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From the Nucleation of Ice Crystals in Clouds to the Formation of Frazil Ice in Rivers

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I. Introduction

It is a well known fact that the phenomenon of supercooling of liquids is apparently universal for the beginning of the solid phase (Young, 1910). Water is no exception. There is considerable supercooling of water droplets in clouds before the appearance of snow or hail. The temperature of freezing of quiet water masses is generally many degrees below 0°C. Thus, it is not surprising to observe that crystals of surface or frazil ice in flowing water also appear at temperatures under 0°C.

But there is quite a difference in the amount of supercooling for different cases. Water droplets might freeze at $-35°C$, but frazil particles will form in rivers with only a few hundredths of a degree of supercooling. There is no coherent explanation in the literature for these discrepancies and we will try here, to synthetize the available knowledge and apply the existing theories to the case of ice apparition in rivers and lakes.

In the first part of this paper we will see that the Mason-Biggs theory of heterogeneous nucleation for water droplets is applicable to the case of ice formation in water samples of finite volume if there is a critical temperature above which the foreign particles can not become active except in the case of agitation. In that latter case, Dorsey's extension of the theory seems acceptable.

In the second part of the paper we will show that the small amount of supercooling attained in rivers and lakes can be explained by the generalized theory of heterogeneous nucleation when the thermal boundary layer in air and water is taken into account. This would stand for big masses of still water or for laminar and turbulent flow in nature.

II. Freezing of Water Droplets

The temperature of freezing of water droplets in clouds is usually very low, of the order of $-20°C$ and occasionnally as low as $-35°C$.

Research work by physicist has shown, long ago, that this temperature is mainly dependent on the presence of foreign particles in the droplets. Mason (1958) says that we can imagine, in the following way, the freezing of a droplet. As the temperature is lowered the molecular arrangement of the supercooled water particle is getting closer and closer to that of ice. If there is no foreign particle, nucleation will occur by a lucky orientation of water particles in space and time to form the crystalline structure of ice. However, the presence of a foreign substance of favorable crystallographic form will give a better orientation to the molecules under the interfacial force field and will maintain this configuration for a longer time in the Brownian motion of the fluid. The probability that the water molecules in contact with this particle will attain the critical configuration to start the solid phase will be much increased. Thus, it is clear that the presence of favorable foreign particles will decrease the amount of supercooling before the freezing of the droplet.

We thus see that there are two different types of freezing of water droplets; the heterogeneous nucleation in presence of foreign particles and the homogeneous nucleation in very pure water. As the latter case has no practical interest we will not discuss it here.

The theory of heterogeneous nucleation has been developed by Langham and Mason (1958) with the empirical results of Biggs (1953).

Laboratory experiments have shown that the number of foreign particles which are active as nucleus for the formation of ice can be given by the relation:

$$n = n_0 e^{a|T_s|}, \tag{1}$$

where:

n : concentration of active particles at the supercooled temperature T_s,
n_0: concentration of active particles at 0°C,
a : more or less favorable characteristic of nucleation of the foreign particles.

The probability that a droplet of volume V has at least one active nucleus at supercooled temperature T_s is, from Poisson's law:

$$P = 1 - e^{-Vn}. \tag{2}$$

Equations (1) and (2) give:

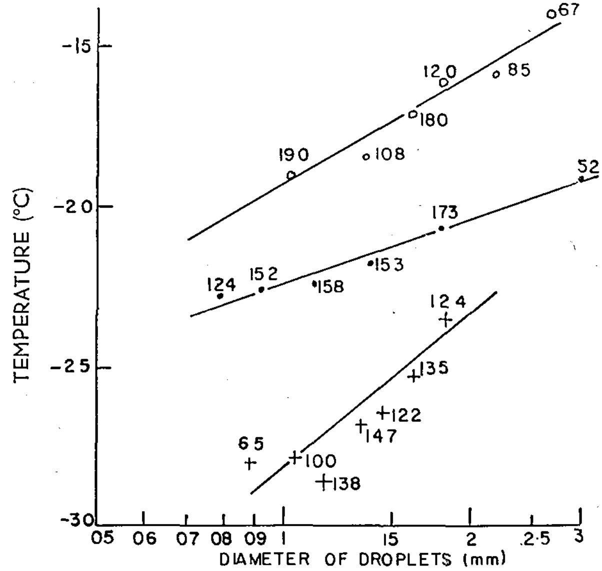

Fig. 1. Median temperature of freezing for groups of water droplets in function of their diameter for three water samples of different purity and foreign particles (From Langham and Mason)

