

# Thermal Properties of Water in Restrictive Geometries

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Melting and freezing transitions are examples of cooperative phenomena. They are dramatic changes on account of their suddenness of occurrence, and because of the discontinuities that they cause in various intensive quantities (volume, heat capacity, viscosity, self-diffusion rate, etc.). These sharp changes come into existence only because of the presence of an enormous number of interacting molecular degrees of freedom. Normally melting and freezing are observed for matter in bulk, comprising roughly Avogadro's number ( $6.022 \times 10^{23}$ ) of molecules, and for all intents and purposes this can be reckoned as infinitely large.

However there are exceptional circumstances wherein melting and freezing are observed for much smaller aggregates of molecules. In the case of water it is possible to induce melting and freezing in sufficiently small systems that the phase transitions ought to exhibit modifications due to finite size effects. This might be expected to occur for fine droplets in aerosols, for some emulsions of water in oils, and for very small water clusters that can be made to form in polymeric solids (1,2). The phase transition modifications arise not only from the reduced number of molecular degrees of freedom *per se*, but also from the fact that a substantial portion of the material will be present in a boundary, or interfacial, region. One expects modifications in both equilibrium (transition "rounding") and kinetic (supercooling) behavior.

Droplets or clusters in the size range from microns downward are those expected to show measurable deviations from bulk equilibrium behavior. For the sake of quantitative orientation, Table I shows representative numbers of molecules contained in spherical droplets of water in this size range, and it also shows the fraction of those molecules within a typical molecular distance ( $5\text{\AA}$ ) of the surface.

The objective of this paper is to provide a theoretical framework for understanding the melting, freezing, and supercooling behavior of water in small clusters and droplets. Although attention will be focussed on spherical geometry, the basic ideas involved can be generalized to other shapes.

## HYDROGEN BOND PATTERNS IN WATER

Both ice and liquid water consist of space-filling networks of hydrogen bonds. That of the former is regular and static; that of the latter is irregular and mobile. The hydrogen bonds in ice are arranged so that each molecule participates in exactly four bonds, and the bonds are spatially disposed so as to form polygons with only even numbers of sides (hexagons, octagons, decagons, ...) (3). The random network in the liquid evidently contains polygons of both even and odd numbers of sides

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TABLE I. Contents of spherical water droplets.<sup>a</sup>

Cluster Diameter (microns)	3.00	1.00	0.30
Number of Water Molecules in Cluster	$4.73 \times 10^{11}$	$1.75 \times 10^{10}$	$4.73 \times 10^8$
Number of Molecules Within 5Å of Surface	$4.72 \times 10^8$	$5.25 \times 10^7$	$4.71 \times 10^6$
Fraction of Molecules Within 5Å of Surface	0.0010	0.0030	0.0100
Cluster Diameter (microns)	0.10	0.03	0.01
Number of Water Molecules in Cluster	$1.75 \times 10^7$	$4.73 \times 10^5$	$1.75 \times 10^4$
Number of Molecules Within 5Å of Surface	$5.20 \times 10^5$	$4.57 \times 10^4$	$4.74 \times 10^3$
Fraction of Molecules Within 5Å of Surface	0.0297	0.0966	0.2710

<sup>a</sup> The droplets are at 0 °C, and are presumed to possess the macroscopic liquid density up to the geometric surface.

intermixed (4); a variety of defect structures is present as well, including broken bonds and bifurcated hydrogen bonds. Thus the invariant fourfold coordination in ice is replaced upon melting by indefinite coordination that varies from one to five, and averages about 2.5 near the melting point (4). Needless to say, the hydrogen bonds that are present in liquid water are much more strained on the average than those in ice.

The famous density maximum in liquid water at 4 °C represents a balance point between two opposing tendencies. On the one hand there is the continuation of the process initiated at the melting point, namely conversion of bulky hydrogen bond structures to more compact forms (the negative volume of melting signifies this change). On the other hand there is present the natural thermal expansion of all liquids, which tends to accelerate in magnitude with increasing temperature. It is plausible to suppose that the first of these is associated with gradual disappearance in the liquid of unstrained polygonal and polyhedral bonding patterns, as they are replaced by highly strained and bond-broken arrangements that permit more efficient packing of molecules.

