Experimental study of sudden solidification of supercooled water.

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Nina balanced the piece of ice two or three times in her hand and threw it forward with all her strength. A sudden thrill seemed to vibrate across the motionless waters to the distant horizon, and the Gallian Sea had become a solid sheet of ice!

Jules Verne, Off on a Comet

Abstract

The two independent methods of measurement of the mass of ice created at sudden solidification of supercooled water are described. One is based on the calorimetric measurement of heat which is necessary for melting the ice and the second interprets the volume change which accompanies the water freezing. Experimental results are compared with the simple theoretical calculation and possible systematic errors are discussed in detail and incorporated into the data evaluation.

Introduction

Supercooled water is a liquid phase which exists at temperatures below the actual freezing point. This effect has been well known for centuries; firstly it was published by Joseph Black in 1775 but probably it was noticed earlier by Gabriel Fahrenheit [1,2]. In nature the highly supercooled water can be found in clouds where supercooling of small droplets can even reach minus 40°C.
Not only water but also other liquids can be supercooled. For instance a very large supercooling can be reached easily with sodium acetate which is employed in so called heating pillows. After initialization of crystallization the heat is revealed which keeps the pillow warm for tens of minutes.
The sudden solidification of a supercooled liquid is a spectacular experiment which is attractive for people of any age. In this paper a quantitative measurement of the mass of solidified ice is presented. The theoretically calculated value is compared with the results of two independent methods. The systematic errors of experimental methods are discussed in detail.

Theoretical background

The effect of supercooling is a result of minimalization of Gibbs free energy and using so called classical theory of homogeneous nucleation can be relatively simply explained in the following way.
The process of freezing starts with the creation of a tiny crystalline nucleus. The appearance of the bulk of the new phase causes a decrease of Gibbs free energy by the value ΔG_V which is

proportional to the volume of the newly created phase. But this is accompanied with the creation of a new liquid - solid interface which leads to energy cost by surface energy ΔG_S proportional to the interface area. The total change of Gibbs free energy is then given by

$$\Delta G(r) = \Delta G_V + \Delta G_S = -Ar^3 + Br^2, \qquad (1)$$

where r is the diameter of the nucleus (supposing it to be spherical) and A and B are the constants. The graph of the function $\Delta G(r)$ is plotted in Fig. 1. In general the spontaneous process is one with a drop in Gibbs free energy. But at the beginning of the nucleus growth Gibbs energy increases, thus the very small nucleus is likely to dissolve rather than grow. In this way a liquid is able to exist in a nonequilibrium state at temperatures below the freezing point.
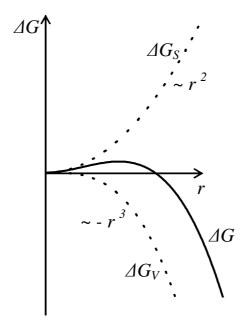

Figure 1 The Gibbs energy as a function of nucleus radius.

For the spontaneous solidification the nucleus must overcome the energy barrier ΔG_{crit} through the random fluctuation which corresponds to the critical nucleus radius r_{crit}. The height of this barrier can be significantly lowered at the surface of another phase or at the surface with elastic stress in the vicinity of scratches or other surface defects. This is called heterogeneous nucleation.

The solidification of supercooled water can be artificialy initialized in two ways:

1) Using a strong elastic wave in liquid for instance by bumping the plastic bottle onto a table.

2) More softly by putting a tiny piece of ice into the supercooled water. This piece of ice significantly exceeds the dimension of the critical nucleus and the solidification will start immediately.

Once the solidification is initialized the new phase grows very quickly. But simultaneously latent heat of freezing is released which warms the liquid-solid mixture until the melting point

is reached. At this moment the solidification is stopped. For supercooling by a few degrees centigrade the amount of ice can be quite small. It can be calculated easily from the calorimetric equation

$$m_W c \cdot (t_m - t_s) = m \cdot l_s, \qquad (2)$$

where m_W is the mass of supercooled water, m mass of ice, c specific heat, l_s latent heat of freezing, t_m melting point temperature and t_s temperature of supercooling.

From Eq. (2) we get

$$\frac{m}{m_W} = \frac{c}{l_s}(t_m - t_s). \qquad (3)$$

Inserting the numerical values gives an amount of 1,2% of solidified ice per one degree of supercooling. Because a maximal possible supercooling of larger volumes of water is only a few degrees centigrade, the amount of solidified water is typically very small, only a few percent. Thus the description of freezing the supercooled Gallien Sea in the famous Jules Verne novel is not exactly accurate. The sea cannot become "a solid sheet of ice" but rather only a weak mixture of water and drift-ice.

