# Surface Melting of Ice

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The present theories of surface premelting are based on the assumed mechanism whereby a liquid layer is formed because the free energy of the surface is thus minimized. It is shown experimentally here that this mechanism is not possible in the case of ice, for which surface melting below 0 °C is, however, well documented. A mechanism of surface melting, unique for ice, is then proposed. It is based on a concept according to which the surface phase equilibrium temperature differs from that of the bulk material. The new theory predicts the onset temperature of premelting on ice in quantitative agreement with recent experimental data. It also explains regelation of ice and explains why water reaches a density maximum above its freezing point.

## 1. Introduction

Surface melting is an actively discussed topic in physics today. Its understanding is essential in many applications including friction, adhesion, coating technology, and material properties. Much attention has also been focused on ice, the surface of which has been subject to rigorous study and debate since Faraday in 1859 proposed[1] that regelation and extreme slipperiness of ice are caused by a thin film of water. Recently, this attention has been motivated by the importance of surface melting of ice in many natural phenomena, such as thunderstorm electrification and frost heave. The widely held theories of the ice surface[2−7] are based on the same idea as that of other surfaces, that is, the free energy of the surface is at its minimum when a liquid layer exists. This would be the case if the contact angle $\theta$ of water on ice is zero. We show here experimentally that, on the contrary, $\theta >> 0°$ under the conditions where such a contact angle experiment is relevant. We then propose an alternative theory of surface melting of ice and use it to explain some fundamental properties of ice and water.

## 2. Contact Angle and Surface Energy

When a liquid drop is placed on a solid surface, the equilibrium is given by the Young−Dupré equation

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \qquad (1)$$

where $\theta$ is the contact angle between the drop and the solid surface and $\gamma_{sv}$, $\gamma_{sl}$, and $\gamma_{lv}$ are the surface energies of the solid/vapor, solid/liquid, and liquid/vapor interfaces, respectively. If the surface energies are such that $\gamma_{sv} > \gamma_{sl} + \gamma_{lv}$, the free energy of the surface system is minimized when a liquid film exists on the solid surface. It is generally assumed that this kind of minimization can freely take place. In such a situation $\theta = 0°$. This forms the basis of the present understanding of surface melting[8,9] and has been applied extensively to various materials including ice.

In the case of ice, the application of the energy minimization principle is originally based on experiments[10,11] that show zero contact angles of water on ice at temperatures close to 0 °C. These experiments, from which the currently used value of the surface energy of ice $\gamma_{iv}$ was derived, have later been criticized on the grounds that equilibrium did not exist.[12] Some further experiments[12−14] have indicated that $\theta$ may be somewhat above 0°. We note the following fundamental problem with regard to all these experiments. Assuming that, for *any* reason, there is a water layer on the ice surface, then a water drop will necessarily spread on it. Thus, it is circular logic to claim that the zero contact angle resulting from these experiments proves anything about surface energies or the mechanism that causes the surface layer to melt. A contact angle experiment on ice with a liquid-like layer is irrelevant because the true ice/vapor interface, the properties of which the experiment is supposed to reflect, is not present in the system at all.

In order to determine a thermodynamically meaningful contact angle $\theta$ and the surface energy of ice $\gamma_{iv}$, one needs to make experiments under conditions where the liquid-like layer does not exist. According to experimental evidence,[11,14,15,22] these conditions are met only at ice temperatures below at least −15 °C.

We have performed sessile drop contact angle measurements of water on ice at −25 °C. In order to find an equilibrium, i.e., no phase change, while the drop attains its equilibrium contact angle, hot water was used. The drop temperature was varied between 0 and 100 °C. Air temperature was −25 °C and relative humidity 40%. Distilled water was used for making the ice and the drops. The drops were placed on a 20 mm thick smooth ice surface using a PVC injector. The injector was preheated to the nominal water temperature. The actual drop temperature at contact was estimated to be 1−5 °C lower than the nominal temperature measured before the water was sucked in the injector. This estimate is based on calculations of drop cooling and infrared thermal video imaging with 1 °C resolution. The drop placement and deformation were recorded by a video camera equipped with a microlens. Data were processed using a digital imaging system and the contact angles measured by adjusting lines on the image produced by a computerized graphic analyzer. No change in the initial contact angle during eventual drop freezing was observed when viewed in slow motion.