The volumetric properties of small water droplets or clusters can be measurably influenced by the significant fraction of material in the surface region (see Table I). The structural character of the hydrogen bond network in the bulk phase is certain to be modified in the interfacial region if the droplet has either a free surface or is in contact with hydrophobic material. Obviously more broken bonds (*i.e.*, unsatisfied bond positions) must be present. But additionally the organization of those bonds which are present, for example into polygons, will differ statistically from the situation deep beneath the surface. It is generally believed, on the basis of experimental observations, that the surface of ice roughly in the range  $-10^{\circ}\text{C}$  to  $0^{\circ}\text{C}$  is covered by a mobile "liquid-like" layer (3), which ought then to contain odd-sided polygons and bifurcated hydrogen bonds. In a crude sense, surfaces act to disrupt the natural order present in the bulk phase.

This last point leads to an interesting prediction concerning the volumetric behavior of liquid water droplets or clusters. Since their surface regions ought to be more disordered at any given temperature than their interiors, the temperature of minimum volume (maximum mean density) should be displaced below  $4^{\circ}\text{C}$ . The magnitude of this effect presumably would depend on the chemical character of the region outside the droplet or cluster, and is difficult to estimate with precision. However a crude estimate is possible by supposing the outer  $5\text{\AA}$  behaves as a "normal" nonaqueous liquid with thermal expansion  $10^{-3}/^{\circ}\text{C}$ , and the remainder as bulk water. Table II shows the resulting predictions for the temperatures of maximum mean density for the droplet sizes considered in Table I. The depressions are substantial for the smaller sizes.

TABLE II. Temperature of maximum mean density for spherical droplets of water.

Diameter, Microns	$T_{\text{max}}$ , $^{\circ}\text{C}$
$\infty$	3.98
3.00	3.92
1.00	3.80
0.30	3.36
0.10	2.13
0.03	-2.06
0.01	-12.88

## STATISTICAL MECHANICAL THEORY

It is mandatory to consider the underlying statistical mechanical formalism in order to systematize the preceding ideas. For this purpose we will examine the partition function for an  $N$ -molecule water cluster. The isothermal-isobaric ensemble is appropriate (5) since constant normal stress (denoted below by "pressure"  $p$ ) seems relevant to most cases of interest. The partition function for this ensemble,  $\Delta_N(\beta, p)$ ,

depends upon the inverse temperature parameter  $\beta = (k_B T)^{-1}$  and the external pressure  $p$ . We will presume that the droplet is constrained to spherical shape, though with variable radius. The connection to thermodynamics is established by the fact that

$$\ln \Delta_N = -\beta G, \quad (1)$$

where  $G$  is the Gibbs free energy.

An expression for  $\Delta_N$  in terms of molecular quantities is the following:

$$\Delta_N(\beta, p) = \Delta_N^{(0)} \langle \exp(-\beta\Theta) \rangle; \quad (2)$$

here  $\Delta_N^{(0)}$  is a normalizing factor that has no further importance in subsequent analysis, and  $\Theta$  is the sum of the potential energy  $\Phi$  for the water molecules and the pressure-volume product  $pV$ ,

$$\Theta = \Phi + pV. \quad (3)$$

The Boltzmann factor average in Eq. (2) is an *a priori* average over all  $N$  molecule orientations and positions within the spherical cluster volume  $V$ , and over  $V$  with a suitable upper limit.

The evaluation of  $\Delta_N$  in Eq. (2) would be a formidable task even if  $\Phi$  were known in all detail (unfortunately it is not). The reason is that the required average entails a multiple integral of order  $6N$ , since there are three translational and three rotational degrees of freedom per molecule. Table I shows that  $N$  is still huge even for very small clusters.

In spite of this difficulty we can understand the behavior of  $\Delta_N$  to some extent by classifying molecular configurations according to a small number of independent parameters. We choose two such parameters, the quantity  $\Theta$  already introduced and a structural order parameter  $\Psi$ . The latter is intended as a measure of the ice-like order present. Conceivably we could take  $\Psi$  to equal the number of hydrogen-bond hexagons present, however this would not distinguish ice *Ih* from the cubic modification *Ic* that is presumably unstable under conditions of interest here (6). Alternatively and more appropriately  $\Psi$  could represent the number of bonded bicyclic octamers (see Figure 1), that are present in ice *Ih* but *not* in ice *Ic*. For the remainder of this analysis we will use this second choice. By accounting for all the distinct (and overlapping) ways that octamers can be traced out on the perfect ice lattice, we find that the maximum value of  $\Psi$  is  $N/2$ , to within terms of order  $N^{2/3}$ .

