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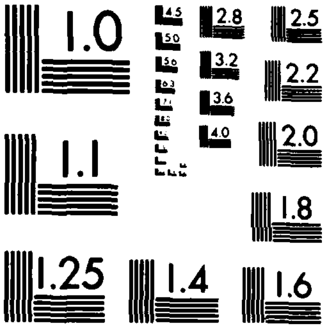

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SUPERCOOLED WATER

by

C. A. Angell

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Department of Chemistry
West Lafayette, IN 47907

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In response to an invitation from Annual Reviews of Physical Chemistry, recent progress in defining and unravelling the anomalies of supercooled water and their origin has been reviewed. Some of the most useful new results have come from binary solution studies. The field is presently in an interesting position with many of the most important properties now measured with acceptable precision and several noncomplimentary theories in circulation to explain them.

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C. A. Angell
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907
(317)494-5256

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SUPERCOOLED WATER

C. A. Angell
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Studies of the supercooling phenomenon in water are hardly a new activity, the first review having been published in 1775.(1) However, it is only in the past decade that a high level of activity, directed particularly at the physical properties of water in the supercooled regime, has been manifested. Apart from the obvious motivation of seeking data on this important liquid over the maximum range of conditions, this activity has been stimulated by the recognition that, as temperature is decreased, certain thermodynamic and transport properties appear to be diverging as at a critical point. This unexpected characteristic has naturally led to an intense curiosity as to the nature of the cooperative phenomenon involved and has promoted an increasing number of experimental and theoretical studies since the first evidence was presented. The position of the 'field' at the moment is an interesting one(2) with many of the fundamental properties now determined with acceptable precision (given the difficulties of performing measurements under conditions of metastability, with the requirement of small sample techniques that this implies) and several non-complimentary theoretical models in circulation to explain them.

Since this is the first review of this subject area to appear in ARPC, we will give some coverage to the earlier, and more scattered studies before developing the subject systematically to its current position.

THE NORMAL LIMIT OF SUPERCOOLING, AND THE POSSIBILITY OF VITRIFICATION

Although the principal interest in the supercooling of water lies in the extraordinary temperature dependences manifested in its physical properties as temperature decreases below 0°C, these measurements can only be performed while the sample remains free from nuclei of the crystalline phase which, once present, will necessarily terminate the measurements in progress. Hence we must first discuss those factors which determine where in temperature a given sample will convert to the stable phase.

In bulk samples the mechanism of generation of the first element of the crystalline phase is almost always heterogeneous in character, i.e., the initial crystal commences to grow on the surface of some solid impurity present in suspension or at the walls of the containing vessel. The heterogeneous mechanism short-circuits the needs for a large free energy fluctuation sufficient to overcome the difference between the free energy per mole of microcrystals of the order 10–20 Å in diameter, and that of the macroscopic crystalline phase which is in equilibrium with bulk water at 0°C. In extremely clean water, nucleation is much less probable hence supercooling more extensive.

Meteorologists and rainmakers have a great natural interest in the efficiency of various impurities in causing the nucleation of supercooled water droplets, since these constitute the substance of high level clouds and their crystallization is often the essential precursor step to the development of raindrops. Much of the early work on crystallization of supercooled water has therefore come from meteorologists. This subject, and the work preceding 1962 is the subject of detailed exposition by Mason in his book Clouds, Rain, and Rainmaking.(3) Important contributions were made by Biggs,(4) Mossop(5) and Mason *et al*.(3) who performed systematic measurements on water samples of different volumes contaminated by controlled quantities of different solid materials, and established more clearly than hitherto a logarithmic relationship between the volume of the sample under study and the temperature to which it could be supercooled before crystallization occurred. The relationship has a simple statistical basis in the probability that the sample under study will contain a seed of sufficient potency to allow a nucleus-producing fluctuation to occur in the 'standard' time of observation. This follows from the assumption that the probability of crystallization is a function only of the fundamental nucleation rate (not valid for viscous liquids) and that the nucleation rate J (nuclei per unit volume per unit time) is determined by events which are random in time and space leading to the relations(3)

$$\begin{aligned} \ln J &= \text{const} + k\Delta T \\ \ln V &= \text{const} + k\Delta T \end{aligned} \qquad (1)$$

where V is the volume in which a nucleation event will be observed in unit time at undercooling ΔT. The parameter k characterizes the shape of the heterogeneous 'seed potency' distribution, while the constant is determined by the concentration of seeds of all types, which may be characterized as the 'total dirtiness' of the sample.

Nucleating impurities seem to be ubiquitous in chemistry and meteorology laboratories, and they can only be removed by very laborious and painful procedures. Such a procedure has been described by Wylie(6) and permitted him to supercool a sample of approximately 1 cc, i.e., a truly bulk sample, to -31°C. This feat has never been repeated. Untreated bulk (>1 cc) samples of water subject to slow cooling in the absence of agitation cannot usually be cooled below -12°C. A less involved procedure for cooling smaller samples contained in 0.5 mm diameter capillaries reproducibly to -34°C has been described by Mossop(5) and utilized by others since. The essential step is the prolonged distillation of the primary water sample to remove, in the first place, nucleating impurities contained in the laboratory atmosphere over the sample, which are swept out by the evolving vapor. It is also essential to avoid mechanical entrapment of droplets of the boiling liquid in the issuing vapor.

Nucleation also frequently occurs, even in very clean water, at centers located in the glass containing vessels.(6,7) The precise nature of these crystallization centers is not known, but they appear to occur randomly in the surface of pyrex and silica glass, and may develop over a period of time due presumably to some leaching action. Coating a glass sample container with silicone can reduce surface nucleation probabilities.(5)

The density of crystallization-inducing impurities in water never seems to be greater than one effective center per 10^{-12}l, so that samples which have been subdivided to this volume, as in the formation of 5 μm droplets emulsions using non-nucleating surfactants,(8-10) seem to supercool reliably to temperatures essentially the same as those found for similar size droplets produced in cloud chambers swept free of all heterogeneous nuclei in preliminary cleansing operations.(5,11) Such samples thus seem to be suitable for performing measurements on water to temperatures approaching the fundamental limit imposed by the 'homogeneous' nucleation phenomenon.(3,12,13) In the latter, microcrystals of dimensions sufficient for thermodynamic stability are generated by the fundamental entropy fluctuations characteristic of the supercooled liquid itself, which become adequate only at and below the 'homogeneous nucleation temperature.' The homogeneous nucleation temperature is itself a function of sample size, though the volume dependence, according to standard nucleation theory,(3,12,13) is much smaller than for heterogeneous nucleation. The relation between the two, as best it is known at this time, is illustrated in Figure 1 taken from the book of Mason.(3) Some additional recent data are to be seen in an article summarizing current Russian work by Skripov.(14)

