COMPRESSION OF ICE IN FREEZING OF SUPERCOOLED WATER IN CAPILLARIES

B. V. Zheleznyi

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When supercooled water is crystallized in a capillary, the ice is found to be strongly compressed [1]. A theory of maximum possible compression is discussed for a rigid cylindrical capillary and its experimental verification is presented.

A phenomenon of strong compression of ice in rapid nonequilibrium crystallization of supercooled water in a capillary is described in [1]. The stresses developed in this case are so large (up to $2 \cdot 10^8\ N/m^2$), that they could cause local destruction of almost any structural material. In view of the fact that this phenomenon is of definite interest for practical use, a special investigation of this phenomenon was carried out on a model of cylindrical capillaries.

We consider a dead end cylindrical capillary partially filled with water from the end face (Fig. 1). Let the length of the column increase on freezing. Due to the effect mentioned above this length is smaller than the length l_0 corresponding to the density of ice at the given temperature and atmospheric pressure. We shall determine the maximum pressure developing in the column and the minimum possible length l. We make the following assumptions which correspond fairly closely to the conditions of the experiment: 1) the capillary is absolutely rigid, 2) $l \gg r$. Since the limiting shear strength of ice is small [2], even at pressures of the order of $10^7\ N/m^2$ the pressure tensor in ice can be regarded close to spherical and the internal pressure in ice may be considered as a hydrostatic pressure. In this case assumption 2) enables one to investigate the problem as a linear one, assuming the pressure in each transverse section of the column constant.

We choose the origin and the direction of the x axis as indicated in Fig. 1. The element of length Δx of the column is acted on by the pressure difference $\pi r^2 \Delta p$ balanced by the tangential force $2\pi r \tau \Delta x$. Passing on to the limit we can write

$$\frac{\partial p}{\partial x} = \frac{2}{r}\tau, \tag{1}$$

where τ is a function of pressure and temperature. The temperature dependence of the force of adhesion of ice at atmospheric pressure has been studied repeatedly [3, 4]. In a limited temperature range near 0°C it can be expressed by the formula

$$\tau = -k_1 t, \tag{2}$$

where $k_1 = \text{const} > 0$, while for lower temperatures

$$\tau \approx \text{const} = \tau_0. \tag{3}$$

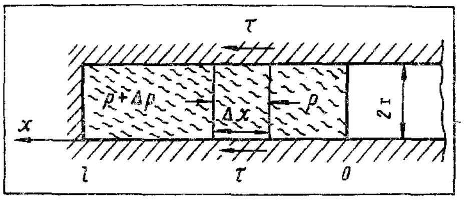

Fig. 1. Diagram illustrating derivation of formula (1).

The dependence $\tau(p)$ for t = const has not been investigated by anyone. But it is just this dependence which is of interest to us, since without knowing it the integration of (1) and a comparison of the theory with the experiment is not possible. Since the increase of the pressure on ice takes it closer to the melting point and is analogous to the increase of temperature, it can be assumed that near the melting pressure the dependence $\tau(p)$ is similar to (2) and can be written in the form

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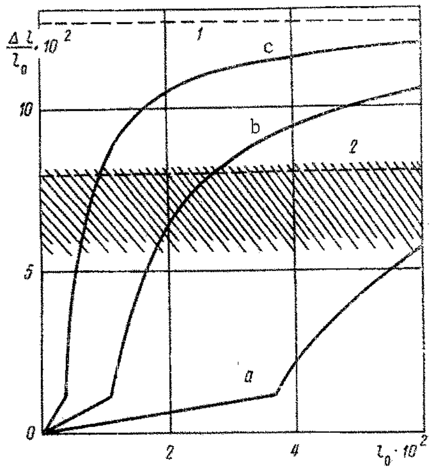

Fig. 2. Dependence of the maximum average compression on the length of the column for the case τ = const, $r = 2 \cdot 10^{-6}$ m, $t = -10°C$: a) $\tau_0 = 3 \cdot 10^3$; b) $1 \cdot 10^{-4}$; c) $3 \cdot 10^4$ N/m^2.