Once the decision has been made to classify configurations according to their  $\Theta$  and  $\Psi$  values, we can write the average in Eq. (2) in a formally simple manner:

$$\begin{aligned} \langle \exp(-\beta\Theta) \rangle &= K^{-1} \iint \exp[w(\Theta, \Psi) - \beta\Theta] d\Theta d\Psi, \\ K &= \iint \exp[w(\Theta, \Psi)] d\Theta d\Psi. \end{aligned} \quad (4)$$

In this expression  $\exp(w)$  stands for the configuration space weight to be assigned to the given  $\Theta, \Psi$  pair.  $K$  is a temperature-independent normalization factor.

The discontinuous liquid-solid transition automatically emerges from the first of Eqs. (4) in the large- $N$  limit. This can be demonstrated by using "peak integration" to evaluate that first integral. This approximation, which becomes increasingly accurate as  $N$  increases, exploits the fact that dominant contributions to that integral arise from regions at which the quantity

$$Y \equiv w(\Theta, \Psi) - \beta\Theta \quad (5)$$

is at a maximum in the two-dimensional  $\Theta, \Psi$  space. By making a local Gaussian approximation for each such maximum we conclude that

$$\langle \exp(-\beta\Theta) \rangle = 2K^{-1} \sum_j (Y_{j11}Y_{j22})^{-1/2} \exp(Y_j). \quad (6)$$

Here  $j$  indexes the maxima, and  $Y_j$  stands for the value of  $Y$  at maximum  $j$ . The quantities  $Y_{j11}$  and  $Y_{j22}$  are the second partial derivatives of  $Y$  at  $j$  along the two principal directions of curvature there.

On physical grounds we expect only two relevant maxima to contribute substantially to Eq. (6), at least when the temperature is around 0 °C and pressure around 1 bar. These two correspond respectively to hexagonal ice and to liquid water. In this temperature range one should keep in mind that  $\Theta$  is dominated strongly by the potential energy part  $\Theta$ ;  $pV$  is far smaller in magnitude. For the "ice" maximum  $\Theta$  is low (many well-formed hydrogen bonds) while  $\Psi$  is high (many characteristic ice-like structures). By contrast the "liquid" maximum will display higher  $\Theta$  (fewer and more strained hydrogen bonds) and lower  $\Psi$  (most bonding patterns not ice-like).

The suddenness of the first-order melting or freezing arises from the fact that the  $Y_j$  are of order  $N$ . It is clear that after exponentiation one of the terms in Eq. (6) will dominate the other almost totally, except in a narrow switch-over temperature range around the transition point. This switch-over range is expected to be proportional in asymptotic width to  $N^{-1}$ , and represents the extent of smearing of the transition due to finite system size. Latent heat is absorbed or discharged over this finite temperature interval if in fact nucleation can occur.

It will be profitable to examine a schematic diagram of the level curves of  $Y$ , for  $\beta$  chosen to make the two maxima equal in magnitude (in the infinite- $N$  limit this will be precisely the thermodynamic transition point). Such a diagram appears in Figure 2. This Figure shows that between the two equal-altitude maxima there will be a saddle point along a ridge line. When  $N$  is reasonably large this ridge line will correspond to side-by-side coexistence of liquid-like and ice-like regions within the droplet, the relative proportions of which determine position along the ridge line. Since an interface must exist between the regions the ridge line will lie below the maxima by an amount of order  $N^{2/3}$ .

