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Hypercooling Temperature of Water is About 100 K Higher than Calculated Before

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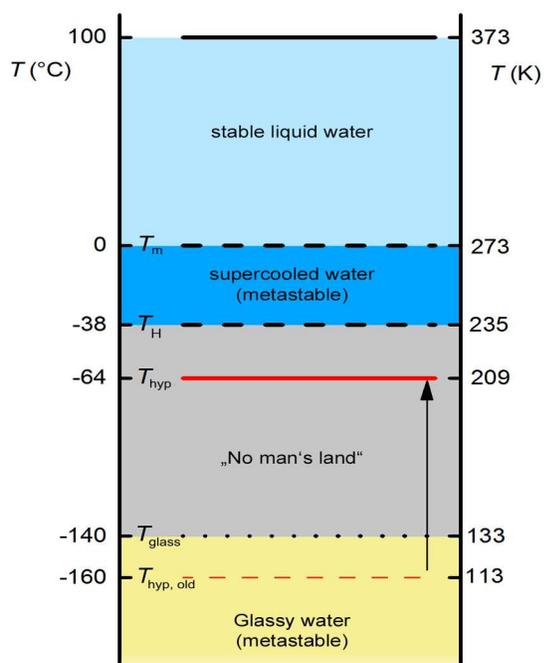
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Abstract

For deeply supercooled liquids the transition from a two-stage freezing process to complete solidification in just one freezing step occurs at the *hypercooling temperature*, a term which seems to be almost unknown in water research; to our knowledge, it has only been mentioned by Dolan et al. for high pressure ice. The reason for the absence of this expression may be that the best estimate to be found in the literature for the hypercooling temperature of water is about -160°C (113 K). This temperature is far below the limit of experimentally realizable degrees of supercooling near -40°C (233 K), which marks the homogeneous nucleation temperature T_H of common pure water; in fact, it is even below the glass transition temperature (133 K). Here we show that, surprisingly, a more thorough analysis taking into account the temperature dependence

of the heat capacities of water and ice as well as of the enthalpy of freezing shows that the hypercooling temperature of water is about -64°C or 209 K — almost 100 K higher than estimated before. One of the most exciting consequences is that existing experiments are already able to reach these degrees of supercooling and it is our prediction that a transition in the freezing behavior occurs at these temperatures.

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3 Usually, supercooled water freezes in two stages: a very fast first stage, in which homogeneous
4 dendritic ice is formed, and a second about 100 to 1000 times slower one, during which the
5 remaining liquid water solidifies entirely within the dendritic network; in the course of this
6 second phase, the partially frozen drop may burst due to the density difference of liquid and solid.
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12 ^{1,2,3,4} The occurrence of this two-stage process is caused by the enthalpy of freezing which can
13 neither be released completely via the surface for droplets bigger than about one cubic
14 micrometer nor be taken up by the newly formed ice. ⁵ Although this fact has been known for
15 water for many decades, it is rarely considered in the manifold research areas of water/ice
16 systems such as atmospheric physics and chemistry or adjacent scientific areas. ⁶ In material
17 sciences, such as metallurgy, it is well established that melts can be highly supercooled to a
18 degree that the enthalpy of freezing can be taken up completely by the solid forming during the
19 phase transition (without heat transfer through the surface) so that here the freezing proceeds in a
20 single stage. ^{7,8,9} This situation is in sharp contrast to the area of water research where, according
21 to our careful study of the literature, the term hypercooling is mentioned only once, namely, by
22 Dolan et al. in context with water investigated under high pressure. ¹⁰

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38 Based on the heat balance Equation 1, ¹ the portion of ice x formed in the first adiabatic
39 freezing stage can be obtained by a comparison of the heat capacities of the liquid $c_{p,l}$ and the
40 solid phase $c_{p,s}$ with the enthalpy of freezing, which is the negative of the enthalpy of fusion
41 ΔH_m , as a function of the degree of supercooling $\Delta T = T_m - T$, if temperature independent values
42 are assumed:

$$x \cdot \Delta H_m = \Delta T \cdot (x \cdot c_{p,s} + (1 - x) \cdot c_{p,l}). \quad (1)$$