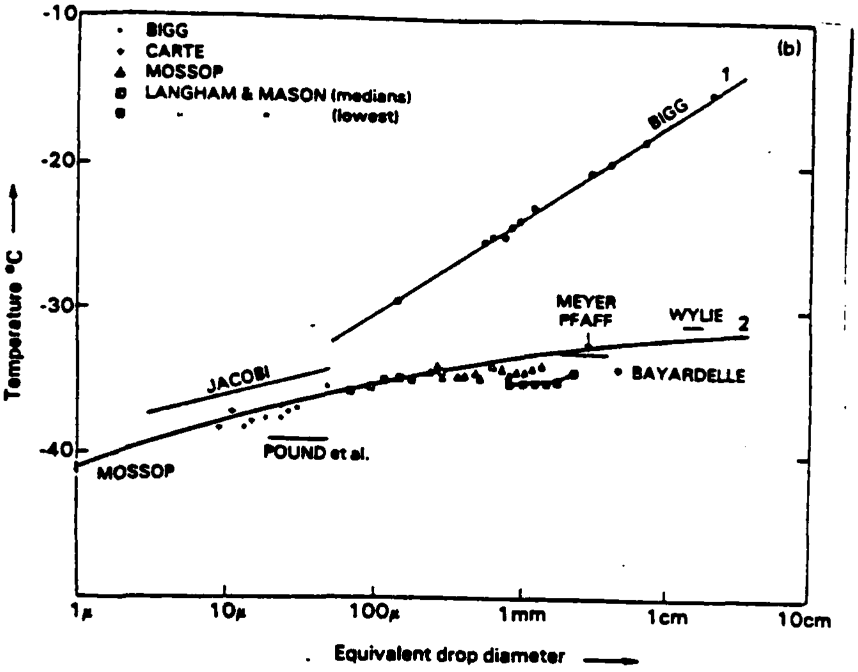

Figure 1. Homogeneous and heterogeneous nucleation temperatures for water as a function of sample volume (after Massu, ref. 3) reproduced by permission).

The lowest temperature to which even the smallest and purest droplets of water (produced in cloud chamber experiments) have ever been supercooled seems to be -42°C,(2,5,11) though scattered and controversial reports of cooling to lower temperatures exist in the literature. The probable reason for this limit will be highlighted in the discussion of physical properties of the supercooled liquid to be given below.

All of the above measurements pertain to observations made at 1 atm. pressure. Just as the freezing point of water is lowered by the application of hydrostatic pressure, so is the temperature at which the nucleation probability becomes high. Thus a question of interest is the extent to which the nucleation temperature of water can be depressed by exercise of the pressure variable. This question has been answered in recent years by two groups studying the behavior of emulsified samples. Xans and Barnaud(16) at the Universite des Bas Pyrenees, studied water droplets immersed in a hydrocarbon dispersant phase using a lanolin surfactant, to measure the nucleation temperatures to pressures of 80 MPa (800 bar), while Kanno, Speedy and Angell(17) using a sorbitan tristearate emulsion recommended by Rasmussen and MacKenzie,(9) extended the measurements to 0.3 GPa. The latter measurements, seen in Figure 2, show that a lower limit of $-92^{o}C$ is reached at 0.2 GPa where a reversal in the pressure dependence of the nucleation temperature occurs due to the preferential nucleation of a denser form of ice, ice(III).

The question arises whether it is possible to cool water so quickly that the nucleation event will be bypassed and a vitreous state of water obtained as a result. Attempts to perform this feat date back over many decades, but except for one unpublished report on the apparent amorphous condition of a sample of water which had been splat-quenched onto a sapphire block,(D. R. Uhlmann, private communication, quoted in ref. 18) no success had been claimed until the recent work of Brugeller and Mayer.$^{(19-21)}$ The latter workers reported that a sample of emulsified water contained an amorphous fraction when jet-quenched at high pressures into a liquid cryomedium such as liquid propane. The evidence presented, which seems fairly convincing although is not universally accepted,$^{(22)}$ was the presence of an exotherm during reheating of the quenched material which occurred at 160 K, the same temperature at which vapor-deposited amorphous solid water ASW$^{(23)}$ (which is clearly a non- crystalline material) crystallizes during steady reheating.

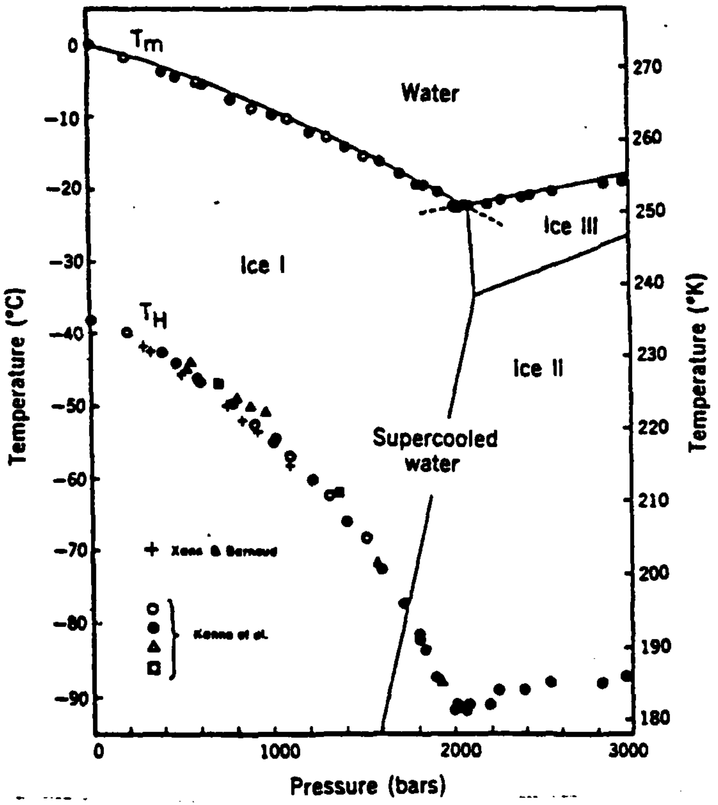

Figure 2. Metastable range for liquid water in the region 0.01-300 MPa defined by emulsion nucleation temperatures. (After Kanno <u>et al</u>. ref. 17, reproduced by permission).

More recently these same workers,(20,21) using an improved technique, have reported the vitrification of pure water jetted through a 10 micron aperture under pressures of 40 mPa into various cryomedia. The exact state of this apparently vitreous material is a little ambiguous at the moment because of uncertainty concerning the role that the cryomedium itself plays in the structure and properties of the resulting amorphous phase. The reheating behavior, for instance, shows different characteristics depending on the extent to which the cryomedium has been removed, e.g., by pumping.(20,21) This is also true of the X-ray structure of the material which shows interesting differences from that of vapor- deposited ASW which evidently cannot be attributed entirely to the presence of elements of the cryomedium.