The scatter of $\theta$ at a fixed water temperature is mostly because drop spreading is not reversible in these experiments. A drop, once advanced over the ice, has warmed the ice/water interface to 0 °C and will not return to the original equilibrium position because a liquid layer would exist at this temperature on the re-exposed surface. In order to avoid underestimation of $\theta$ arising from this irreversibility, we placed drops carefully, trying

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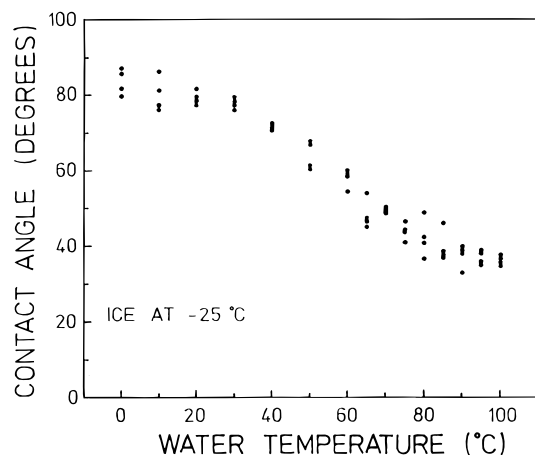


**Figure 1.** Contact angle of water on ice at −25 °C. At water temperatures close to 0 °C freezing takes place at the ice/water interface during drop deformation, while at water temperatures close to 100 °C melting of the base ice occurs. The initial phase equilibrium condition is obtained at a water temperature of about 95 °C.

to avoid flattening due to inertia of the drop. However, the drop was always fully released from the injector prior to contact with ice.

Note that the different temperatures of the two phases, the liquid drop and the base ice, as such, do not distort our experiment because eq 1 concerns the *free* energies of the system. Equation 1 can also be derived by considering the balance of surface tension forces. This derivation, as well, is independent of the temperatures of the interfaces.

On the other hand, one would expect that system is out of the static equilibrium described by the Young−Dupré equation when rapid solidification takes place at the ice/water interface, i.e., when the water temperature in our experiment is close to 0 °C. Generally, therefore, this experiment does not provide relevant contact angles, although corrections to take into account the dynamic condition are apparently possible to make.[16] However, by using sufficiently hot water it is possible to obtain initial static equilibrium, in that essentially no solidification occurs during the process before the drop obtains its final contact angle. This is discussed in detail below.

A simple heat balance calculation using the appropriate heat conductivities for the water drop and the ice shows that in our experiments, where the water temperature is varied, the phase equilibrium exists at the ice/water interface at the time of contact when the drop temperature is 95 °C. Under these conditions the heat flux from the drop to the water/ice interface equals that from the interface to the ice. Thus, freezing occurred in the experiments at temperatures colder than about 95 °C and melting at temperatures close to 100 °C. We verified this by blowing off drops immediately after they reached their equilibrium shape (in a fraction of a second). At water temperatures below 85 °C the ice surface at the position of the blown-off drop was elevated, indicating drop freezing, and at water temperatures at and above 95 °C a crater was formed, indicating melting of the base ice. We conclude that static equilibrium existed at a water temperature close to 95 °C. Under these relevant conditions, where eq 1 is valid, the results shown in Figure 1 indicate a value of 37° for the contact angle.

Inserting our experimental value of $\theta = 37°$ into eq 1 and using $\gamma_{wv} = 60$ mJ m$^{-2}$ (at 95 °C)[17] and $\gamma_{iw} = 29$ mJ m$^{-2}$ gives $\gamma_{iv} = 77$ mJ m$^{-2}$ for ice at −25 °C. This may be compared with $\gamma_{wv} = 79$ mJ m$^{-2}$ at the same temperature,[18] indicating that the surface energy of ice is slightly less than that of water. This is what one would expect from data of other materials that show a higher surface energy of the phase that

has the higher density.[19,20] Extrapolation using the d$\gamma$/d$T$ relationship of water[18] gives $\gamma_{iv} = 73$ mJ m$^{-2}$ at 0 °C, in contrast to the values of 105−109 mJ m$^{-2}$ widely used so far.[11]

The purpose of our experiments was not to derive accurate values for $\gamma_{iv}$ or $\theta$, however. From the point of view of the problem considered here, it is sufficient to know that eq 1 is valid somewhere in the range of water temperatures of Figure 1 and that *nowhere* in this range is $\theta$ even close to zero. The significant result obtained here is, therefore, that the surface free energy of ice $\gamma_{iv}$ is *not* minimized by forming a liquid layer ($\gamma_{wv} + \gamma_{iw}$). We have thus shown that the present theories of surface melting of ice, based on minimizing the free energy of the surface, are unfounded because the basic assumption of $\theta = 0$ °C is incorrect.