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54 Imposing the condition of hypercooling, i.e., of 100% ice being formed in the adiabatic
55 freezing stage ($x = 1$), Equation 1 can be written as: ^{1,2}

$$\Delta H_m = \Delta T_{hyp} \cdot c_{p,s} \quad (2)$$

which leads to the conclusion that $\Delta T_{hyp} = T_m - T_{hyp} = \Delta H_m / c_{p,s}$.

With this approximation Pruppacher predicted the hypercooling temperature T_{hyp} of water to be 113 K (henceforth referred to as $T_{hyp,old}$) marking the highest temperature at which the entire latent heat released in the freezing process can be stored in the newly formed solid phase.¹ The simple heat balance Equations 1 and 2 use constant values for the enthalpy of fusion $\Delta H_m = 6006$ J mol⁻¹ as well as for the heat capacity of the ice $c_{p,s} = 37.8$ J mol⁻¹ K⁻¹ that are valid at the melting temperature T_m for the entire temperature range, although both quantities do depend on the temperature.¹ As the estimated hypercooling temperature of Pruppacher is about 160 K ($= \Delta T_{hyp}$) lower than T_m , about 120 K lower than the homogeneous nucleation temperature T_H of water, and even significantly below the glass transition temperature $T_{glass} = 133$ K,^{11,12} one would surely assume that the hypercooling temperature cannot be reached, neither experimentally nor in nature, even if a revised estimate of T_{hyp} was obtained by considering the variations of the thermodynamic quantities with temperature. This expectation, however, proves to be incorrect as we will demonstrate by performing a more accurate calculation which leads to a *much* higher hypercooling temperature lying in the upper region of "No man's land" (Figure 1).¹¹ The hypercooling temperature T_{hyp} is determined correctly by the condition that the temperature dependent quantities $\Delta H_m(T)$ and $\int_T^{T_m} c_{p,s}(T) dT$ become equal at T_{hyp}

$$\Delta H_m(T_{hyp}) = \int_{T_{hyp}}^{T_m} c_{p,s}(T) dT \quad (3a)$$

Equation 3a thus expresses the fact that, at the hypercooling temperature, the enthalpy of freezing released upon solidification of the entire sample is used entirely to heat the newly formed solid to the equilibrium melting temperature. Equivalently, but reversing cause and

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3 action, T_{hyp} can be obtained in the imaginary process of first heating the supercooled liquid to T_m
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5 and subsequently providing the enthalpy required for this process by releasing the enthalpy of
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7 freezing at T_m
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$$\Delta H_m(T_m) = \int_{T_{hyp}}^{T_m} c_{p,l}(T) dT \quad (3b)$$

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14 The results for T_{hyp} obtained from Equations 3a and 3b are, of course, identical because
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16 the enthalpy is a state function. While the right-hand side of Equation 3a is easily obtained from
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18 literature data for the well-studied heat capacity of water ice, see Equation 5 below, the left-hand
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20 side requires knowledge of the enthalpy of fusion as a function of temperature. To obtain this
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22 quantity, we employ Kirchhoff's law:
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$$\Delta H_m(T) = \Delta H_m(T_m) - \int_T^{T_m} \Delta c_p(T) dT \quad (4)$$

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28 with $\Delta c_p(T) = c_{p,l}(T) - c_{p,s}(T)$, implying that the temperature-dependent heat capacities of both ice
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30 and liquid water are required for the calculation. The heat capacity of hexagonal ice I_h has been
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32 measured in a wide range of temperatures. Here, we represent the data for 180–273 K compiled
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34 by Feistel and Wagner as:^{13,14}
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$$c_{p,s}(T) = 2.1596 \text{ J mol}^{-1}\text{K}^{-1} + 0.13016 \text{ J mol}^{-1}\text{K}^{-2} \cdot T \quad (5)$$