In independent work, Dubochet and McDowell(24) give evidence for the vitrification of tiny drops of pure water caught on hydrophilic carbon film electron microscope screens and plunged into a liquid cryogen, e.g., propane or ethane. The evidence presented is the amorphous state electron diffractogram obtained from the product and the crystallization of this material to Ice I_c observed at ~135-140 K during reheating. A critical cooling rate is observed in their work, since only Ice I_h is found if the film falls into boiling liquid nitrogen, while a nitrogen slush yields Ice I_c. The recrystallization temperature depends on time in a manner similar to that observed for the amorphous vapor deposit by Dowell and Rinfret,(15) though seems to be lower than expected from DSC observations carried out at various heating rates.(25,31) For instance, Dubochet <u>et</u> <u>al</u>(24(b)) find that crystallization occurs after 100 sec at 140 K, whereas even at a constant heating rate as low as 1 deg per 100 sec, crystallization in Skripov's deposits(14,25) did not occur until 158 K. There is an unresolved problem in determining the extent to which a given kinetically unstable glass is nucleated during the cooling process, and when the density of nuclei in the material is large enough that the material should be regarded as microcrystalline even though amorphous to X-rays or electron diffraction. Heavily nucleated glasses should crystallize more readily during heating than their nucleus-free equivalents. Detailed comparisons of the quenched droplet and vapor-deposited ASW diffractograms are awaited with interest; partial incorporation of the cryogen in clathrate structures could help explain an apparent reduction in kinetic stability compared with the vapor deposit which can itself be studied at leisure at 140 K.(23)

The importance of the liquid-vitrification work is two-fold. Firstly and less significantly, the retention of an amorphous material on quenching an initially liquid state implies that at least transiently the liquid existed, though not necessarily in a state of internal equillibrium, throughout the extended temperature range between -40°C where it would normally crystallize and the temperature of final vitrification which is not exactly known for the cooling schedule employed. Of greater importance is the opportunity which now exists to resolve the following important problem concerning the relation between liquid water and the much studied vapor-deposited ASW.

The latter material, which is obtained by deposition of water molecules from the vapor onto a cold substrate, and which has been much studied in recent years,(23) (but which falls somewhat outside of the scope of this review since it is palpably a <u>solid</u> rather than a <u>supercooled</u> <u>liquid</u> state of water) is somewhat mysterious at this time. Two different groups(28,29) have reported the existence of a glass transition temperature in the range 130-140 K, the apparent increase of heat capacity at which leads to an incompatibility with the known excess entropy of liquid water at the lowest temperature to which it has been studied. Johari(30) pointed out that it was not possible that a liquid state with the observed excess of heat capacity over that of the amorphous solid could arrive at 0°C, on heating, with as little total entropy as liquid water is known to possess at that temperature. The argument requires either that amorphous solid water is thermodynamically unconnected with ordinary liquid water or that there is some error in the glass transition and heat capacity measurements. It now seems probable that the latter is the case, for reasons given immediately below, and the jet-quenched vitreous material may well provide the evidence to substantiate this claim.

In an attempt to improve the quantitative understanding of the glass transition in the vapor-deposited vitreous material MacFarlane in this laboratory(31) carefully deposited material into a differential scanning calorimeter pan at ~90 K under appropriate slow deposition, high vacuum, conditions(23) and affected a cold transfer to a Perkin-Elmer DSC-2 differential calorimeter. Repeated efforts including cycling, and annealing at 130-140 K, using the highest sensitivities of the DCS-2 have failed to reveal any glass transition phenomenon in the temperature range expected, while the deposit always crystallized sharply at 158-160 K during the final heating scan. Thus the observations of Sugasaki _et al_(29) are either made on a material with different properties from that deposited in MacFarlane's experiments, or are the result of some experimental artifact.

MacFarlane and Angell(32) have concluded from the DSC studies that the vapor deposited material, which has been shown to be a rather defect-free random network structure,(23) has no glass transition in the range up to 160 K and cannot be expected to exhibit one at higher temperatures because, as with most splat-cooled metallic glasses, the deposit relaxes more rapidly towards the crystalline state than towards the internally equilibrated amorphous state (though a shoulder which appears consistently on the low temperature side of the crystallization peak could prove to be an enthalpy relaxation effect, i.e., a glass transition, competing with the exothermic crystallization). In support of this argument, we note that ice nucleates and grows from glass-forming aqueous solutions at a lower temperature than ASW crystallizes, despite the much greater glass-forming tendency of the former. The failure of extrapolations from binary solution data to correctly predict the relatively high temperature of this 'intrinsically unobservable' glass transition must be due to the same factors which cause the glass transition temperature of silica and zinc chloride to be rapidly depressed by addition of second components,(33) viz., the disruption of the relaxation-resistant network structure by the network-incompatible second components. If the heat of crystallization of the jet-quenched water samples, when free from cryoliquid contaminant, can be shown to be the same as that of the vapor deposited vitreous water then the proposed reassignment of the glass transition temperature to some value above 160 K (which is in principle undeterminable at 'normal' heating rates hence is, in a real sense, fatuous in concept) will be confirmed.

Summarizing this section, liquid water can be conveniently studied in its metastable states down to approximately $-40^{\circ}C$ at 1 atm. pressure decreasing to $-92^{\circ}C$ at 2 kbars of pressure, and an extension of this range for ultra-fast measurements (not yet designed) is perhaps possible in principle for measurements performed on microscopic particles during cooling processes at rates of the order of 10^7 deg sec^{-1}. A continuity of non-equilibrium states between liquid water and amorphous solid water has not yet been positively established, though it appears more possible now than previously.

STRUCTURE AND PHYSICAL PROPERTIES OF SUPERCOOLED WATER

In the following pages we will consider the various measurements which have been made, not only on water, but also on various aqueous solutions on which the focus of attention has been the solute modification of pure water properties and implications for the nature of water itself. These properties will be considered under the separate sections, Structural Characteristics, Thermodynamic Properties, and Transport and Relaxation Properties. In the description of these properties we will repeatedly take note of the functional forms for temperature and pressure dependences of physical properties exhibited description of these properties we will repeatedly take note of the functional forms for temperature and pressure dependences of physical properties exhibited by both pure water and its solutions, though we will postpone a detailed discussion of these forms to a concluding section in which the various models, aided by computer simulations, will be discussed. Inevitably, some overlapping of the interpretive material into the experimental sections will be necessary in order that the experiments which have been performed appear generally coherent in their design and sequence. Considerable use will be made of recent review articles by the author,(2) Lang and Ludemann.(34) For a popular level account of the anomalies of supercooled and superheated water, see ref. 35.

Sampling techniques

Since as the previous section has indicated, it is extremely difficult to free bulk samples of water of all nucleating impurities, the pursuit of knowledge of the physical properties of water substantially below $0^{o}C$ has for the most part depended on the use of one or other 'small sample' technique. The choice of technique has depended to various extents on the patience and ingenuity of the individual investigators, but for convenience can be summarized under three headings, as has been done in more detail in Ref. 2. The references given are examples, and are not intended to be exhaustive.