### 3. The Mechanism of Surface Melting of Ice

We next propose another explanation for the origin of the liquid-like layer. The surface energy of an interface can be defined as

$$\gamma = \int_{\infty}^{0} P(z)\, dz \qquad (2)$$

where $z$ is the distance from the interface and $P$ is the potential due to the net inward pull resulting from the difference in molecular forces at the bulk side and on the other side of the interface. The interface energy $\gamma$ is thus the energy per unit area that is required to form the interface either by exposing it from the bulk or bringing molecules from the bulk onto the surface. The potential $P$ can be interpreted as a pressure exerted on the thin interface layer.

This surface pressure $P$ is the net molecular force due to imbalance caused by the interface divided by the surface area and can be seen as the macroscopic representative of the net effect of the complex microscopic forces within the interfacial layer. A way to visualize the surface pressure is to consider a surface just exposed by cleaving a bulk material. Prior to molecular rearrangement ot the surface, there is the net inward pull due to the imbalance of molecular forces and the corresponding surface pressure that causes the surface to rearrange its structure. Upon rearrangement the surface attains a new quasi-equilibrium structure. It is reasonable to assume that this new structure is as if the corresponding pressure was applied to a bulk material. The surface pressure within the interface is not considered in classical thermodynamics because classical thermodynamics simplifies the surface between phases as a discrete boundary.

The quantitative relation between the surface pressure $P$ and surface energy $\gamma$ can be derived by applying the Lennard-Jones potential energy function. The attractive force per unit area between two semi-infinite parallel plates at a distance $z$, based on the Lennard-Jones potential, is (e.g. ref 20)

$$P(z) = \frac{2\pi q^2 A}{6z^3}\left[1 - \left(\frac{z_0}{z}\right)^6\right] \qquad (3)$$

where $q$ is the number of molecules per unit volume, $A$ is the attractive constant, and $z_0$ is the equilibrium distance between the molecules in the bulk material.

The surface energy $\gamma$ can be expressed in term of the Lennard-Jones potential as[20]

$$\gamma = \frac{\pi q^2 A}{16 z_0^2} \qquad (4)$$

Combining eqs 3 and 4 yields

$$P(z) = \frac{16\gamma}{3}\frac{1}{z}\left[\left(\frac{z_0}{z}\right)^2 - \left(\frac{z_0}{z}\right)^8\right] \qquad (5)$$

We are now interested in total net force per unit area exerted by the underlying molecular layers to the outermost surface, in order to find the onset temperature of surface pressure melting. There is no force between the outermost molecular layer and the second molecular layer because upon cleaving these are at the equilibrium distance $z_0$. The net force arises from the layers at the distance $2z_0$, $3z_0$, etc. Thus, the total pressure $P_0$ at the surface based on eq 5 is

$$P_0 = \frac{16}{3}\frac{\gamma}{z_0}\sum_{n=2}^{\infty}\left(\frac{1}{n^3} - \frac{1}{n^9}\right) \qquad (6)$$

The sum term in eq 6 equals 0.200, so that

$$P_0 = 1.067\frac{\gamma}{z_0} \qquad (7)$$

For ice with $\gamma_{iv} \approx 75$ mJ m$^{-2}$ and[11] $z_0 = 2.74 \times 10^{-10}$ m, eq 7 gives $P(0) \approx 290$ MPa. A surface energy of 29 mJ m$^{-2}$ is related to the ice/water interface at equilibrium.[17] The corresponding equilibrium surface pressure from eq 7 is 110 MPa. The pressure difference $\Delta P$ between a free ice surface and the phase equilibrium condition is, therefore, 180 MPa.

The effect of pressure is to alter the equilibrium melting temperature $T_m$, as first shown experimentally for ice by Lord Kelvin[21] already in 1850. The interface pressure due to molecular forces acts across an equilibrium ice/water interface and, therefore, in both phases. Thus, the equilibrium temperature change is given by the Clausius−Clapeyron equation

$$L_f = \frac{dP}{dT_m}(\nu_l - \nu_s)T_m \qquad (8)$$

where $L_f$ is the heat of fusion and $\nu_l$ and $\nu_s$ are the specific volumes of the liquid and the solid. The essential assumption here is that the thermodynamics of the interface can be treated according to the conventional laws of physics, an assumption already widely utilized in the Gibbs−Thomson relation, that predicts the internal surface pressure and equilibrium melting temperature for a curved surface. We extend this by noting that surface pressure in both phases, ignored in classical thermodynamics, already exists at a flat interface due to net molecular forces and that this affects the melting temperature.