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44 Experimental data for the heat capacity of supercooled liquid water have only been obtained
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46 above the homogeneous freezing temperature. At this point, the essential work of Murphy and
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48 Koop comes into play.¹⁵ They extrapolated the known experimental data for the heat capacity of
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50 supercooled water (236–273 K) of Archer and Carter as well as of Angell et al. by modifying the
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52 predicted data of Starr et al. for lower temperatures.^{15,16,17} Here, we use the nominal values of
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Murphy and Koop for an integrable fit which covers the entire temperature range from 180–273 K (Figure 2, solid red line):¹⁵

$$c_{p,l}(T) = (a_0 + a_1 \cdot T) \cdot \left(a_2 + \frac{a_3}{(T-a_4)^2 + a_5} \right) \quad (6)$$

with the following parameters: $a_0 = -227.52 \text{ J mol}^{-1} \text{ K}^{-1}$, $a_1 = 1.962 \text{ J mol}^{-1} \text{ K}^{-2}$, $a_2 = 0.2218$, $a_3 = 79.929 \text{ K}^2$, $a_4 = 222.222 \text{ K}$, $a_5 = 209.653 \text{ K}^2$. At low temperatures, the interpolation of Murphy and Koop is designed to reproduce the thermodynamic properties of amorphous solid water (ASW, also referred to as “glassy” water). Since the publication of their correlation, new data for the properties of ASW have become available: Chonde et al. were able to measure the heat capacity of ASW at temperatures as high as 205 K using ultra-fast microcalorimetry.¹⁸ This fast method allowed them to extend their measurements to temperatures that are more than 50 K higher than the 150 K at which Speedy et al. obtained their data for the enthalpy of crystallization,¹⁹ upon which the correlation of Murphy and Koop is based. These new and higher enthalpies of crystallization were supported by data reported by Sepulveda et al..²⁰ Furthermore, very recent measurements of the vapor pressure of ASW in comparison to ice I_h by Nachbar et al.,²¹ which agree with earlier data by Shilling et al.,²² provide the required free-energy difference between ASW and hexagonal ice at 205 K. We checked that the new set of thermodynamic data at 205 K is consistent with the fit of Murphy and Koop, which was based on 150 K as a reference temperature for ASW, and found good agreement within the quoted uncertainties. A revision of the correlation of Murphy and Koop is, therefore, not required.

In the next step, Equations 5 and 6 are inserted into Equation 4 to calculate the temperature-dependent enthalpy of fusion $H_m(T)$ (Figure 3, solid red line) which equals the heat storable in solid water ice (Figure 3, solid blue line) at 209 K, our best estimate of the