THIN FILMS (TWO-DIMENSIONS MACROSCOPIC) The use of thin film techniques has proven appropriate for certain spectroscopic studies,(36) and crystallization has been suppressed at least to $-31^{o}C$. Some controversial(2) reports of much deeper supercooling exist in the literature.(37,38)

CAPILLARY SAMPLES (ONE-DIMENSION MACROSCOPIC) This technique has been used for certain PVT determinations where the length of a thread of water is conveniently measured in glass capillaries,(39-41) and also for spin-echo diffusion(42) and viscosity(43) measurements, and ESR studies.(44) Sample survivals down to -33°C have been reported several times. In 1-2 μm diameter samples, supercooling to below -35°C is reported,(44,45) but much caution against interference of surface effects on the physical property under study must be exercised.(45)

DROPLET SAMPLES (NO DIMENSIONS MACROSCOPIC) The use of single droplets of diameter ~1 mm down to -33°C has been reported(47) but the common droplet technique has involved the use of emulsion methods, in which various surfactants have served.(8-10) A popular and generally successful choice has been developed by Rasmussen and Mackenzie using span 65 (sorbitan tristearate) with a light hydrocarbon dispersant phase.(8) These have served for extensive PVT(8) spin lattice relaxation(48) and even spectroscopic(49) studies. At the limit of the droplet technique we find the possibility of studying 'nanoscopic' (as opposed to 'microscopic') samples in newly developed micro-emulsion systems in which the only -OH groups are those of the water itself.(50,51)

Structural Characteristics

In the last few years both scattering and resonance spectroscopy studies of the structural characteristics of water have been extended to subzero temperatures using thin film, capillary, and droplet sample techniques, in some cases reaching to the homogeneous nucleation temperature. Bundles of silica capillaries were utilized by Bosio *et al*(52) to study the elastic scattering of neutrons and X-rays respectively from samples down to -20°C, from which isochoric temperature differential structure factors (which are less subject to correction errors than the structure factors themselves) were obtained, to the structure factor for comparison with known behavior in the normal temperature regime. In this manner they were able to observe sharpening of features related to the D-D, and D-O ordering in the liquid and see, through the oppositely directed shifts of first and second S(Q) peaks, the consequences of increasing the rigid and tetrahedral hydrogen bonding developing with decreasing temperature. This work extends to lower temperatures an initial isochoric study by Egelstaff et al(53) Emulsion samples have also been briefly studied but background difficulties have made resolution of the results unsatisfactory so far (J. Teixeira, private communication).

Capillary samples have also been used by Bosio et al(54) to perform small angle X-ray scattering studies and thereby to obtain information on the increase in mean-squared density fluctuation which compressibility measurements had earlier shown set in at the lower tempertures. The small angle X-ray measurements give specific information on the correlation length of the fluctuations, which prove to be of order 8 Å at -20°C. Reduction in the mean-squared density fluctuations on addition of ethanol were also demonstrated by this technique. This is of special interest because viscosity and conductivity measurements suggest structuring in the solution is increased (see below). Quasielastic neutron scattering studies have also been carried down to -20°C, and the results will be referred to in discussion of transport properties below.

A number of studies of the vibrational spectra of water under supercooled conditions have been reported in the last few years. Raman spectra for water, D_2O and their solutions, have been studied by several groups(55-57) at temperatures ranging down to -24°C, while infrared spectra in both the intermolecular far IR region(58) and the intramolecular overtone regions have been examined, in the latter case reaching as low as −35°C at 1 atm.(49) and −60°C at 20 MPa.(59)

D'Arrigo <u>et al</u>(55) have reported the polarized Raman spectra of pure water in the range 95°C to −24°C, using a remarkable source of pure water produced in phials by the firm Angellini SpA. Despite its large ~10 cc volume, these water samples may be supercooled repeatedly to at least −24°C while remelting precisely at 0°C. D'Arrigo <u>et al</u> showed that whereas spectra in the range of 0–95°C repeatedly yield the much-discussed isosbestic point at 3370 cm^{-1}, the spectrum at −24°C deviates markedly from this pattern (see Figure 3). These authors considered the distinction to lie in the presence of heterophase fluctuations involving microscopic incipient true ice nuclei. The latter interpretation is not directly supported by the more detailed study of Bansil <u>et al</u>(56) who examined both the 3400 region and the low frequency region at temperatures down to −20°C, though increases in the temperature dependences of the 'bonded' OD stretching band were noted in the supercooled region. An extrapolation of the bandwidth to the temperature of 140 K, the expected T_g, where data on the vapor-deposited amorphous solid are available(23,59,60) showed close concordance (2450 cm^{-1} FWHH = 80cm^{-1} vs. 2447 cm^{-1} FWHH = 60 cm^{-1}, respectively) which argues in favor of a continuity of structural states between liquid and amorphous solid (though according to MacFarlane's and Angell's recent conclusions,(32) see earlier section, the comparison should be

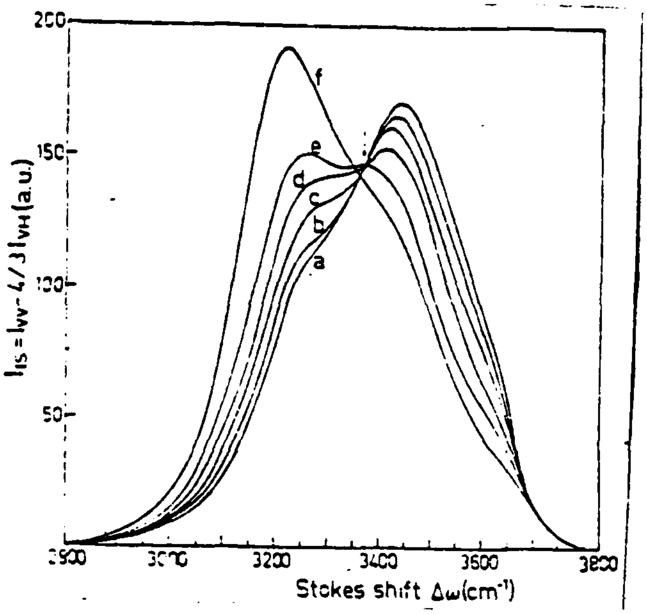

Figure 3. Polarized Raman spectra of water in the temperature range 95 to −24°C. (After D'Arrigo <u>et al</u> ref. 55 reproduced by permission).

made at a higher temperature. Bansil et al argued for two classes of hydrogen bonds (not water molecules), strong and weak, on the basis of their observations.

A subsequent careful study of the composition dependence of the 3400 cm^{-1} region for H_2O in dilute solution in D_2O by Wiaufe-Akenten et al(61) has identified the low frequency component of both H_2O and D_2O Raman spectra as a feature determined by intermolecular coupling. The weakening of the coupling for more weakly hydrogen bonded molecules leads to the high frequency feature (see Figure 3). These results were considered more consistent with a continuous distribution of hydrogen bond strengths in the total structure, i.e., with a continuum model for the liquid.