$$\ln\left(\frac{1}{1-P}\right)=Vn_0 e^{a|T_s|}\,.$$

If tests results are processed in a way that for a volume V and a temperature $-T_s$, 50% of the droplets are frozen, we then have $P=1/2$, which gives:

$$|T_s|=\frac{1}{a}\left\{\ln\frac{(\ln 2)}{n_0}-\ln V\right\}. \tag{3}$$

It is seen from Fig. 1, that the experimental results closely verify this theory. Each curve corresponds to a different concentration of foreign particles, the highest value at the origin of each, on the graph, representing the highest concentration n_0. The slope of these curves depends on the affinity of nucleation of the particles, a.

III. Freezing of Water Samples

Dorsey (1948) has made many tests to determine the temperature of freezing of water samples of finite sizes. His results on specimens of many cubic centimeters can be summarized in the following way:

The temperature of nucleation is much closer to 0°C than for droplets.

It is constant for a same sample.

It is independent of the cooling rate.

It is quite influenced by the state of agitation of the sample. The agitation lowers the maximum temperature of supercooling.

There is somewhat a contradiction with these results and the Mason-Biggs theory of nucleation of water droplets. This comes from the fact that the empirical law eq. (1) giving the number of active nucleus is extended down to 0°C but it has never been found experimentally that there is any nucleus of foreign particles which are active at temperatures above a few degrees of supercooling. This law should probably have been written:

$$n=n_0 e^{a(|T_s|-|T_c|)}\,, \tag{4}$$

where T_c is a critical temperature below which the foreign particles become active, depending on the crystallographic form of these particles.

If such a correction is entered into the results of eq. (3) we then get:

$$|T_s|-|T_c|=\frac{1}{a}\left\{\ln\left(\frac{\ln 2}{n_0}\right)-\ln V\right\}. \tag{5}$$

This more general formula is represented on Fig. 2, where we see that starting from a certain critical size, the temperature of nucleation does not depend on the size of the sample.

We will now have to dwell further in the heterogeneous theory of nucleation as extended by Dorsey (1948) to explain the case of freezing with agitation of rubbing. His own statement is given here:

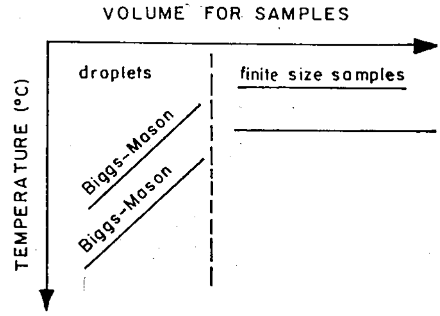

Fig. 2. Representation of the generalized theory of heterogeneous nucleation of water

"It is generally agreed that the molecules of a liquid that are immediately adjacent to a foreign body are packed quite closely together, are bound quite strongly to the body, and have a preferred orientation with reference to the interface between the body and the liquid. In successively more distant layers, the packing becomes less close, the binding weaker, and the orientation less complete, until presently the status characteristic of the liquid in bulk and far from foreign bodies is attained."

"For simplicity, this entire group of layers, ··· is called the absorbed layer of liquid."

"If the absorbed layer can be so torn that a sufficient number of loosened molecules remain in one another's field of force for such a time and with such a degree of freedom that they can reorient themselves and become bound together in the manner characteristic of an embryo that can persist and grow at the existing temperature, they will do so."

"He defines an embryo of a crystal as any structural aggregation of the molecules of the melt that maintains its identity as an individual, distinct from the ambient melt, for an interval that is long as compared with the mean time between consecutive molecular collisions ···." The embryo retains its identity, although it may continually exchange molecules with the melt.