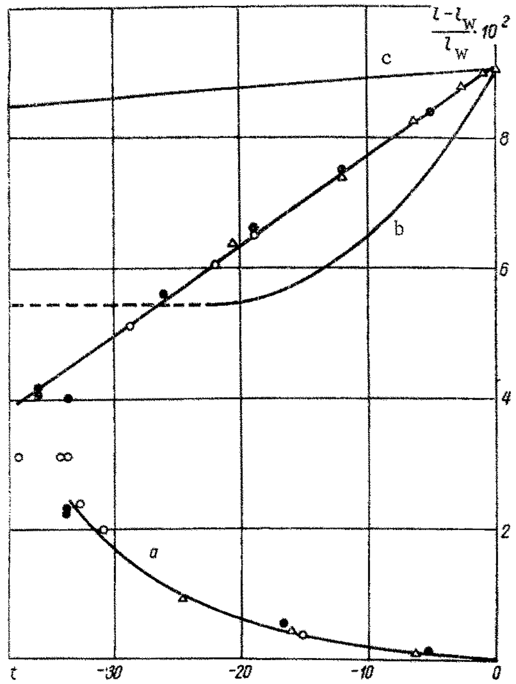

Fig. 3. Experimental temperature dependence (from three experiments) of the length of ice column in quartz glass capillary ($r = 2 \pm 0.3 \cdot 10^{-6}$ m, $l_0 = 4.4 \cdot 10^{-2}$ m): a) water at p = 0, b) ice I at $p = p_t$, c) ice I at p = 0.

$$\tau = k(p_t - p), \tag{4}$$

where k = const, while at pressures far from p_t (3) is valid.

The integration of Eq. (1) with the condition p = 0* at x = 0 gives

$$p = \frac{2\tau_0}{r} x, \tag{5}$$

for the case (3), and

$$p = p_t \left[1 - \exp\left(-\frac{2k}{r} x \right) \right], \tag{6}$$

for the case (4).

It is obvious physically that the maximum pressure in the ice in the capillary cannot exceed p_t, since in such a transition the pressure is removed by a negative change of volume. If (3) were valid for all p, then according to (5) the value p_t will be attained for

$$l \geqslant l_t = \frac{p_t r}{2\tau_0}. \tag{7}$$

According to formula (6) p_t cannot be attained. It is interesting to determine the conditions, in which it is generally possible to attain p_t in a cylindrical capillary. According to (1) this is possible in the case where l_t, which is equal to $r/2 \int_0^{p_t} dp/\tau(p)$, is finite. It is clear that if ice has nonzero adhesion strength in the entire interval $0 \leq p \leq p_t$, then p_t is attainable; if $\tau(p) \to 0$ for $p \to p_t$, then it is well known from analysis that the integral $\int_0^{p_t} dp/\tau(p)$ converges only under the condition

$$\frac{\tau(p)}{(p_t - p)^\lambda} > c > 0 \quad \text{for} \quad p \to p_t, \quad 0 < \lambda < 1, \tag{8}$$

where c and λ are some constants. Condition (8) is the general condition for attainability of p_t in a cylindrical capillary.

*Here and below we disregard the atmospheric pressure for brevity, taking it arbitrarily equal to zero.

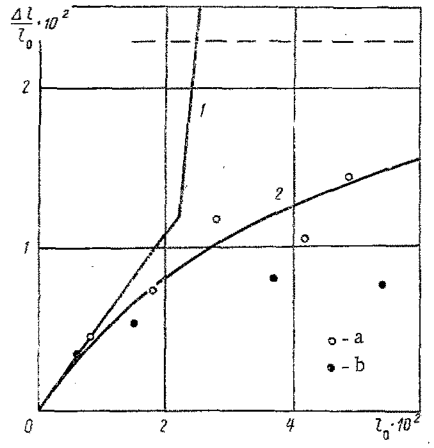

Fig. 4. Experimental and theoretical dependence $\Delta l/l_0$ (l_0): a) r = 2 ± 0.3 · 10^{-6} m; b) r = 7.5 ± 0.5 · 10^{-6} m; 1) from formula (11), (12); 2) from formula (13); computed values for r = 2 · 10^{-6} m; τ_0 = 5 · 10^3 N/m^2, k = τ_0/p_t, t = −10°C.

In order to change over from the known distribution p(x) to l it is necessary to know the dependence ρ(p). In the literature only the data for p = 0 and p_t are available [2]. We have assumed that the dependence ρ(p) for ice is of the form

$$\rho = \rho_0 + \alpha p - \beta p^2, \tag{9}$$

where α and β are constant coefficients depending on temperature. In order to find the third point on the curve ρ(p), which is necessary for determining α and β, we have assumed that the linear expansion coefficient δ of ice for p = 5.9 · 10^7 N/m^2 in the temperature range −5 to −10°C is equal to 4 · 10^{-5} deg^{-1} (for p = 0 δ = 5.2 · 10^{-5} deg^{-1} [2]). This assumption makes it possible to descend along an isobar from the point −5°C on the melting line of ice to the point on the curve ρ(p) corresponding to −10°C. Even though it is highly arbitrary, it cannot introduce a significant error, since the correction introduced for the thermal expansion of ice is generally small. Under this assumption the following constants of Eq. (9) are obtained for −10°C with p expressed in N/m^2 and ρ in kg/m^3: ρ_0 = 918.2, α = 2.15 · 10^{-7}, β = 1.275 · 10^{-16}.