Polarized and depolarized Raman spectra for the same frequency region have been reported by Yeh et al,(57) who also studied the low frequency 175 cm^{-1} band in the depolarized spectrum. This band is believed to be an intermolecular H-bond stretching mode. A strong increase in its intensity observed with temperature decrease in this work was interpreted in terms of water molecule cluster $(H_2O)_5$ build-up in view of the C_{2v} symmetry requirement.

Overtone IR studies have been made up to 200 MPa using emulsion samples of both pure H_2O, and H_2O-D_2O mixtures, only the former giving adequate spectra in the high pressure regime. From the former, Angell and Rodgers(49) were able to obtain information on the uncoupled overtone bonds and to show that the band commonly attributed to 'weak' or 'broken' hydrogen bonds decreases to very small intensities at the low temperature extreme leaving behind a broad structured band which could be attributed to the fully bonded or vitreous structure and had features in common with, though shifted to high energies from, the corresponding ice I_h band. This band compared well in shape with the spectrum of H_2O-glycerol glasses observed at $-100^{\circ}C$. The results could not be interpreted within the framework of a simple two-state model, but seemed consistent with the Stillinger-Rahman concept of 'exciting across the centroid,'(50) the latter being a static population of H-bonds of intermediate strength. Increase of pressure was found to reduce the enthalpy change associated with this process.(49(b)) However, contrary to expectations from two-state models, the number of broken bonds does not increase with increasing pressure except perhaps at the lowest temperatures. This would imply that the strikingly anomalous consequences of increasing pressure on water come about not through 'breaking' hydrogen bonds but through redistributing the bonds already present so as to have fewer groupings of strong bonds which are responsible for the low density fluctuations (see Interpretations section later).

In the far infrared, L. Boehm(58) has shown that decrease of temperature to -12°C (or to -60°C using H_2O + propylene glycol solutions), results in a very considerable sharpening and shift to lower frequencies of the interesting feature at 170°C cm^{-1} reported by Williams et al(62) in the normal temperature regime. The band which is usually assigned to a translational quasi-lattice mode, is also observed clearly in Raman scattering studies, and Bansil et al(63) have recorded temperature effects essentially the same as those of Boehm.

Thermodynamic Properties

PVT MEASUREMENTS The outstanding anomaly characteristic of water in its stable region is the density maximum at 4°C, and it has been a natural since earliest times to enquire into the behavior of the density in the negative expansivity region when measurements are extended below 0°C. The first reported measurements date back to 1837 when Despretz performed accurate density studies to -9°C.(64) Using capillary samples, such measurement have been extended more recently to -34°C(39) while emulsion methods have pushed the low temperature limit down to -37°C.(9) The results indicate that supercooling water is rapidly approaching the low density of ice at the lowest temperatures of measurements, and reasonable extrapolations indicate that, had the crystallization event not occurred, the ice and water density plots would intersect in the vicinity of $-(45\text{–}50^\circ C)$, see Figure 4.

The peculiarity of this behavior is best displayed through the derivative property, the thermal expansivity, which is found, at $-34^\circ C$, to be more than three times as negative as it ever becomes positive at higher temperatures (except near the critical point). The behavior of the density, and the consistency of the expansivity measurements in the supercooled region between different capillary and emulsion(9) measurements, and their overlap with those of the bulk material, is well demonstrated in Figure 4.

The expansivity measurements for D_2O were extended to high pressures by Kanno,(41,65) who found a systematic shift of the density maximum (at $11^\circ C$ for normal pressure) to lower temperatures with increasing pressure. At the limit of the study the TMD occurred at $-24^\circ C$ at 120 MPa. These measurements have recently been extended to <u>negative</u> pressures of the order of 20 MPa in a clever experiment by Henderson and Speedy,(46) using a Bourdon-type tube technique. At -20 MPa the density maximum for H_2O occurs at $7^\circ C$, continuing the pattern observed at positive pressures. Extensions of these measurements using remarkable microcapillary spirals have permitted observations to $-18^\circ C$ under negative pressures, (Henderson, B. and Speedy, R. J., private communication).

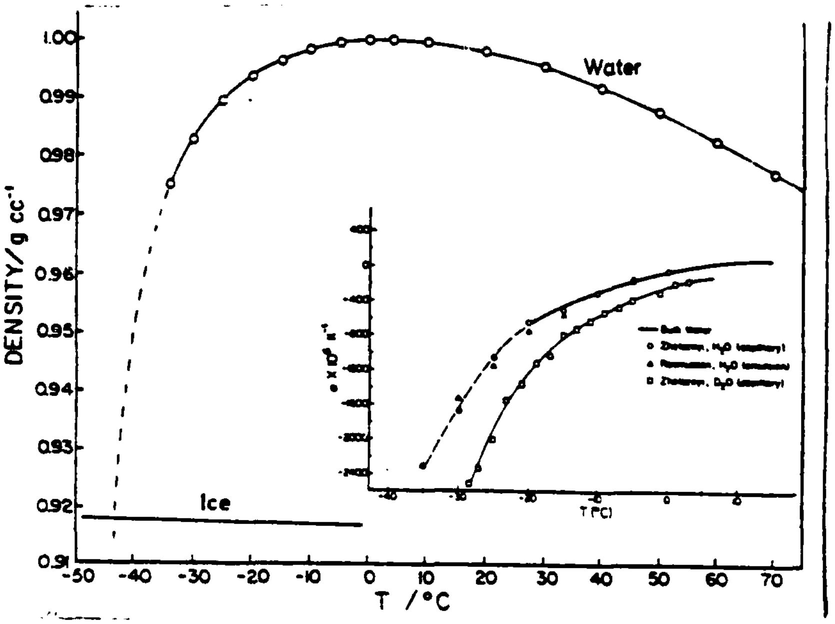

Figure 4. Density and expansivity dependence on temperature in normal and supercooled states. of H_2O and D_2O (from ref. 2 by permission).

Comparable anomalies in the compressibility κ_T were recorded by Speedy and Angell at low pressures(40) and extended to pressures of the order of 200 MPa by Kanno and Angell.(41,65) The variations follow closely the course predicted by polynomial extrapolations of precise measurements in the stable region,(66) and have recently been reconfirmed by new extrapolations of PVT data obtained recently using a novel piezo thermal method by Ter Minassian *et al*.(67) Their Figure 5 is reproduced here. The heat of compression data of these authors extend the knowledge of water to 600 MPa at temperatures ranging down to -28 K.