The stability of an embryo depends on its size. An embryo of a given kind can be in equilibrium at a given temperature only if it is of a particular size. "That size will be called the *critical size* ··· Embryos larger than the critical size will mature into macroscopic crystals; those smaller than the critical size will decay ··· Hence, at any given temperature the initiation of a *viable* (one capable of growing) embryo requires the existence of an embryo of at least critical size."

Dorsey distinguishes between a simple embryo (one composed of molecules of the melt only) and a complex embryo (one with a foreign particle as a center and molecules of the melt adhering to it). The initial structure of the very small embryo is not known, but it is tought to undergo a progressive (not necessarily continuous) change toward the structure of a true macroscopic crystal as it grows.

"His theory assumes that the absorbed layer can be so torn by various means, including the impact of free molecules of the melt, and that both the spontaneous and the mechanically initiated freezing of a supercooled melt may be, and at least at the higher temperatures are, initiated solely in that manner."

"If the absorbed layer can be so damaged by molecular impacts as to give rise to viable embryos, then the spontaneous freezing of a supercooled melt can obviously be initiated in that manner. And if the layer can be so damaged by molecular impact, it can surely be so damaged by other means, including gross mechanical ones."

Thus this extension of the theory of heterogeneous nucleation by Dorsey is the only one that can explain the fact that agitation, rubbing and supersonic radiations can nucleate a sample of finite size of water at a higher temperature than that of quiescent water.

IV. Apparition of Border Ice in Rivers and Lakes

Border ice is the first type of ice to appear in a lake because the water cools down at a higher rate in shallower water or in areas of laminar flow along the banks of a river. In calm water or in laminar flow there is no intermixing of the top layer with the bottom layers and the temperature differences are important either in the vertical direction or in the horizontal one away from the banks.

In a river the top layer adjacent to the bank will go through undercooling considerably while the temperature underneath and in the middle of the river will still be much above freezing point. Figure 3 shows considerable supercooling at the surface along a vertical section in a laminar flow.

There might be two related mechanisms of freezing in such circumstances.

The first one will occur right in contact with the bank. Because the solid bank is more conductive than water, it will be colder than water and the particles of water in contact with it will first attain the critical temperature of nucleation depending on the foreign particles present in the water body or the bank itself. Ice will nucleate and adhere to the banks. The ice front will then progress away from the bank in the supercooled water. There are abundant particles in river water which are very favorable as nucleus of ice formation.

The second mechanism will occur away from the bank. The surface layer will supercool up to the critical temperature of nucleation of the water. There will then be a prism of supercooled water at the surface as shown in Fig. 3. Nucleation will start and propagate quickly on the surface giving up the latent heat of fusion taken away in this supercooled layer. Figure 4 shows the actual measurement of the temperature of an ice crystal growing in such a case.