Since the mass for a given ice column is constant, for a rigid capillary we can write

$$\int_0^l \rho dx = l_0 \rho_0. \tag{10}$$

Combining (10), (9), and (5) for $l \le l_t$ we have

$$\Delta l = l_0 - l = \frac{\tau_0 l^2}{\rho_0 r}\left(\alpha - \frac{4}{3}\beta\frac{\tau_0 l}{r}\right). \tag{11}$$

For $\beta \ll \alpha$ (which happens in our case), considering that $\Delta l \ll l_0$, instead of (11) we can write

$$\frac{\Delta l}{l_0} \approx \frac{\alpha \tau_0 l_0}{\rho_0 r}. \tag{11'}$$

For the case $l \gg l_t$ instead of (10) we must write

$$l_0 \rho_0 = (l - l_t)\rho_* + \int_0^t \rho dx, \tag{10'}$$

which together with (9) and (5) leads to

$$\frac{\Delta l}{l_0} = A - \frac{B}{l_0}, \tag{12}$$

where

$$A = 1 - \frac{\rho_0}{\rho_*}; \quad B = l_t\left(1 - \frac{\rho_0}{\rho_*}\right) - \frac{\tau_0 l_t^2}{r\rho_*}\left(\alpha - \frac{4}{3}\beta\frac{\tau_0 l_t}{r}\right).$$

The complete graph of the dependence $(\Delta l/l_0)(l_0)$, constructed for three different values of τ_0 from formulas (11), (12) for the case r = 2 · 10^{-6} m, t = −10°C, is shown in Fig. 2. The initial segments of the curves are almost rectilinear, which corresponds to (11'). A discontinuity of the curves occurs at $\Delta l/l_0$ = 1.18 · 10^{-2}, which denotes that p_t is attained. The subsequent behavior of the curves is hyperbolic, corresponding to (12).

Line 1, corresponding to $\Delta l/l_0 = 1-\rho_0/\rho_*$, is a common limit of the curves. In practice, however, even with the fulfilment of (3) the curves of $\Delta l/l_0(l_0)$ cannot go above line 2 corresponding to the density of supercooled water at -10°C. In general a physical limit of the relative compression of ice (averaged over the entire volume) in a rigid capillary is the region (shaded in Fig. 2; its lower boundary is undefined) corresponding to the density of super cooled water, as without the application of an external active force the volume of the ice cannot become smaller than that of the liquid from which it is formed. The attainment of this limit is manifested in the fact that the freezing occurs without a change of the volume, which has been actually observed by us repeatedly in the experiment in freezing of long columns at $\tau < -30$°C.

Combining (10), (9), and (6) we get

$$l_0\rho_0 - l\rho_t = \frac{\alpha p_n r}{4k\gamma}(z+2\gamma-3)(z-1), \tag{13}$$

where

$$z = \exp -\frac{2kl}{r}; \quad \gamma = \frac{\alpha}{\beta p_t}.$$

Formula (13) does not give the discontinuity in the dependence $\Delta l/l_0(l_0)$ and $\lim_{l_0\to\infty} \Delta l/l_0 = 1-\rho_0/\rho_t$.

Formulas (11)-(13) have been derived for the column in a dead-end capillary. For a column, which is free both ends and has a length L, the maximum length deficit $\Delta l/l_0$ will be equal to the value of $\Delta l/l_0$ for a column in a dead-end capillary of length L/2.

For an experimental investigation of the dependence of $\Delta l/l_0$ on l_0, r, t we have used the procedure described earlier [1]. Certain changes are made in the equipment; a built-in low-inertia electric heater is used and the upper glass is electrically heated. The capillaries are drawn from prewashed tubes of optically pure quartz glass and doubly distilled water is used for the experiments. The experiment is conducted in the following order: after measuring the length of the column of liquid in the capillary at 0°C it is frozen (after appropriate supercooling) and then the length of the column of ice is measured as the temperature increases by 3-6°C.

On maintaining the capillary at a constant temperature after the next temperature increase the length of the ice column, while increasing, approaches the minimum possible value for the given temperature (we call it extremal) asymptotically. In order to shorten the time required to attain this length, after maintaining the capillary at a constant temperature for some time the temperature is lowered by stages through 0.3-0.6°C until the length of the ice column practically remains unchanged on maintaining t = constant for 5 min (the reading accuracy of the comparator is $\pm 1 \cdot 10^{-6}$ m). The average temperature between the last points is taken as corresponding to the given (extremal) length of the column.