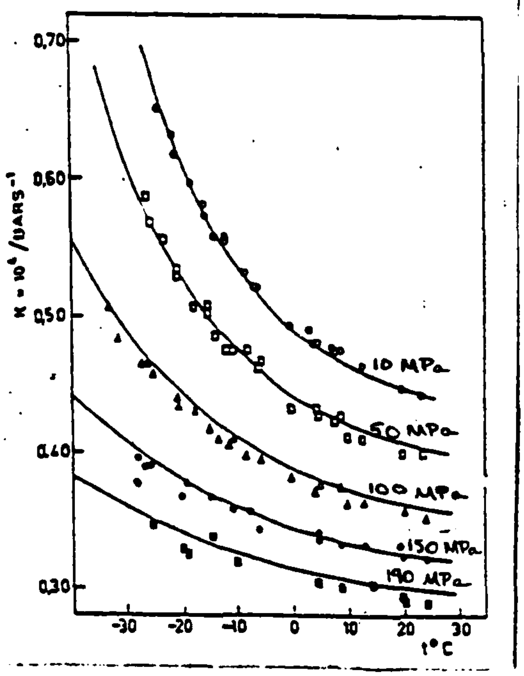

Figure 5. Compressibility behavior of water up to 200 MPa by extrapolation from stable range, compared with experimental data of ref. 65. (After Ter Minassian *et al*, ref. 67, reproduced by permission.)

It was the finding that the low pressure compressibility and other properties could be fitted to a critical type equation

$$X = A_x(T/T_s - 1)^{-\gamma} \tag{2}$$

with a singular temperature just below the homogeneous nucleation temperature which first drew general attention to the interest potential of water in the supercooled region.(40) The singular temperature obtained by constrained fitting of a critical point equation to the compressibility dataproves to follow closely the homogeneous nucleation temperature over a range of pressures,(41) essentially as shown later (in Fig. 7) from the analysis of NMR relaxation data. It seems rather clear from these relations that there is a close connection between the suggestive temperature dependences of these intensive thermodynamic properties and the eventual crystallization event, though the basis for the connection remains at this time a matter of some controversy.

The adiabatic compressibility has been determined by ultrasonic measurements to -26°C by Bacri and Rajonarison(68) at 925 MHz and extended to -34°C by Trinh and Apfel,(47) using an ingenious levitated droplet technique and 54 KHz waves. κ_S determined in the latter work shows an interesting maximum value at about -32°C, a feature which is mimicked at slightly higher temperatures by C_v.(69) Both variations make a striking contrast with the constant pressure properties. No sign of the κ_S maximum is seen in the 925 MHz study. Hypersonic (55 GHz) measurements by Teixeira and Leblond(70) using the Brillouin scattering technique down to -20°C accord better with the 925 MHz velocities, but show a different absorption α/f^2 suggesting a dispersion due to structural relaxation may be at hand. Further work is needed in this area. κ_S maxima like that observed by Trinh and Apfel have been observed in H_2O + ethanol solutions by Conde et al.(71) The ultrasonic studies have been the subject of a detailed review by D'Arrigo.(72)

HEAT CAPACITY The heat capacity of supercooled water is a property which lends itself to measurement by the emulsion technique, and for this reason its value is known over the widest temperature range of all the intensive thermodynamic properties. Early measurements by Rasmussen et al(73) and Angell et al(18) have recently been refined,(74) and correlated with similar striking variations encountered in the superheated regime—an observation of which more will be made later in this review. Combination of C_p with the above PVT data has yielded the constant volume heat capacity C_v which has a maximum at -23°C.(69)

OTHER THERMODYNAMIC PROPERTIES The vapor pressure, which is at the same time the most fundamental, and the longest-known of the deeply supercooled water properties has been on record since Regnault's pioneering work to -32.8°C in 1847,(75) and recently confirmed by less extensive measurements of Bottomley.(76) Since it is only in the second derivatives of the free energy that the anomalous character of supercooled water becomes clearly displayed, the vapor pressure measurements themselves show little to excite the curiosity.

The remaining thermodynamic property of which some knowledge is available in the supercooled regime, is the low frequency relative permittivity. This was first determined using an emulsion technique by Hasted and Shahidi(77) and quickly supported with emulsion measurements using a different analysis by Hodge(78) and more recently by the co-axial resonator spectrometer technique of Bertolini et al who reached -21°C using a non-emulsion sample of approximately 0.1 cc volume. Hermiz(79) (J. B. Hasted, private communication) has recently found some reason to doubt the viability of the initial emulsion measurements, though the results are well supported by independent measurements using different techniques. This reviewer is unable to account for the difficulties in emulsion preparation conscientiously reported by Hermiz in this connection.(79)

SOLUTION MEASUREMENTS It is not possible to review in full detail the findings of the numerous binary solution studies which have now been reported but we will summarize briefly their intentions and results. To do this we must first introduce some of the basic ideas which have been proposed to understand the origin of the curious thermodynamic characteristics reviewed above.

Common to all interpretations is the notion that, with decreasing temperature, the hydrogen bonding interactions amongst the water molecules become more effective and the 4-coordination requirement established by the ice rules results in an increasing open network character (commonly, though in some ways misleadingly, referred to as 'ice-likeness') being generated in the molecular assemblage. It is in the next order of refinement, namely, in specification of the types of configurations encountered at the microscopic level, that the different interpretations show their distinctions. One class of model(9,72) considers the structured groupings to be characterized by actual crystalline ice-like arrangements of molecules describable as Frenkel heterophase fluctuations, and generating in effect ultramicrocrystals from the otherwise water-like assemblages. A second class(40,81,82) insists less on the symmetry of ice but expects that the low density fluctuations have the volumetric characteristics of ice, while allowing the arrangements to be spatially random in accord with the 'random network' concept.(82-84) A third group(85-86) emphasizes the importance of 5-membered ring groupings such as are exhibited in clathrate hydrate compounds but not in the ices. Originally conceptualized by Pauling as a favored arrangement in stable liquid water, this idea draws some support from the manner in which such groupings can introduce a cooperative characteristic into the structuring of water with decreasing temperature.(85,86)

With these basic notions now introduced, one can discuss the motivation for solution property studies. These are several-fold.