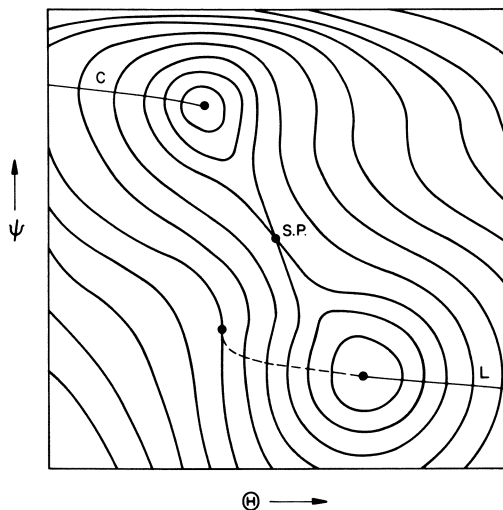
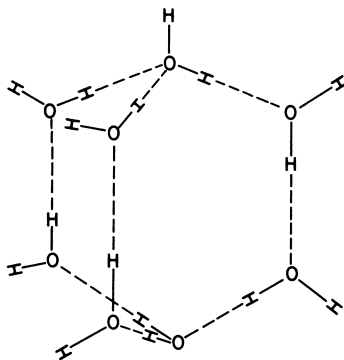
At the temperature for which Figure 2 is shown the two maxima are the positions of the  $Y_j$  that are to be inserted in Eq. (6). These may generically be designated by  $Y_L$  and  $Y_C$ , for "liquid" and "crystal", respectively. They are the positions of simultaneous contact for a horizontal plane resting atop the  $Y(\Theta, \Psi)$  surface.

As temperature varies,  $Y_L$  and  $Y_C$  will shift from the locations of the maxima shown in Figure 2. The shifts can be identified with points of rolling contact for the initially horizontal plane as it is tipped so as to remain parallel to the  $\Psi$  axis. This rolling constraint arises from the fact that  $\beta$  multiplies only  $\Theta$  in  $Y$  in the first integral of Eq. (4). The  $\Theta$ -direction slope of the rolling plane is just  $\Delta\beta$ , the change in  $\beta$  from its initial value at the horizontal orientation.

Under the supposition that  $Y(\Theta, \Psi)$  is continuous and at least twice differentiable in its two variables, the loci of rolling contact (one through each maximum in Figure 2) will be at least piecewise continuous curves. These curves trace out the dominant  $\Theta, \Psi$  "structure" for the liquid and solid phases, and they are indicated in Figure 2 as full curves in the respective ranges of thermodynamic stability.

The relative positions of the two maxima on the  $Y$  surface will change with  $N$ , even after accounting for the fact that  $\Psi$  and  $\Theta$  are extensive quantities in the large- $N$  limit. The presence of the structure-disrupting surface has a greater influence on an ice phase than on a liquid phase. As  $N$  declines,  $\Psi/N$  decreases and  $\Theta/N$  increases for both maxima, but the changes are larger for ice than for liquid. Further-

**Figure 1.** Bicyclic octamer structure, a pattern of hydrogen bonding that appears exclusively ice Ih. Several isomers are possible, depending on the disposition of hydrogens along the given linear hydrogen bonds.



**Figure 2.** Level curves for  $Y$  at the melting temperature (maxima at equal altitudes). Curves  $C$  and  $L$  are loci of rolling contact for a plane parallel to the  $\psi$  axis. The dotted portion of the  $L$  curve corresponds to supercooled liquid, and it ends at a point with vertical tangent.

more these shifts, if viewed at constant  $\beta$ , will be associated with a change of relative altitude of those maxima. This latter effect causes the previously mentioned broadening of the reversible thermodynamic transition with decreasing  $N$  to be accompanied by a shift to lower temperature.

## SUPERCOOLING

Nucleating the crystal phase from liquid cooled just below the thermodynamic freezing point can kinetically be especially difficult in small clusters. This stems partly from the fact that impurity "seeds" are less likely to be present in any given cluster, and partly from the proportionality of homogeneous nucleation rates to the volume of the system. Consequently supercooling becomes the rule rather than the exception, and this fact has been useful in laboratory studies of supercooled water (7). It should be stressed that a range of  $N$  values evidently exists which on the one hand is small enough to prevent nucleation, while on the other hand it is large enough so that the intensive properties observed for the supercooled water are essentially independent of system size.

Considering this situation it is thus useful in Figure 2 to continue the rolling loci through the respective maxima to map out metastable phase extensions. In principle this is just as possible for  $Y_C$  as for  $Y_L$  though melting of a crystal usually is immediately initiated at its already amorphous surface. [A water inclusion in the interior of an AgI crystal, or some other epitaxial structure-promoter, might provide an exception.] The metastable extension for the liquid is indicated in Figure 2 as a dashed curve.