The experimental determination of the amount of solidified ice is an interesting experimental problem. The ice is weakly dispersed in water, cannot be easily separated from the water and, at usual room temperature, melts very quickly. So direct weighing of ice is not possible and other indirect methods must be employed.

Calorimetric method

The calorimetric method is based on the measurement of the latent heat of melting ice. Due to the very high value of latent heat this, the method is relatively sensitive even if the amount of ice is very low.

The experimental procedure is the following: Immediately after the solidification has ended, the water with the ice is quickly moved into a calorimeter. During gentle continuous stirring, room temperature water is added into calorimeter until all the ice is melted and then the resulting temperature is measured[1]. The process is described by the calorimetric equation

$$\left(m^* c + K \right) \cdot (t_1 - t) = m \cdot l_s + m_W \cdot c \cdot (t - t_m), \qquad (4)$$

where m^* is the mass of added water at room temperature, K the heat capacity of the calorimeter, t_1 temperature of the room temperature water and t the resulting temperature of water after the ice has melted. (expected to be slightly above 0°C). From this equation we can easily obtain:

$$m = \frac{1}{l_s}\left[\left(m^* c + K \right) \cdot (t_1 - t) - m_W \cdot c \cdot (t - t_m) \right]. \qquad (5)$$

The heat capacity of calorimeter K is obviously difficult to measure with any precision. Because typically the mass of added water m^* is small, the heat capacity of the added water could be comparable with the heat capacity of the calorimeter and this will result in a large error of calaculated mass m. To avoid this it is better to cool down the calorimeter to 0°C before the experiment. Thus the temperature of the calorimeter is practically not changed

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[1] Using room temperature water to melt the ice limits the experimental errors. In this case there is no need to take care about possible temperature changes caused by a heat exchange between the water and the ambient air.

during the experiment and there is no need to measure the calorimeter heat capacity. In this occasion Eq. (5) turns to the equation

$$m = \frac{1}{l_s}\left[m^* c \cdot (t_1 - t) - m_W \cdot c \cdot (t - t_m) \right].$$

(6)

Method based on the volume increase after solidification

This method is based on the well-known fact that the density of liquid water is about ten percent larger than the density of ice. During solidification the total volume of the water ice mixture increases. In this experiment a volume change below 1% is expected so we have to use a sufficiently sensitive method for the determination of the change in volume.

The volume of the supercooled water V_W can be calculated as

$$V_W = \frac{m_W}{\rho_w},$$

(7)

where ρ_W is the density of liquid water. Similarly the volume of water ice mixture V_{W+I} is given by

$$V_{W+I} = \frac{m_W - m}{\rho_W} + \frac{m}{\rho_I},$$

(8)

where ρ_I is the density of solid ice. From Eq. (7) and (8) we get

$$m = \frac{(V_{W+I} - V_W)\rho_W \cdot \rho_I}{\rho_W - \rho_I} = \frac{\Delta V \cdot \rho_W \cdot \rho_I}{\rho_W - \rho_I}.$$

(9)

The volume change $\Delta V = V_{W+I} - V_W$ is measured by a shift of a coloured water bead in a tiny horizontal glass tube which is hermetically fixed to the cap of the bottle containing the supercooled water, see figure 2. The volume calibration of the glass tube can be made by weighing the tube filled with water. For the temperature measurement, a tiny thermocouple gauge has to be slipped into a second glass tube which is sealed at the bottom end. In this way direct contact of the supercooled water with the metal surface of the thermocouple, which can cause an unwanted heterogeneous nucleation of ice, is avoided.

The nucleation is started by hitting the bottle on the table. This can cause an air strike in the tube which can split the coloured water bead (green spot in Fig. 2). To avoid this a capillary tube is inserted between the bottle and measuring tube to atenuate the air strike.
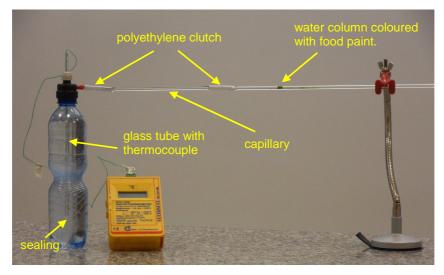
Figure 2: The experimental arrangement.