Equation 8 yields $dT_m/dP = -7.43 \times 10^{-8}$ °C/Pa in the case of ice. The additional pressure of 180 MPa, consequently, reduces the melting temperature $T_m$ of the uppermost surface of ice by 13 °C. The origin of the liquid-like layer of ice is, therefore, very simple; at temperatures warmer than about −13 °C an exposed ice surface is above its melting point. This predicted melting temperature is remarkably consistent with recent X-ray scattering studies,[22] which show surface melting of ice at −13.5 ± 2.6 °C for the basal and at −12.5 ± 1.9 °C for the nonbasal surfaces.

The proposed mechanism is unique for ice. For normal materials, which contract on freezing, the term $(\nu_l - \nu_s)$ in eq 8 is positive; that is, the effect of surface pressure is to raise $T_m$. Surface melting of these materials is nevertheless possible if $\theta = 0°$ and if the conventional free energy minimization effect overrules the pressure effect very close to $T_m$. This theory also suggests that, at least on some material surfaces, freezing of a liquid should occur above the freezing point. This has been observed on, for example, liquid crystals and alkanes.[23] It is significant that the origin of the liquid-like layer on ice is

different from that on other materials. The ice surface melts due to the surface pressure, whereas surface melting of other materials, when it occurs, results from minimizing the free energy. This fundamental difference is supported by the evidence of the unique nature of the ice surface, starting from Faraday's classic experiment on regelation.[1] He showed that when two pieces of ice close to $T_m$ are brought into slight contact, they freeze together; a behavior not shown by other materials. The theory proposed here explains regelation by freezing of the surface pressure-induced liquid layer as the surface disappears on contact. Interestingly, Thomson[24] tried to explain Faraday's results by pressure melting already in the 1840s. However, his idea was that the liquid layer was formed by external impact pressure and froze when the pressure was released. This was later shown not to be the case.[11,25]

## 4. The Thickness of the Liquid-like Layer

Considerable attention has been paid to evaluating both theoretically[2−5,26−30] and experimentally[14,15,22,31−36] the thickness of the liquid layer on ice. We consider the predictions of the surface melting mechanism proposed here in this regard.

The surface pressure derived in eq 6 can similarly be calculated for any molecular layer depth below the surface. One may then use eq 8 to find the depth at which the pressure corresponds to the phase change at a given temperature. Such calculations, however, critically depend on the assumed form of the potential function. For example, if we take the Lennard-Jones form represented by eqs 3 and 5 the pressure can be approximated only by considering the effect of the nearest molecular layer that exerts a net force and neglecting the small repulsive term. The approximation following from eq 5 is then $P(z) \approx z^{-3}$, and considering eq 8 the liquid-like-layer film thickness $z \approx \Delta T^{-1/3}$. If an exponential form[2] is chosen for the potential function, then $z \approx \ln(13 \text{ °C}/\Delta T)$ is the corresponding approximation. Both of the above dependencies of the melted layer thickness on ice have been predicted by earlier theories[2−9,24,26] and also have experimental support.[15,22] Thus, while the theoretical explanation for the fundamental mechanism of surface melting presented here differs from the earlier state-of-the-art, its prediction for the temperature dependence of the liquid-like layer on ice is very similar.

Quantitatively, we have performed numerical calculations on the thickness of the melted layer based on this theory and the Lennard-Jones potential function, i.e. by eqs 6 and 8, so that the value of $n$ in eq 6 is varied for each depth. These results are qualitatively in good agreement with the X-ray measurements[22] and the optical measurements[15] as discussed above. The quantitative values of the liquid-like layer thickness as predicted by this theory are close to those measured by optical ellipsometry.[15] As mentioned above, the predicted onset temperature of −13 °C for surface melting is, however, in excellent agreement with the X-ray data. More precise comparisons with this theory and the experiments in regard to the thickness of the liquid-like layer on ice are not attempted here due to the uncertainty of the form of the potential function that should be chosen and the discrepancies in the results of various experimental studies.[41]

The interfaces between crystal grains in polycrystalline ice also involve a surface energy. The grain boundary energy is[11] approximately 60 mJ m$^{-2}$, for which this theory predicts a liquid film at grain boundaries above −8 °C. The film thickness is related to grain boundary sliding, and the theory can therefore be used as input in modeling the creep of ice and, for example, glacier flow. Interfaces between ice and other materials may also be considered in the light of the theory proposed here. This

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is of interest because of adhesion and friction of ice. The interface pressure is unrelated to the direction of the molecular forces, so that ice molecules are under positive pressure regardless of whether the other material is hydrophilic or hydrophobic. The temperature range and thickness of the resulting liquid film are related to the surface energy of the interface, as discussed above. The observed behavior that the adhesion[5,11] and static friction[37] of ice increase with decreasing temperature down to −10 to −20 °C depending on the other materials is in agreement with the theory.