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3 hypercooling temperature. Our calculation of the enthalpy of fusion leads to the same results as
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5 the one presented by Koop and Murray²³ with the difference that their polynomial fit is only
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7 consistent with the heat-capacity data for liquid water suggested by Murphy and Koop¹⁵ down to
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9 230 K and, therefore, should only be applied above this temperature, whereas our fit based on
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11 Equation 6 covers the entire temperature range of interest down to 180 K.^{15,23} In principle, the
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13 hypercooling temperature could be also calculated without knowledge of the heat capacity of the
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15 solid phase via Equation 3b. The boundaries of the shaded region in Figure 3 mark the upper and
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17 lower limits of the enthalpy of fusion, which take into account the uncertainties that Murphy and
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19 Koop assign to their extrapolation of $c_{p,l}$ (Figure 2);¹⁵ these extremes establish an upper limit of
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21 T_{hyp} of about 216 K and a lower limit of 157 K.
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27 For temperatures above 240 K the experimental results of calorimetric measurements of
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29 $\Delta H_m(T)$ are considerably smaller than the calculated data, cf. black dots and white squares in
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31 Figure 3 (up to 1 kJ mol⁻¹ which means 20%).^{24,25,26}, which indicates the tendency to an even
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33 higher hypercooling temperature. The authors of the respective studies explain this discrepancy
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35 with the occurrence of metastable forms of ice (according to Ostwald's step rule),^{24,25} which is in
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37 agreement with the results of molecular dynamics (MD) simulations and Raman spectroscopy.
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39 Other authors predict the formation of stacking disordered ice I_{sd} or ice I_0 from supercooled
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41 water.^{27,28,29,30,31,32,33,34,35,22}
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46 If stacking disordered ice I_{sd} was formed, the hypercooling temperature would be shifted
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48 downward by about 2 K as marked by the crossing point of the red and blue dash-dotted curves in
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50 Figure 3,^{22,36} which is caused by the lower enthalpy of fusion of ice I_{sd} (the difference being
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52 about 155 J mol⁻¹ as suggested by Koop and Murray) and the lower melting point of 266 K.²³ In
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54 any case, the new calculated hypercooling temperatures of $T_{hyp} = 209$ K for the formation ice I_h
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3 and 207 K for the case that ice I_{sd} is formed are about 100 K higher than the best known value up
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5 to now and, unlike the previous estimate by Pruppacher,¹ they are not below the glass transition
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7 temperature T_{glass} , but rather close to the homogenous nucleation temperature T_H . This finding
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9 leads to the conclusion that several research groups could already have realized hypercooled
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11 water experimentally.^{37,38,39}
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15 On the one hand, Bartell and Huang as well as Manka et al. used laval nozzles to get very high
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17 cooling rates to supercool water nanodroplets to 200 K and 202 K respectively, which is just
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19 below the calculated hypercooling temperature for the bulk phase of 209 K.^{37,38} On the other
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21 hand, Xu et al. succeeded in reaching even higher degrees of supercooling at temperatures around
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23 180 K by means of a completely different method, applying a nanosecond infrared laser for
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25 pulsed-heating of cold ice.³⁹ As small droplets are affected by pronounced effects of the surface
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27 tension, which modify the physical properties due to the enhanced vapor pressure (for a 100 nm
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29 droplet the melting point is lowered by 1 K) via the Kelvin equation and lead to an enhanced
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31 inner pressure described by the Young-Laplace equation, the hypercooling temperature should be
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33 shifted for smaller droplets below 100 nm. The effect of enhanced pressure is mentioned by
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35 Dolan et al. who describe liquid water below the hypercooling temperature at a pressure of 7
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37 GPa.¹⁰ A detailed study of the influence of the Kelvin effect on the freezing behavior of small
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39 droplets will be part of a future publication. Nevertheless, these observations show that the
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41 hypercooling temperature of water is not only a theoretical physical limit but, contrary to the
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43 current opinion, is experimentally achievable which could have important consequences in water
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45 research.
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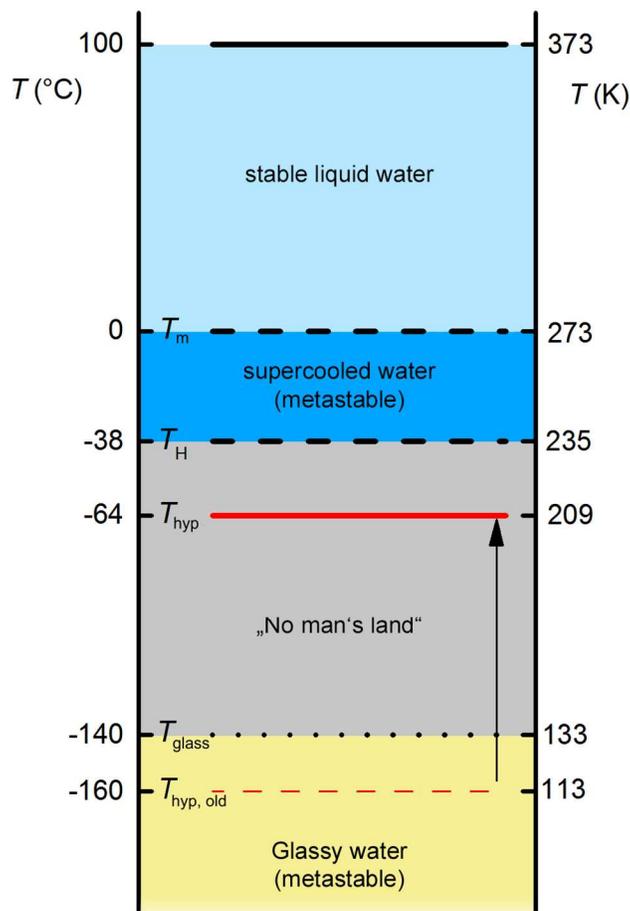