The differential geometry of our constrained rolling contact demands that the contact loci cross the level curves only at points where the latter have tangents parallel to the  $\Psi$  axis. It is important to recognize that this requirement can lead to sudden disappearance of a locus. In mathematical terms the locus can suffer a "catastrophe", with an endpoint that itself has a vertical tangent. Such a catastrophic endpoint hence would manifest a diverging rate of change with temperature of the concentration of ice-like structural elements measured by  $\Psi$ .

The possible existence of an endpoint for the supercooled liquid locus is particularly interesting in view of the experiments of Angell and coworkers (7,8,9,10). They find that pure water at ordinary pressures (even very finely dispersed) cannot apparently be supercooled below about  $-40^\circ\text{C}$ , and that virtually all physical properties manifest an impending "lambda anomaly" at  $T_s \cong -45^\circ\text{C}$ . The most striking features of this anomaly are the apparent divergences to infinity of isothermal compressibility, constant-pressure heat capacity, thermal expansion, and viscosity. We now seem to have in hand a qualitative basis for explaining these observations.

The supercooled liquid catastrophe, if it exists, would necessarily be associated with diverging fluctuations in the structural order parameter  $\Psi$ . This stems from the fact that the  $Y$  surface develops a vanishing curvature in the  $\Psi$  direction as this endpoint is approached. Because the bicyclic octamer elements are bulky, fluctuations in their concentration amount to density fluctuations. Diverging density fluctuations then imply diverging isothermal compressibility. Furthermore the infinite slope of the metastable liquid locus at its endpoint implies the divergence of thermal expansion. Potential energy fluctuations remain essentially normal, so constant-volume heat capacity remains small. But the volumetric divergence creates an unbounded constant-pressure heat capacity.

Thus far we have seen that differential geometry of the  $Y(\Theta, \Psi)$  surface *can* produce a metastable liquid catastrophe, not that it *must*. Demonstration of the latter

will have to invoke the special character of the interactions in water, specifically the strong directionality of hydrogen bonding which produces tetrahedral coordination.

The key observation seems to be that the structure-measuring octamer units ought to experience a mean attraction for one another in the liquid medium. They are in fact geometrically suited to link up through directed hydrogen bonds, and indeed it is so that the extended lattice of ice Ih can be entirely broken into bicyclic octamer units (11). In addition an isolated octamer unit embedded in a locale of strained and broken bonds would be in great jeopardy, for those neighboring defects would exert torques and forces that would distort it severely and often past the point where it would continue to qualify for inclusion in  $\Psi$ . The net result is a statistical tendency of the surviving octameric units to aggregate, and the lower the temperature the greater the degree of aggregation.

This thermally-sensitive sorting out process will not segregate bicyclic octamers alone but will also include a few other types of well-bonded (and bulky!) species. Figure 3 shows two which qualify, each fused to an octamer without mutual distortion. The first includes pentagons; the second is a structure which appears in cubic ice. Because bonding arrangements such as these exist one must keep in mind that the strongly bonded aggregates are not automatically ice Ih fragments.

The aggregation or clumping of bulky and well-bonded structures is clearly going to be a cooperative process, and as such it will produce long-range coarsening of the texture of the fluid medium. This process is entirely analogous to that which creates long-range fluctuations at the critical point of a condensing gas. In the present case it will produce divergent  $\Psi$  fluctuations as already discussed above. On structural grounds it appears most natural for the aggregates to grow in a dendritic, rather than globular, fashion.

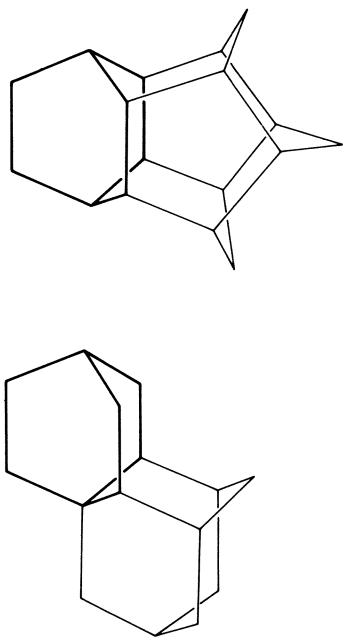
Just as in that analogous case of conventional critical fluctuations it is useful to introduce a correlation length  $\xi$  for the scale of inhomogeneity (12). In the present context  $\xi$  gives an average linear dimension for regions of anomalously high (or low) concentration of the structural units defining  $\Psi$ . As temperature declines for the supercooled liquid  $\xi$  increases, becoming infinite at  $T_s$ . Since these structural fluctuations are also density fluctuations it should be possible *in principle* to detect them and to measure their size  $\xi$  by light scattering or small-angle X-ray scattering experiments on strongly supercooled water. *In practice* these experiments would probably be very difficult.

