ANOMALIES IN THE "LATENT HEAT"
OF SOLIDIFICATION OF SUPERCOOLED WATER

D. BERTOLINI, M. CASSETTARI and G. SALVETTI
Istituto di Fisica Atomica e Molecolare del CNR, Via del Giardino 7, 56100 Pisa, Italy

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The latent heat for the solid-liquid transition, measured in supercooled water down to \(-30^\circ\text{C}\), is reported for the first time. These values do not agree with those calculated using the specific heat values at constant pressure \(c_L(T)\) reported in the literature for supercooled water in emulsions. However, values of \(c_L(T)\) obtained working with bulk water down to \(-26^\circ\text{C}\) confirm emulsion data. To account for the observed anomalies we suggest the existence of a metastable phase (or phases) in freshly formed ice, relaxing to the equilibrium \(\text{I}_h\) configuration.

1. Introduction

When supercooled water crystallizes, a large quantity of heat is suddenly released. It increases the sample temperature and, if the phase transition takes place adiabatically, a mixture of ice and liquid water at \(0^\circ\text{C}\) is obtained. When the sample is thermally coupled to a bath with capacity \(C_B\), only part of the latent heat remains in the sample and, if the heat exchange rate and \(C_B\) are sufficiently high, the temperature of the sample does not increase up to \(0^\circ\text{C}\). In these conditions a solid phase at \(T < 0^\circ\text{C}\) results.

When a liquid is supercooled down to \(T_f < T_m\) (\(T_m\) being the melting temperature) and the heat capacities of the liquid \((C_p^L(T))\) and of the solid \((C_p^S(T))\) phases at constant pressure are known in the range \(T_f < T < T_m\), the latent heat \(\lambda(T)\), defined as the difference between the enthalpies of the liquid and the solid phases at \(T_f\) is:

\[
\lambda(T_f) = \lambda(T_m) - \int_{T_f}^{T_m} (C_p^L - C_p^S) \, dT.
\]  

(1)

The behaviour of \(\lambda(T)\) can be calculated using literature values for the quantities in eq. (1). Conversely one can use measurements of \(\lambda(T)\) to obtain for example \(C_p^L(T)\) if \(C_p^S(T)\) is known. \(C_p^L(T)\) has been measured in bulk water down to \(-13^\circ\text{C}\); for further supercooling there are values obtained in emulsions [1].

At the outset of this work we intended to obtain, by measuring \(\lambda(T), C_p^L(T)\) of bulk water at temperatures lower than \(-13^\circ\text{C}\). Indeed this can be done with very thin capillary tubes, owing to the large signals involved, so that the probability of large supercooling is enhanced. In the analysis of our experimental results we found large differences, increasing with supercooling, between the measured \(\lambda(T)\) values and those calculated by eq. (1) using emulsion data, i.e. an anomalous behaviour of the latent heat of freezing. We therefore measured directly \(C_p^L(T)\) of bulk water and succeeded in obtaining \(C_p^L(T)\) of supercooled water in capillary tubes down to \(-26^\circ\text{C}\).

Very good agreement with Angell's emulsion data [1] was obtained so that the observed differences remained unexplained.

After detailed consideration of the experimental apparatus and procedure to eliminate possible artifacts, we conclude that our data support the existence of a transient solid phase (or phases) in the ice just grown from the liquid phase. These ice structures should be metastable in respect of ice \(\text{I}_h\) and they must relax towards the equilibrium phase with a transition heat equal to the difference between the calculated \(\lambda(T)\) value and the measured one. The existence of a state intermediate between the liquid phase and
the equilibrium solid could be relevant to a micro-
scopic theory of the liquid–solid phase transition,
and the explanation of some effects directly related
to the kinetics of the process \([2,3]\).

The aim of this Letter is to report results of the
experiment on which the above conclusion is based.

2. Experimental

In our experiment we used a home-made micro-
calorimeter able to accept water samples in capillary
tubes (0.5–7 cm in length, 0.3–0.9 mm internal
diameter). It is essentially a differential dilatometer,
the sensitivity of which, in terms of relative length va-
riation of the calorimetric cell, is \(\Delta l/l \approx 5 \times 10^{-8}\), \(l\)
being the length of the cell. The quantity we measure
is the temperature increase of the sample cell produc-
ed by the phase transition. The related signal is de-
tected by the instrument with a rise time of 0.2 s, and
a sensitivity of \(4 \times 10^{-3} \text{ J}\). The heat capacities of the
sample cell and the reference one are equal to \(1.9 \text{ J/}
\)°C, and the reset time constant after a signal is 240 s.