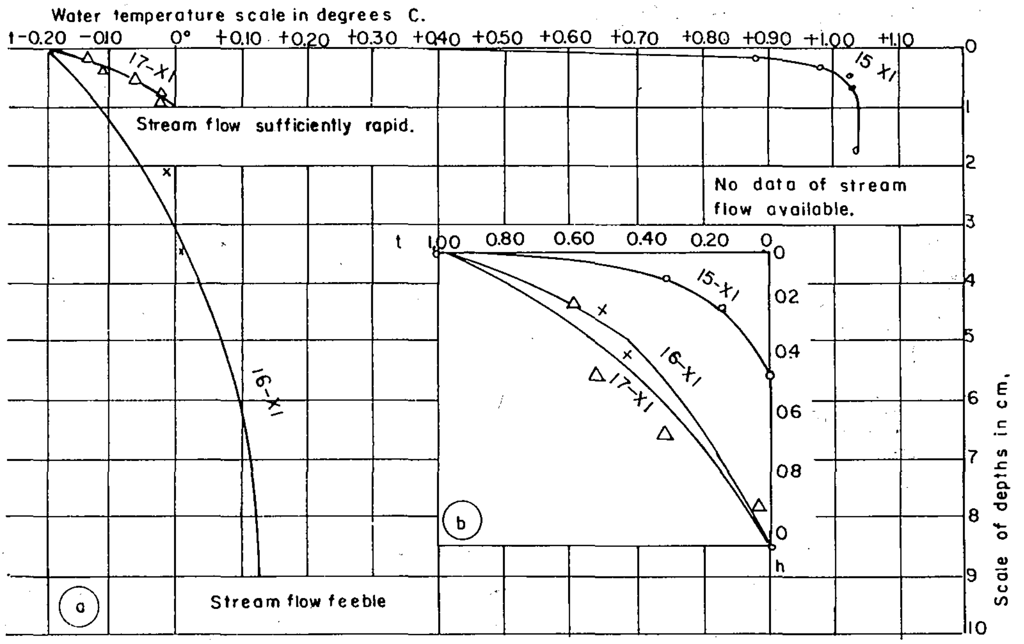

Fig. 3. Dissimilarity of the water temperature in the thin surface layers of the river Neva; a, in the thermometer readings; b, in computed relations

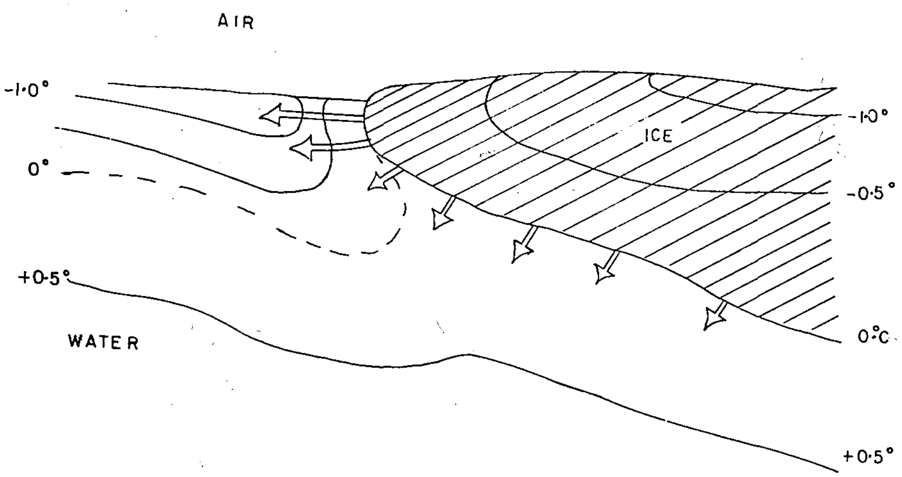

Fig. 4. Growth of ice in supercooled water (*cf.* Devik, 1944)

V. Apparition of Frazil Ice in Rivers

In turbulent flows of river the temperature of supercooling hardly goes over a few hundredths of a degree. For such temperatures, Piotrovich (1956) has shown that ordinary substances in suspension in water are unable to nucleate ice.

We will now see that the theory of heterogeneous nucleation can also be applied to such a phenomenon. Consider the temperature distribution (Altberg, 1936) along a vertical section in an idealized turbulent flow, as shown in Fig. 5. There is a steep temperature gradient at the surface and then an almost uniform distribution in the remainder of the flow. As the water is cooled down the temperature at the surface attains the critical temperature of nucleation at the surface while the remainder of the

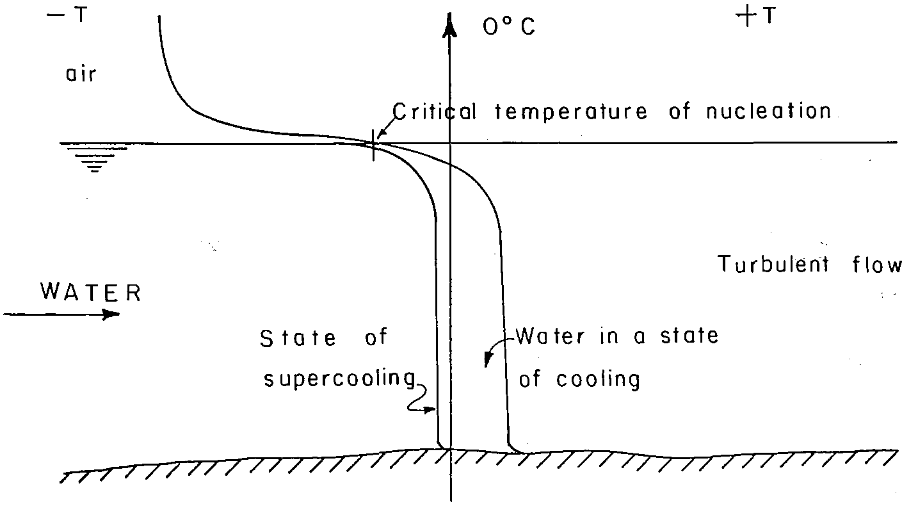

Fig. 5. Distribution of air-water temperature before the appearance of frazil ice