## 5. The Ice−Water Phase Equilibrium

We next consider implications of the mechanism proposed here to the first-order phase transition. As discussed, a surface energy of 29 mJ m$^{-2}$ is related to the ice/water interface at equilibrium causing a surface pressure of 110 MPa and resulting in the melting temperature change $\Delta T = -8$ °C. Thus, the equilibrium temperature 0 °C at the ice/water interface is 8 °C lower than the theoretical melting temperature of the bulk material. In other words, the theoretical melting temperature of bulk ice (and the freezing temperature of bulk water) is approximately +8 °C.

This result may seem paradoxical, but its relation to the observed phase diagram can be readily explained by the fact that macroscale phase change without forming an interface is hypothetical. For example, although we suggest that bulk water is below its hypothetical freezing temperature between 0 and +8 °C, any permanent icelike molecular arrangement at these temperatures is impossible because it would form an ice/water interface. Such an interface immediately melts because of the surface pressure. The situation is similar to conventional supercooling, the difference being that below 0 °C there is a finite critical nucleus size that initiates freezing, whereas above 0 °C this size becomes infinite.

Heating bulk ice close to the bulk melting point, on the other hand, is unlikely because upon heating melting occurs at 0 °C or earlier due to interfaces at grain boundaries and impurity particles and possibly even in vacancies in the molecular ice lattice. In any case, this kind of heating would be difficult to observe because all temperature measurements of bulk material are made at or through an interface.

## 6. Density Maximum of Water

As explained above, bulk water at temperatures between 0 and +8 °C is below its freezing temperature, but is unable to form permanent ice clusters due to immediate surface melting. This is consistent with the so-called mixture model concept for water, which recently has been verified.[38] On statistical grounds one would then expect some icelike properties at these temperatures because of atomic mobility in a liquid. In the light of the present theory it is, therefore, not surprising that the water density versus temperature curve deviates from its normal behavior already well above 0 °C, resulting in the density maximum at +4 °C.

We have thus described here the *mechanism* that causes the anomalous density maximum of water, a property that has waited for an explanation for more than 100 years.[39] We relate the density maximum to the anomalous volume expansion at freezing, as a result of which bulk water is below its hypothetical freezing temperature already at +8 °C.

## 7. Concluding Remarks

In summary, we have presented a concept that shows a surface equilibrium melting temperature different from that of the bulk

material. In the case of ice this results in surface melting. The results are in qualitative agreement with recent molecular dynamics simulations.[27] Our concept is, however, more general and is derived from first principles.

The concept here where the surface layer of ice is at a pressure higher than the bulk is similar to that of Fukuta[40] but is in sharp contrast with the model of Dash et al.,[6,7] which involves a liquid layer at a lower thermomolecular pressure. Knight[41,42] has argued that all formulations involving pressure differences across the interfacial layer are inconsistent with the thermodynamic equilibrium and that the existence of the liquid state on the ice surface violates the Gibbs phase rule. Our position regarding this issue is that the pressure increase in this model is limited to the interfacial region idealized as a discrete dividing surface in classical thermodynamics and that the phase rule ignores the surface contributions to the thermodynamic properties of the system. In fact, we propose that the concept put forward in this paper may be used more generally in looking at the phase equilibrium in an unconventional and possibly fruitful way. For example, one could formulate a new kind of phase diagram in which the pressure axis represents the total pressure at the interface, i.e. the sum of the external pressure of the thermodynamic system and the surface pressure. In such a formulation each phase line is determined also by the interfacial surface energy of the interface between the two phases.

The theory developed here is verified for ice by its quantitative agreement with experimental data on the surface melting onset temperature and the temperature dependence of the thickness of the liquid-like layer, as well as by its ability to predict the unique nature of the ice surface and the density anomaly of water. We cannot suggest any new experiments to further verify this theory. The following situation is relevant, however. Suppose that a molecularly thin water film on an ice surface is suddenly submerged into bulk ice at 0 °C. If the film freezes, then the melting temperature in the bulk is above 0 °C, because only in the presence of a thermal gradient can the latent heat released in freezing be transferred away from the contact area. This experiment is precisely what Faraday did in 1843 when he brought two thawing ice spheres into contact at room temperature. The spheres immediately froze together. It is virtually impossible to explain[11] how the initial contact is formed when the temperature is below 0 °C nowhere in the system, unless the bulk equilibrium freezing temperature is above 0 °C. Hence, the most convincing piece of evidence to support the theory presented here comes from Faraday's original experiment made over 150 years ago.

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