The reproducibility of the experimental results for each column can be judged from Fig. 3, on which the results of different experiments with the same column in the liquid as well as solid state are plotted with different symbols. Plotted on the same figure are the lines corresponding to relative lengthening (volume changes) for water and ice at atmospheric pressure and ice I on the melting line; accurate data for the density of ice I on the line of transition into ice III and II are not known to us and tentatively it can be taken constant in the range -22 to -40°C.

The change in volume on freezing of one and the same column in different cases is different, but after a sufficient increase of temperature the lengths of the column measured in different experiments are practically equal (Fig. 3). The segment of the curve $l-l_w/l_w(t)$, on which the results of different experiments coincide, is taken as the segment in which the length of the ice column is extremal.

In order to exclude the effect of small conicity on the computed value of l_0 the length of the ice column at 0°C (after maintaining at a constant length) is taken corresponding to the normal density of ice at 0°C and 1 atm. This point together with the length of the column of the liquid at 0°C is used as the datum.

The overall experimental error is estimated as $\pm$0.3-0.6°C in temperature. This accuracy is determined not by the accuracy of measurement of temperature ($\pm$0.2°C), but by the accuracy of agreement of the determined temperature of the given extremal length of the column. It should be noted that, after the growth of the column has been stopped by cooling to a certain temperature t_1, a heating to a temperature $t_2 > t_1$ is generally required to resume its growth. In the present work as a rule, we determined the extremal length at the time when the growth stops, and not when it starts. We have not carried out a special investigation of this hysteresis.

Figure 4 presents experimental results of determination of $\Delta l/l_0$ at -10°C for ice columns of different lengths in capillaries with $r = 2.0 \pm 0.3$ μm and 7.5 ± 0.5 μm. Each point represents the average value for the column of a given length, obtained in several experiments. The dependence $\Delta l/l_0(l_0)$, computed from formulas (11), (12) (curve 1) and formula (13) (curve (2) for $t = -10$°C, $r = 2$ μm, $\tau_0 = 5 \cdot 10^3$ N/m^2, $k = \tau_0/p_t$, is also shown in the same figure. The dashed line represents the limit of formula (13) for -10°C.

The large spread of the experimental points, and also the smaller difference between the capillaries $r = 2$ μm and 7.5 μm than that expected from formulas (11)-(13), is, in our opinion, mainly due to nonidentical properties of the surfaces of different capillaries, which in turn is due to different reasons: random conditions during the drawing of the capillaries, incidence of impurities etc. The adhesion strength has a strong dependence on the properties of the surface; for example, it can change by an appreciable factor depending on the nature of the surface [4]. Small deviations from cylindricity and variations of the average radius for different capillaries can also affect the scatter.

The experimental points for the capillary with $r = 2$ μm lie close to curve 2. This leads to the conclusion that the force of adhesion of ice to the walls actually decreases with the increase of the pressure and the dependence $\tau(p)$ is close to (4). Using (4) we can estimate the maximum pressure p_{max} in the column from formula (6). Thus, for $l_0 = 10^{-2}$ m we have $p_{max} \simeq 4 \cdot 10^7$ N/m^2 for the capillary with $r = 2$ μm (for the assumed value of k).

The value $\tau_0 = 5 \cdot 10^3$ N/m^2 coincides in order of magnitude with the value $\tau_0 = 7 \cdot 10^3$ N/m^2 obtained by Jellinek [4] for the strength of adhesion of ice to optically polished quartz glass for zero rate of displacement at -4.5°C. Considering the influence of the surface roughness mentioned above, it can be asserted that there is a satisfactory qualitative agreement between the theory and experiment.

The results of our experiments do not enable us to conclude whether or not condition (8) is satisfied for temperatures higher than t_T; nevertheless their nature is certainly in favor of nonfulfilment of this condition. Not even in a single case did we obtain results definitely indicating a compression exceeding the limit of formula (13) for $t > t_T$. Clearly, from Fig. 3, for $t < t_T$ such compressions were obtained repeatedly. This indicates that a significant part of the ice in the column exists in the form of ice II or III (compare [1]) and, hence, p_t is attained.

NOTATION

r	is the radius of the cylindrical capillary;
t	is the temperature, °C;
$t_T = -22$°C	is the triple point temperature for water–ice I–ice III;
l	is the minimum length of column of compressed ice for a given temperature t, having equilibrium length l_0 at the same temperature t and at atmospheric pressure arbitrarily taken equal to 0;
p	is the average internal pressure in ice;
p_t	is the pressure of ice I–water transition (or ice I → ice III or II transition) at a given t;
τ	is the specific adhesion strength of ice to capillary wall;
ρ	is the density of ice I at p, t;
ρ_0	is the same as p at p = 0 and t;
ρ_*	is the density of water (or ice III or II) at t and p_t;
$\Delta l = l_0 - l$;	
ρ_t	is the density of ice I at t, p_t;
l_w	is the length of column of water at 0°C.

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