Figure 1: According to the new calculation, the hypercooling temperature T_{hyp} of water is shifted into the upper part of the "No man's land" region by taking the variations of the enthalpy of fusion and the heat capacities with temperature into account, --- $T_{hyp,old}$ according to Pruppachers's approximation (thin dashed red line), - T_{hyp} our new calculation (thick red line). The schematic illustration of the different regions has been adopted from Mishima and Stanley.¹¹

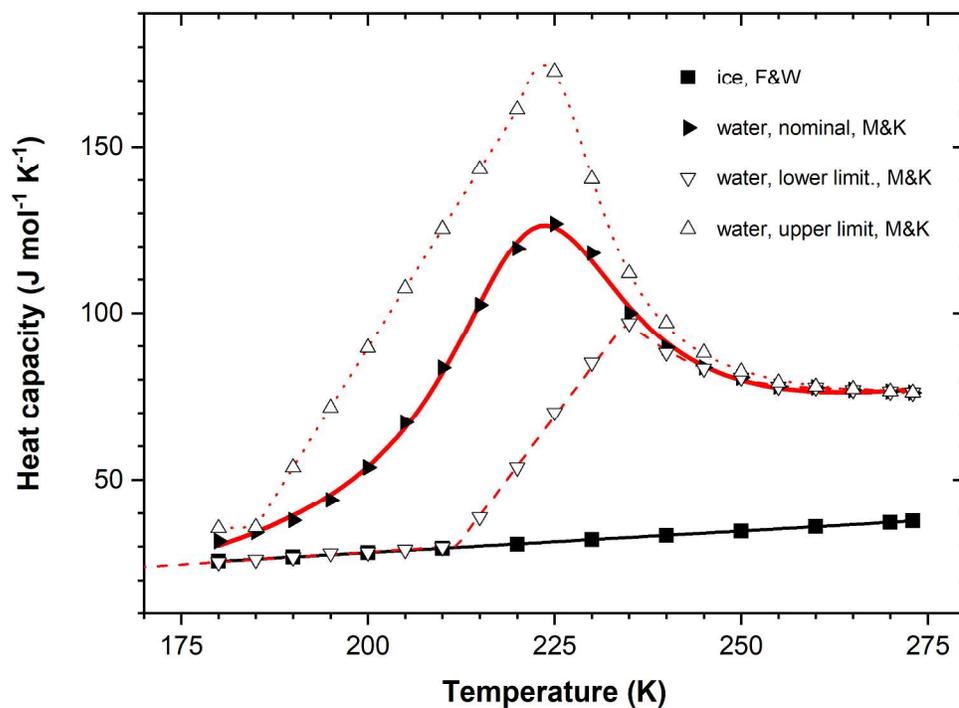


Figure 2: Heat capacities of liquid water based on Figure 6 of Ref. 18 (triangles, Murphy and Koop, M&K) and of ice I_h (squares, Feistel and Wagner, F&W).^{15,13} The solid red line represents an integrable fit (Equation 6) for the temperature range of 180–273 K. The dotted and dashed red lines indicate the uncertainties that Murphy and Koop assign to their extrapolation of the experimental heat-capacity data.