flow is still above 0°C. Viable heterogeneous embryos are formed on the surface. As they start to give up the heat of fusion of ice, they are carried underneath and disappear in the warm water. Thus the temperature at the surface will remain, from now on, at this value. The body of water will continue to cool down and we will attain supercooling of the whole flow section.

The degree of supercooling attained by the whole water mass can then be explained with the help of some observations we have made in a frazil ice flume (Michel, 1963). We found that:

The degree of supercooling increases with the rate of cooling of water.

A supercooling of 0.04°C was attained in a test during a light snow fall.

The physical explanation of the mechanism of supercooling is thus apparent. A number of seeds per unit surface area either falls in the water in the form of snow or are formed as viable embryos in the top highly supercooled layer of the flow. These seeds have a finite growth velocity depending on their state and the ambient water temperature. There is thus a finite amount of heat that can be given to the water as these seeds form ice and grow. On the other hand, there is also a given amount of heat taken away from the water per unit volume. The bigger the embryos get, the more heat they will give. We then observe the temperature curve given in Fig. 6.

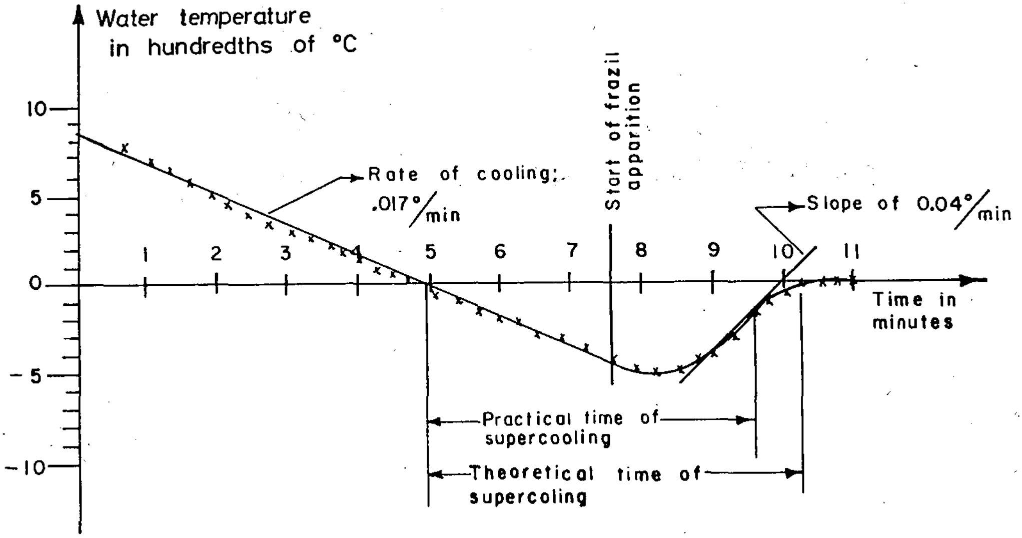

Fig. 6. Temperature of water during frazil ice production

We see that it takes a small amount of supercooling for the viable embryos to start the nucleation, and frazil particles to appear. The rate of water cooling drops considerably and the maximum temperature of supercooling is attained. Finally we have a more or less asymptotic approach of the water temperature to 0°C.

VI. Conclusion

From the preceding short synthesis it would appear that the theory of heterogeneous nucleation is universal for the appearance of ice in nature. First developed to explain the formation of ice crystals in clouds it is applicable for finite size water masses with Dorsey's hypothesis and finally for the apparition of frazil ice in rivers. This particular case has never been elucidated in a convenient manner and it can be quite simply connected to the more general phenomenon if use is made of the thermal boundary layer of turbulent flows in nature.

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