Experimental errors

There are a few possible sources of experimental errors. Firstly, the water temperature in the PET bottle is certainly not homogeneous but the thermocouple measures temperature at a single point. It is not possible to homogenize the temperature by intensive stirring because this can cause an undesirable initialization of the solidification. It was proved experimentally that the vertical temperature gradient of supecooled water in a 500 ml PET bottle can even reach 1.5°C. Due to the negative value of thermal expansion cofficient (see Fig. 3) the temperature is higher at depth.

The main problem in the calorimetric method is warming of the water-ice mixture. Due to this effect the measured mass of ice will always be smaller than in reality. But this effect can hardly be quantified. On the other hand a more detailed analysis of systematic errors can be done in the method based on volume increase in ice solidification.

When water is freezing, the temperature of the water-ice mixture grows from the temperature of supercooling t_s to melting temperature t_m. This happens in a few seconds. Due to thermal expansion the volume of water is changed according to the equation

$$\Delta V_W = V_W \beta_W (t_m - t_s), \tag{10}$$

Where, as before, V_W denotes the original volume of supercooled water and β_W is the thermal expansion coefficient of water. It is well known that the thermal expansion coefficient of water is negative in the range from 0°C to 4°C, but it remains negative also for supercooled water below freezing point, see Fig 3. That is why the quantity ΔV_W is negative and this systematic error decreases the measured mass m of ice.
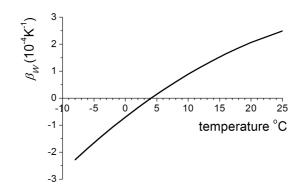
Figure 3: The thermal expansion coefficient of water [3].

Thermal expansion of the PET bottle also plays an important role. When the temperature of the water-ice mixture grows, the inner volume of the bottle ΔV_B increases by the equation

$$\Delta V_B = V_W \beta_B (t_m - t_s),$$ (11)

where β_B is the thermal expansion coefficient of PET, $\beta_B = 1.17 \cdot 10^{-4}$ K^{-1}. This systematic error also decreases the measured mass m of ice.

Finally, the thermal expansion of air in the glass tube must be taken into account. We can suppose that the air in the PET bottle above the water surface has the same temperature as the supercooled water. When the solidification starts, a volume of this air is pushed into glass tube and there it is warmed to room temperature. This increase of air volume ΔV_G can be calculated from well known isobaric law

$$\Delta V_G = \frac{t_o - t_s}{T}(V_{W+I} - V_W),$$ (12)

where t_o is room temperature and T is a mean value of t_o and t_s expressed in kelvin. This effect increases the measured volume and thus increases the measured mass m.

All three effects mentioned above can be simply incorporated into a calculation by modification of equation (9)

$$m = \frac{(\Delta V - \Delta V_W + \Delta V_B - \Delta V_G) \cdot \rho_W \cdot \rho_I}{\rho_W - \rho_I}.$$ (13)

The following numerical example can provide a quantitative insight into the significance of particular systematic errors. Let us assume that we have a 500 ml of water supercooled to a temperature -5°C. Theoretically 31,4 g of water turns to ice during solidification, that corresponds to a volume change 2,84 ml (equations (3), (7) and (8)). When water is warmed up from its supercooled temperature to ice melting temperature, due to thermal expansion its volume is decreased by the value -0,293 ml (equation (10)). For this calculation the mean value of the water thermal expansion coefficient in the range from -5°C to 0°C was used, $\beta_W = -1.17 \cdot 10^{-4}$ K^{-1}. At the same time the inner volume of the PET bottle is increased by 0,293 ml

(Eq. 11)[2]. And finally cold air pushed from the bottle to the glass capillary and tube expands by 0,266 ml. As a result of all these effects, the measured volume change is 0.320 ml smaller than in reality. Thus the total systematic error is about 10%.

Results and discussion

The results of three selected experiments are listed in Table 1[3]. In all cases the calorimetric method provides smaller values than the volume change method. This can be explained by the previously mentioned thermal gain (i.e negative thermal loss) during the experiment. The calorimetric method requires more time to empty the PET bottle, move the water-ice mixture into the calorimeter and wait until the ice is melted. On the other hand the volume change method is very fast and the measurement is finished a few seconds after the solidification starts. So in this case the thermal gain can be considered to be negligible.

