ventilation is that in pulse pump systems air forces the lung to expand, whereas in aspiration systems air is sucked into the already expanding lung (5). In fishes using a buccal pulse pump, such as the bowfin, Amia calva, the mouth cavity expands to fill with air and compresses to pump air into the lung. The lung begins to fill only after the mouth is closed, and buccal cavity diameter decreases as lung diameter increases (Fig. 1).

The use of aspiration to fill the lungs in polypterid fishes is demonstrated by the pattern of buccal and lung diameter change shown in Fig. 1. Unlike Amia lung diameter, Polypterus lung diameter increases rapidly while the mouth is still open, and the buccal and lung diameters increase simultaneously. This pattern indicates that air is sucked into the lungs through the open mouth, rather than being forced in by a buccal pump. A mouthful of air is usually pumped onto the lungs at the end of inhalation, but this buccal air contributes less to the total ventilated volume than does the aspirated air (6)(Fig. 1, Polypterus, lung diameter increase after mouth is closed). Sometimes, however, the buccal air is simply expelled from the opercular openings at the end of the airbreath. X-ray cine films also show that polypterid fishes exhale through the opercular openings and inhale through the mouth: they do not, as others have suggested, breathe through the spiracles (7).

Aspiration breathing requires the generation of negative pressure in the body cavity surrounding the lungs. We have measured considerable negative pressures in the pleuroperitoneal cavities of two polypterid species, Polypterus senegalus and Erpetoichthys calabaricus. X-ray cine films synchronized with pressure measurements show that the most negative pleuroperitoneal pressure occurs at

Museum of Comparative Zoology, Harvard University, Cambridge, MA 01238