

MELTING POINTS OF SMALL ICE CRYSTALS AND A CAPILLARY  
THEORY OF MAXIMUM UNDERCOOLING OF WATER

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NOTICE: Because the progress in the research at the University of Vermont has led to results more significant than those which were hoped for at the time when the 1956 Eastern Snow Conference was being planned, Dr. Skapski asked the permission of the Conference to present, instead of the originally announced paper, "Melting Points of Thin Ice Sheets," his last work dealing with a new theory of supercooling of water, which is summarized below.

By melting point we understand the temperature at which liquid and solid coexist in equilibrium. Under normal conditions under which the solid and the liquid contact each other in relatively flat 'interface,' the melting point is determined only by pressure, and is thus constant under atmospheric pressure.

If, however, we consider a very small ideally spherical crystal — and we know that very small crystals tend to round up their edges considerably and can approach this shape — the 'interface tension'  $\sigma_{SL}$  (in ergs/cm<sup>2</sup>) existing in this interface (which is now curved instead of being flat) influences the equilibrium by depressing the melting point of the crystal. This depression of the melting point  $\Delta T = T_m - T$ , is given thermodynamically by

$$\Delta T = \frac{2T_m\sigma_{SL}}{q_f\rho_s r} \quad (1)$$

where  $T_m$  is the 'normal' melting point in degrees Kelvin,  $q_f$  is the heat of fusion in ergs per gram,  $\rho_s$  is the density of the solid, and  $r$  is the radius of the spherical crystal.

It is evident from Eq. (1) that the depression of the melting point (or, in other words, the undercooling  $T$  of the liquid which is in equilibrium with the small crystal) is directly proportional to  $(1/r)$  and thus increases with the decreasing size (radius) of the crystal. If we neglect the changes in  $q_f$  and  $\rho_s$  as relatively small, this dependence will remain linear as long as the interface tension solid/liquid ( $\sigma_{SL}$ ) retains its macroscopic value.

The value of the interface tension  $\sigma_{SL}$  can be calculated from Skapski's next neighbours theory of capillarity.<sup>1/</sup> For water/ice its value is 27 erg/cm<sup>2</sup>.

The question now arises whether the  $\Delta T$  will increase steadily with the decreasing radius until the crystal has been reduced to the minimal group of molecules which still exhibits crystalline symmetry, such as a unit cell? The answer to this question is again given by the next neighbours theory of interface tension developed by Skapski.<sup>2/</sup> It follows namely from this theory that the interface tension solid/liquid disappears when the crystal is still relatively large, composed of hundreds of molecules. The minimal or rather 'critical' radius below which the interface tension ceases to depress the melting point of the spherical crystal any more, comes out from the theory to be:

$$r_{\min} = 3.5 k N^{-1/3} V_s^{2/3} \quad (2)$$

where  $k$  is a packing factor of the order of magnitude of

unity,  $N$  is the Avogadro number, and  $V_s = (M/\rho_s)$  is the molar volume of the solid.

By inserting the meaning of  $r_{\min}$  into Eq. (1), we obtain

$$T_{\max.} = \frac{2T_m\sigma_{SL}}{q_f\rho_s} \times \frac{1}{3.5 k N^{-1/3} V_s^{2/3}} \quad (2)$$

where  $T_{\max}$  is the maximal possible depression of the melting point of the spherical crystal, and consequently the maximal undercooling of the liquid which is in equilibrium with this crystal.

Let us apply Eq. (3) to the case water/ice. Substituting the numerical values, namely:

$$\begin{aligned} T_m &= 273^\circ\text{K}, \sigma_{SL} = 27 \text{ erg/cm}^2, \\ q_f &= 80 \times 4.19 \times 10^7 \text{ erg/gram}, \\ \rho_s &= 0.92, V_s = 19.6 \text{ cm}^3, \end{aligned}$$

and putting  $k = 1$  (which involves only a small error), we obtain:

$$T_{\max.} = 43^\circ\text{C.}$$

in reasonable agreement with the experimentally found maximum undercooling of water. The corresponding  $r_{\min} = 1.12 \times 10^{-7}$  cm.

The theory is general and applies to all non-ionic substances, metallic and non-metallic, provided their molecules are not too elongated (it does not apply to fatty acids, for example). The main theoretical conclusion is that the temperature of maximum undercooling is a definite fraction of the normal melting temperature, if both are expressed in degrees Kelvin:

$$T_{\max.\text{und.}} = AT_m \quad (4)$$

The fraction  $A$  has nearly the same numerical value for several substances. In case of metals, for instance, we have

$$T_{\max.\text{und.}} = 0.81 T_m$$

which holds for most metals within an error smaller than 3%. For water, the relation is

$$T_{\max.\text{und.}} = 0.843 T_m.$$

It seems very interesting that the phenomenon of maximum undercooling can be treated as an equilibrium problem under the influence of capillarity and that such a treatment leads to correct numerical relations.

## REFERENCES

1. A. S. Skapski, A Theory of Surface Tension of Solids, Acta Metallurgica, 1956 (in print).
2. A. S. Skapski, A Capillary Theory of Maximum Undercooling in Metals, Acta Met., 1956 (in print).