The presence of strongly bonded regions, presumably composed of low-mobility molecules, obviously will inhibit hydrodynamic flow just as polymer dissolved in low-molecular-weight solvent does. Furthermore this effect will amplify as temperature declines. Thus it is not surprising that viscosity should experimentally diverge at  $T_s$ .

It is in the nature of random mixing statistics for the various strongly-bonded units in a low-density fluctuation region that several bicyclic octamers would occasionally link up to form a larger fragment of ice Ih. Such events become more and more likely in a given amount of supercooled liquid as temperature declines toward  $T_s$ . These multiple octamer structures are the most likely precursors of a nucleation event. Thus the supercooled liquid contains literally the seeds of its own destruction. This observation rationalizes the inability experimentally to supercool pure water below about  $-40^\circ\text{C}$  without spontaneous freezing. The only way to avoid this fate seems to be to use much smaller clusters and high cooling rates; perhaps condensing clusters within thin film polymeric media might be a suitable preparative technique which would permit the required subsequent rapid cooling.

The droplet size range for convenient observations of supercooling





*Figure 3. Bonding of bicyclic octamer units (heavy lines) to unstrained structures that do not occur in ice Ih. Oxygen atoms occur at vertices, and hydrogen bonds between water molecules are illustrated only schematically by lines. In the lower part of the diagram the octamer is fused to a structure occurring in ice Ic.*

anomalies was mentioned earlier. Unfortunately this range shrinks as the temperature of measurement declines toward  $T_3$ . Firstly, the rapid increase in homogeneous nucleation rate as temperature decreases places ever more stringent upper limits on droplet size. Secondly, the correlation length  $\xi$  must remain small compared to droplet diameter to maintain size-independence of intensive properties; but this causes the minimum permissible size to increase as  $T_3$  is approached from above. The situation seems inexorably to draw a veil of unobservability about the lambda anomaly at  $T_3$ , while still permitting the careful experimentalist to infer its properties by extrapolation.

## CONCLUSIONS

It is appropriate to end this theoretical discourse with a statement about the future role of computer simulation studies, which have much to offer this field. Pure water has been the object of intense study by this approach and a lot has been learned (4,13). More recently molecular dynamics computer simulation has turned to the modelling of alkanes and polymers (14,15). It seems natural and inevitable to combine the two specialties to illuminate molecular motions and structure for water droplets in alkane or polymeric hosts.

Thus far the  $N$  values feasible in digital computer simulation has fallen below those shown in Table I. The largest number that has been used to date is 1728 (13). However rapid advances in computer technology, including especially parallel processing capabilities, are likely to increase this number by at least an order of magnitude. That increase would cause overlap with the smallest cluster size considered in Table I.

Specific polyhedral structures such as those in Figures 1 and 3 cannot be detected in the liquid phase by any known experimental method. However a digital computer can be instructed to identify these patterns in the course of a simulation study. The mean concentration of bicyclic octamer units could thus be determined at any given temperature, along with their tendency to aggregate in regions whose mean size  $\xi$  could also be determined.

Studies of this sort could provide vital quantitative underpinning for the qualitative ideas presented here. The resulting expansion of knowledge ought to go far toward completing our understanding of melting and freezing in water, of its supercooled state, and of its behavior in small clusters.

## ABSTRACT

When water is finely dispersed as an aerosol, an emulsion, or as small clusters in polymeric host media, its thermal behavior can deviate significantly from that exhibited by bulk water. The reasons for these deviations are examined, and a statistical-mechanical approach for their study is proposed. A rough estimate is obtained for the depression of the temperature of maximum mean density for small spherical droplets. An explanation is advanced (in terms of specific structural fluctuations) for the singular behavior of strongly supercooled water that has been observed in emulsions near  $-40^\circ\text{C}$  by Angell and collaborators.

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