An initial venture has been based on the idea that, since the open structures are determined by the peculiar charge distribution around the water molecule, they will be interrupted by the presence of hydrophilic solutes such as ions and other strongly hydrogen bonding molecules. It is then supposed that such binary solutions may, at sufficient concentrations, provide a basis for deducing, by extrapolation to pure water, the properties of water in the <u>absence</u> of framework-building water-water interactions. This has been the particular focus of Oguni and Angell(69,87) in their attempt to separate an 'anomalous' component from the total thermodynamic properties in order to better assess the appropriateness of critical laws for the 'anomalous' part of the thermodynamic properties. Startling decreases in C_p on solute additions are observed in the deep supercooling region.(69)

Stimulated by the suggestion of Stillinger,(85) there has been considerable activity(88-91) in seeking solution information on the behavior of hydrophobic solutes around which the water molecules can build clathrate cages. Such induced cage-building could be viewed as a positive structuring influence in which case it is anticipated that the singular state would be reached more rapidly with decreasing temperature and the anomalous behavior therefore enhanced. Indeed early studies by Wada(92) had indicated that the temperature of the density maximum of water was initially increased by incorporation of ethanol into the system. These ideas have been tested using thermodynamic measurements by Oguni(88) who has studied the variation of the homogeneous nucleation temperature for ice with solute concentration for many solutes, and most recently by Sorensen,(90) who studied the partial molar volume of solutions with hydrazine and t-butyl alcohol as solutes at temperatures down to -30°C. Except for Wada's observation, no increases in the anomalous thermodynamic characteristics have been observed (however, see Transport Properties). Indeed decreases in κ_S as abrupt as those observed for C_p with all-hydrophilic solutes(111) have been observed for EtOH additions by Conde et al (by light scattering measurements:(71) an interesting maximum in κ_S vs. T was observed in solutions of >5% EtOH in this work). However, the clathrating concept has survived since it has been recognized(88-91) that the actual mean-squared density fluctuations, which determine the magnitude of κ_T, α, and C_p(40) can be damped by including guest molecules into cages.

Transport and Relaxation Properties

It is in the transport properties of supercooled water that we find some of the most unusual behavior, and also some of the best evidence for the reality of the putative singularity underlying the behavior of this extraordinary liquid.

VISCOSITY The most familiar, though not the most fundamental, of the transport properties is the shear viscosity, which at 1 atm. pressure has been now studied over a temperature range extending from 150 to -35°C with a high degree of concordance amongst the different investigations. The earlier measurements in the supercooled state made by Hallett(42(a)) using a cold capillary viscometry technique, have recently been extended to -35°C by Osipov *et al*(43) using a briefly described moving slug method. The accuracy of the data at the lower extreme appear to be about ±1% and the entire temperature range can be fitted, (see Figure 9 below) to the singular equation, Eq. (2) above, with a singular temperature of 228 K in excellent agreement with the most recent and probably reliable determination made by electrical conductance methods to be described below.

More striking than the highly non-Arrhenius temperature dependence (which after all is seen qualitatively in many viscous liquid systems, though in detail fitting a different equation form) is the anomalous presure dependence of the viscosity. Though not yet studied below 0°C, the existing data supported by results of diffusivity and relaxation time measurements at lower temperatures, show clearly that a striking *negative* presssure dependence of the viscosity develops as the temperature falls below 20°C. Such an anomaly is actually to be expected from theories which link the transport properties, i.e., the rate of exploration of the system's phase space, with the configurational entropy of the liquid,(93) since a Maxwell relation,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad (3)$$

shows S increases with P in a negative expansivity regime. Studies of the viscosity at subzero temperatures and pressures to 200 MPa are currently being performed by M. Rogalski in the author's laboratory using a micro-falling ball (mercury bead) viscometer and strengthened capillary tube pressure vessel-sample containers. The shear viscosity is expected to show an increasingly well resolved minimum at around 150 MPa as the temperature decreases.

The bulk viscosity, which can be obtained from combining shear viscosity and ultrasonic absorption measurements, has been given less attention for experimental reasons, but its behavior down to -20°C is known to be similar in character to that of the shear viscosity.(68,70)

DIFFUSIVITY The most fundamental of the transport properties is the self diffusion coefficient since no external stress is required to manifest, or measure, the property. Data have been obtained below 0°C both by tracer,(94) and NMR spin-echo methods,(42) the latter appearing more reliable and extending to -31°C. Combined with high pressure measurements performed utilizing the latter method,(95) the diffusivity shows the positive pressure dependence expected from the viscosity behavior, though the maximum on the high pressure side is not very clearly defined. Self-diffusion measurements on <u>emulsion</u> samples are possible in principle using a pulsed gradient NMR spin-echo technique, though the interval between pulses must be kept extremely short in order for free diffusion conditions to be maintained during the experiment. Since viscosity, but not self-diffusivity, diverges near the common critical and consulate points, the comparison of diffusivity and viscosity down to the low temperature limit in the case of water should be a matter of some interest.

Some detail on the diffusion process is available from incoherent quasi-elastic neutron scattering expriments which were recently extended to -20°C by Chen et al(96) This work clearly resolved two Lorentzian components to the (instrument-resolution-function-corrected) quasi-elastic spectrum. The broad component characterized by a halfwidth Γ_b of $(3.3\ \text{ps.})^{-1}$ at 294.4 K was associated with rotational relaxation (the NMR rotational correlation time at the same temperature is 3.2 ps.). The sharp (s) component was linked to proton translational diffusion and, using a jump diffusion model for the analysis, a characteristic jump length was extracted from a plot of Γ_s/DQ^2 vs. Q^2 . The mean jump distance was 1.23 Å, independent of temperature between 253 and 273 K. This corresponds to the proton moving from one hydrogen bond site to another via a partial molecular rotation across the tetrahedral angle. According to the model this motion would occur on average every 1.1 ps at 298 K and every 5.7 ps at -20°C, the temperature dependence being that of the diffusion coefficient.

This characteristic time and its implied temperature dependence is longer than that associated with the breaking hydrogen bond on the basis of depolarized light-scattering (discussed at the end of this section) though the two processes would seem to be closely linked. It may be pertinent to observe that jumps of the distance described only make sense in the context of a highly structured system, and a proton that 'disconnects' in a non-structured micro-region will behave in a less regular manner.

NMR RELAXATION The deepest penetration of the supercooled regime achieved for any mass transport or relaxation property has been for the case of spin-lattice relaxation times, for which sample dimension is not a problem, and the emulsion sampling method may be used. Normal pressure studies on emulsions were first made by Hindman _et al_.$^{(48,97)}$ and the technique has since been exploited with great success by Lang and Lüdemann$^{(34,98-100)}$ who, using Yamada's HF-strengthened glass for sample containment,$^{(101)}$ have explored the pressure regime up to 300 MPa, and pushed the measurements down to as low as -86°C.

The results of Lang and Lüdemann's measurements, conducted variously on ^{1}H, ^{2}H, and ^{17}O nuclei, have been most enlightening. Most spectacular, perhaps is the observation of a T_1 minimum for protons and deuterons under applied pressures of the order of 200 MPa near -80°C. The implication of the minimum is that water under these conditions is in a highly viscous condition.

Orientation correlation times for the water molecule have been deduced from such measurements for all 3 nuclei, and their concordance is demonstrated in Figure 6 for the pressure range 5-150 MPa, plotted in the Eq. (2) form. The support given this simple equation by these data, which extend over some 3 orders of magnitude in τ_2, is rather impressive. The variation of T_s with pressure closely mirrors that of T_h in the same way as found for the compressibility. The relationship, for both H_2O and D_2O, is shown in Fig. 7.