The sample temperature was measured with an ab-
solute precision of 0.2°C. The temperature gradients
in the cells slow down in times smaller than the rise
time of the instrument. The temperature increase of
the sample cell in a \(\lambda(T)\) measurement was typically
1°C.

The apparatus, when adapted directly to measure
\(C_p^L(T)\), becomes a differential calorimeter. The proce-
dure to measure \(C_p^L(T)\) is the following: the two cells
are fed measured amounts of electrical power for a
fixed time, one cell containing the water sample; if
the currents are chosen to give zero differential out-
put of the instrument at the temperature \(T_0\) (for ex-
ample +5°C), then in runs at different temperatures
signals related to the heat capacity of the sample with
respect to \(T_0\) are obtained. The temperature increase of
the cells was 1–2°C. We have accounted for this in
analyzing the results. The mass \(m\) of the water sample
was measured using a microbalance which gives (with
a sensitivity of \(10^{-5} \text{ g}\)) the weight of the capillary
tube with and without the water sample (typically
the \(\text{H}_2\text{O}\) content was 30–40 mg). Twice-distilled
water in ampoules (Angelini, Verona) was used in all
the measurements reported here.

The agreement between the latent heat of fusion
we measured at 0°C and the values in ref. \([4]\) gives a
check on the reliability of each run.

3. Results and discussion

The values of \(\lambda(T)\) obtained down to \(-30^\circ\text{C}\) are
shown in fig. 1; the solid line represents eq. (1) using
for \(C_p^L(T)\) data from ref. \([1]\), while the dashed curve
is obtained from data reported in ref. \([5]\) as the more
reliable for supercooled water. A curve like the solid
one shown in fig. 1 has been derived by Franks \([6]\)
using the same emulsion data. The experimental points
were calculated using the relation

\[
\lambda(T_f) = (T' - T_f)C_B/m + \int_{T_f}^{T'} C_p^L(T) \,dT,
\]

where \(m\) is the mass of the sample and \(T' - T_f\) is the
temperature increase of the sample cell during the
freezing. This increase and \(T_f\) are the quantities mea-
sured in the experiment. In deriving \(\lambda(T)\) from eq. (2),
we have taken into account the corrections (1–2%) due
to the finite value of the instrumental reset time
constant (≈240 s) which is larger than the freezing
time (3–7 s) but not negligible.
At constant sample volume we have worked with different tube diameters (0.3–0.9 mm) and consequently with different heights of water in the capillary tubes. In this way we varied the heat exchange rate $\Gamma$ of the sample to test for a possible dependence of the results from the condition of the freezing process. Only when $\Gamma$ was strongly reduced, by thermally insulating the sample tube with another capillary tube containing it did the experimental points appear significantly affected. The black triangles in fig. 1 refer to these measurements. They are higher than the curves, but by an amount within experimental error. The important feature is that $\lambda(T)$ from these measurements was 8% higher than other determinations where samples were well coupled to the thermal bath. In these latter conditions the latent heat anomaly disappeared.

In fig. 2 are shown measured $C_p^l(T)$ values down to $-26^\circ C$ together with the curve fitted to Angell's data [1] for emulsion water. The good agreement and the noticeable anomalous behaviour of $\lambda(T)$ in fig. 1 (at $-26^\circ C$ the separation between the two curves in fig. 1 is $\approx 7\%$ and greater than 10% at $-30^\circ C$) strongly suggest that the anomaly cannot be, at least down to $-26^\circ C$, traced back to the recently suggested differences in the physical properties between bulk water and water in emulsions [5]. As the experimental points in fig. 1 are lower than the curves from eq. (1), we must account for a loss of energy in the heat balance. Thus we must introduce in the thermodynamic cycle followed by the water sample some process not considered in deriving eq. (1). The anomaly disappears when, for small enough $\Gamma$, the ice sample explores temperatures much higher than $T_f$ (see fig. 1); this implies that the temperature increase of the ice sample causes a change in its structure, the related heat release being equal to the anomaly at $T_f$.

Our conclusion is that one must postulate the existence of a transient structural phase (or phases) in ice obtained from sufficiently supercooled water. When the temperature of the ice sample remains sufficiently low the "mean life" of these transient phases must be greater than a few seconds, the time interval during which the experimental signal attains its maximum.

References