The systematic error corrections according to Eq. (13) increases the values by the 10% as was expected. But these values (which can be regarded from theoretical considerations as the best ones) are in all cases larger than the mass of ice theoretically calculated from Eq. (3). The theoretical values are probably underestimated. The temperature in the bottle was measured near to the bottom of the bottle where the temperature is the highest and that is why the theoretically predicted amount of ice is lower than in reality.

initial mass of water (g)	supercooling (°C)	mass of ice (g)			
		theoretically calculated from Eq. (3)	calorimetric method, Eq. (6)	volume change method	
				without corrections Eq. (9)	with corrections Eq. (13)
500	- 5,4°C	34,0	34,8	37,7	41,1
525	- 4,7°C	31,1	21,3	29,6	33,2
525	- 4,6°C	30,5	22,3	29,6	33,1

Table 1: A list of experimental results.

Practical hints for the experiments

The supercooled water can be prepared most easily in winter when the outdoor temperature is about minus 5°C. Put the bottle with water outside and wait for a few hours or overnight. But usually the weather condition is not suitable and we must cool the water indoors. The standard fridge or freezer is not convenient; the temperature in a fridge is too high and in the freezer too low for successful supercooling. It is not necessary to use distilled water.

Reliable cooling can be achieved using an ice-water-salt mixture. It is good to work with more than one bottle together because in some cases the solidification starts spontaneously. To supercool three 500ml PET bottles we need about one kilogram of crushed ice mixed with half a liter of water. Salt is added while stirring continuously until a temperature of about minus 7°C is reached. When the initial temperature of water in the bottles is near to zero, it takes about 30 min to get a sufficient supercooling. When we have the possibility to measure

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[2] The mean thermal expansion coefficient of water and thermal expansion of PET has the same absolute value, but this is only a coincidence.

[3] This is a random selection from a larger number of experiments.

the temperature inside the bottles (which is necessary for the quantitative evaluation of the experiments described above anyway), we can recognize immediately when the unwanted spontaneous solidification starts: the temperature grows to freezing point rapidly and persists there for a long time.

The experiment must be conducted as fast as possible to limit warming from the ambient air. We should prepare all requisites in advance: measuring glass tube with coloured water bead, calorimeter vessel cooled to freezing point, bottle with room temperature water for melting the ice in the calorimeter, a very sensitive thermometer for measurement of the final temperature in the calorimeter.

At the beginning of the experiment we carefully take out the bottle from the cooling mixture. At that time the measuring glass tube should already be fixed to the bottle. We mark the position of the coloured water bead in the glass tube. Then we hit the table with the bottle to start solidification. We observe the shift of the water bead along the tube until its movement is stopped and mark the final position of it. As fast as possible we empty the created water-ice mixture from the bottle into the calorimeter. Whilst stirring continuously, we slowly add the room temperature water until all the ice is melted; the temperature gauge is immersed in the calorimeter all the time. At the end we read the final temperature t of the water. The mass of added room temperature water can be easily determined by weighing the empty calorimeter and the bottle with room temperature water before and after the experiment.

Conclusion

In this paper three possibilities for the determination of an amount of ice created in sudden solidification of the supercooled water are described.

1. Direct calculation from the calorimetric equation (3). This is the simplest way but its precision is limited by the inhomogeneous distribution of the temperature of supercooled water which limits the accuracy of the measurement of the real degree of supercooling.

2. Calorimetric method is based on the measurement of the heat consumption which is necessary for melting the ice, Eq. (5) or (6). In this method the heat exchange brings about a systematic error which decreases the measured mass of ice.

3. Measurement of volume increase in solidification. In this method a few systematic errors affect the measured value but they can be easily evaluated and successfully suppressed. Thus this method provides the most reliable way for measurement of the amount of solidified ice.

None of these methods requires any special experimental equipment and can be easily conducted at secondary school. Also, the theoretical background of the experimental method including the systematic error suppression does not exceed the level of secondary school physics but it is not trivial. Thus these experiments can be interesting problems for student projects or other individual student's experimental work.

References

[1] J Black, The Supposed Effect of Boiling upon Water, in Disposing It to Freeze More Readily, Ascertained by Experiments. *Phil. Trans. 65, (1775) 124-128.*

[2] J Güémez, C Fiolhais and M Fiolhais, Reproducing Black's experiments:freezing point depression and supercooling of water *Eur. J. Phys*. 23 (2002) 83–91.

[3] See for instance http://www1.lsbu.ac.uk/water/anmlies.html.