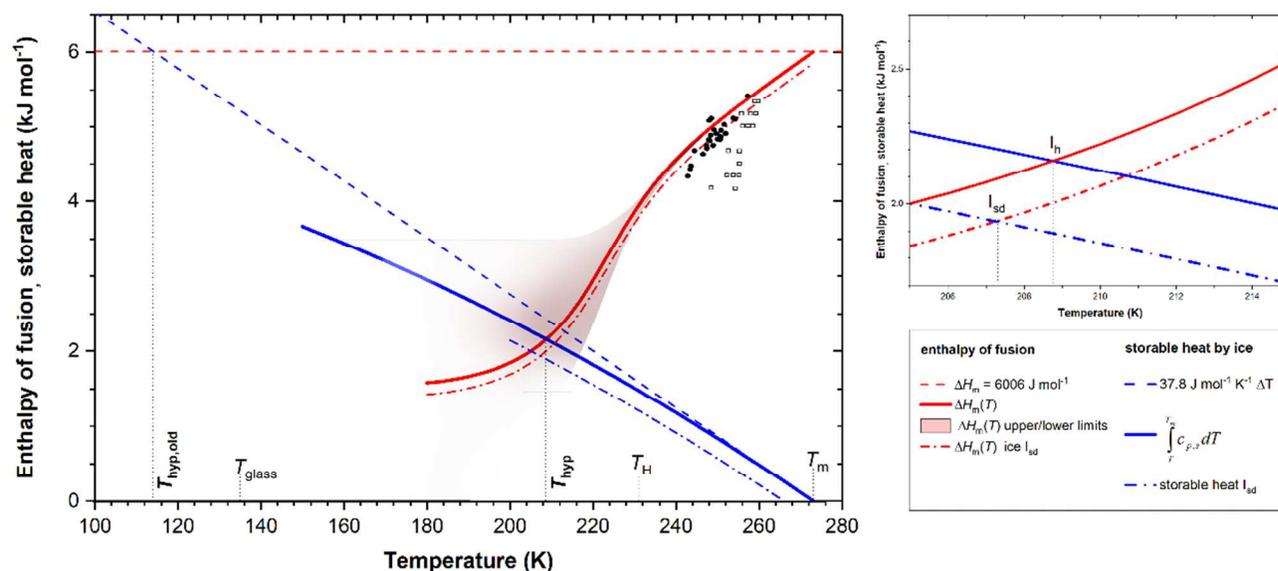


Figure 3: Hypercooling temperature of water: If the heat that can be stored in the ice (blue lines) is larger than the enthalpy of fusion released in the freezing process (red lines) at a given temperature, the water is *hypercooled*, compare Equation 3a. This means that the water can freeze in one single step in contrast to merely undercooled water which needs two freezing steps due to thermodynamic reasons. The new calculated hypercooling temperature T_{hyp} of hexagonal ice I_h (marked by the intersection of the solid lines) is 209 K, almost 100 K higher than the approximate limit of 113 K estimated by Pruppacher (marked by the crossing of the dashed lines, cf. Equation 2). For stacking discorded ice I_{sd} the hypercooling temperature is about 207 K due to the enthalpy of fusion being reduced by a constant value of 155 J mol^{-1} (red dash-dotted line) according to Koop and Murray.^{23,22} Note that the huge difference between "old" and "new" hypercooling temperature is mainly caused by the pronounced decrease of the enthalpy of fusion with temperature. The measured values of Cantrell et al. (white squares) and Bertolini et al. (black dots) are up to 20% smaller than the calculated values for the enthalpy of fusion,^{24,25} which could be an indication of an even higher hypercooling temperature if the ice formed is metastable.