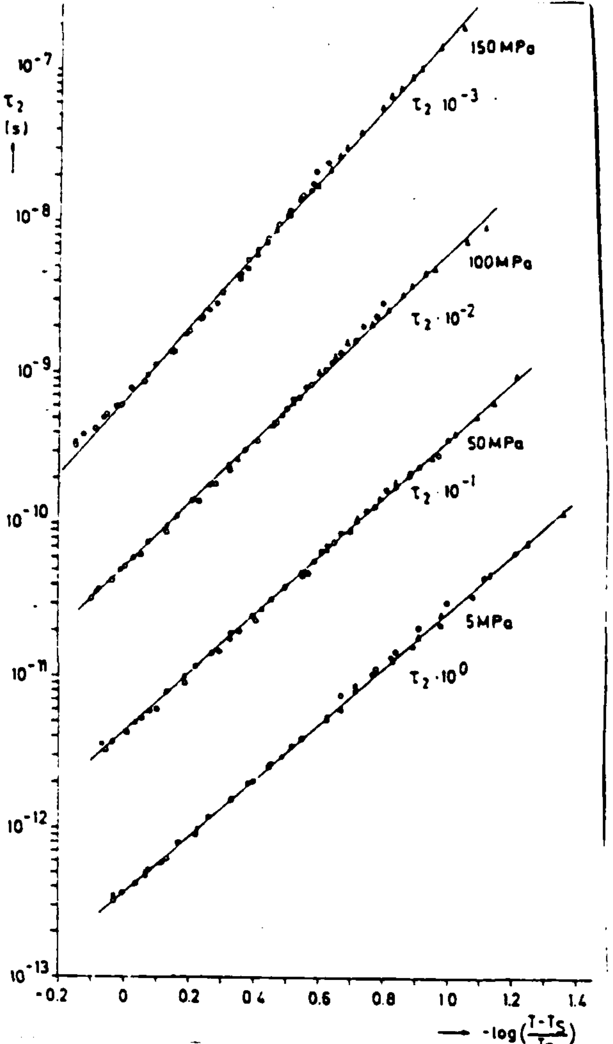

Figure 6. Test of Eq. (2) for τ_2 obtained from ^{1}H(98), ^{2}H(99), and ^{17}O(100) nuclear spin-relaxation time data.

For pressure above 150 MPa, Lang and Lüdemann find Eq. (2) less satisfactory, or at least indistinguishable in its ability to describe the behavior from the familiar Vogel-Tammann-Fulcher equation

$$X = A_x \exp \pm B/(T-T_o) \qquad (4)$$

which describes the transport properties of most viscous liquids. Thus the growth of the density and entropy fluctuations which seem responsible for the low pressure anomalies of water is inhibited by increasing pressure and their effects are displaced to lower temperatures where their influence on the transport properties is finally masked by the cooperative relaxation phenomena characteristic of the viscous regime.

In the high pressure regime, the physical significance of the VTF equation parameters can be critically examined.(34,41,65) The pre-exponent has the role of an attempt frequency and might be expected to correlate with the vibrational frequency observed in the IR spectrum, hence to exhibit an isotope effect which is predictable viz.,

$$\frac{\tau_0^{-1}(D_2O)}{\tau_0^{-1}(H_2O)} \approx \sqrt{\frac{I(D_2O)}{I(H_2O)}} = 1.38$$

The extent to which this expectation is borne out, and the additional expectation - that the T_o parameter for D_2O fall some 5° above that for H_2O as is found from direct glass transition temperature measurements on H_2O and D_2O solutions - is upheld, may be judged from the following table of best fit parameters, presented by Lang and Lüdemann.(34)

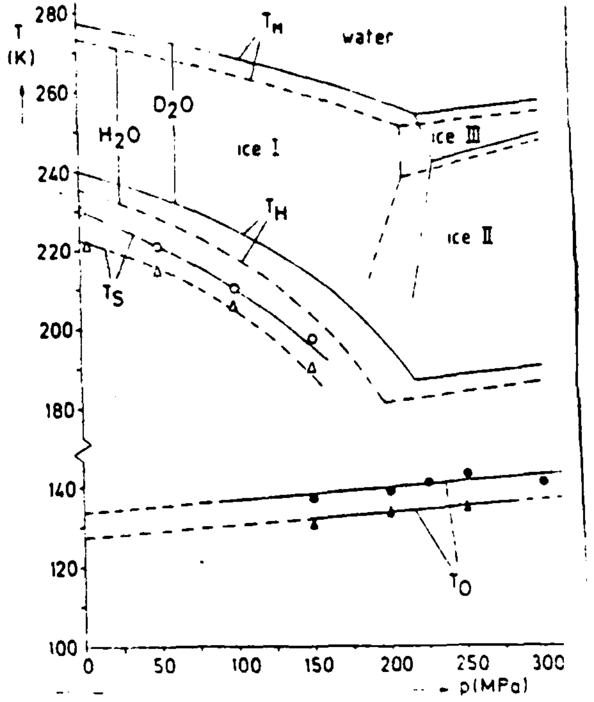

Figure 7. Comparison of the singular temperatures T_s for H_2O and D_2O obtained by Eq. (2) analysis of relaxation time data, with the homogeneous nucleation temperature T_h. Also shown are the "ideal" glass temperatures T_o obtained from Eq. (3) fits to data above 150 MPa. (After Lang and Ludemann, ref. 34, reproduced by permission).

Table 1 Parameters of the VTF-equation obtained from the least squares fitting of τ_2 to Eq. (4) (σ = standard deviation)

p [MPa]	$T_0 \pm 2$ [K]		$B \pm \sigma$ [K]		$(\tau_0 \pm \sigma) \times 10^{-4}$ [s]		Corr.-coeff.	
	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O
150	137	131	633 ± 3	652 ± 5	6.6 ± 0.3	4.6 ± 0.3	0.9998	0.9996
200	139	134	604 ± 3	623 ± 7	6.1 ± 0.5	4.6 ± 0.5	0.9997	0.9992
250	143	135	563 ± 3	581 ± 5	7.0 ± 0.6	5.9 ± 0.3	0.9997	0.9986

The value the Eq. (4) T_o is in accord with thermodynamic estimates, as best they can be made at the moment.(41) These results lend support to the notion discussed later that the transport properties of water (and its dilute solutions) be analyzed as a superposition of anomalous components of Eq. (2) form and a background component of Eq. (4) form.

OTHER RELAXATION AND DYNAMICS STUDIES Information on the reorientational motions of the water molecules can also be obtained from the dielectric relaxation phenomenon which has been studied by various workers(102,103) using different techniques penetrating as far as -21^o into the supercooled regime. The most recent of these studies and also the one to achieve the lowest temperatures is that of Bertolini _et al_(103) who used a coaxial resonator technique requiring samples of only 0.1 cc, and achieved good accuracy in their data. These workers were able to show that the single relaxation time characteristic of water in its normal regime(102) is retained down to the lowest temperatures studied. This phenomenon is somewhat uncommon amongst molecular liquids and seems restricted in general to the monohydric alcohols. Its occurrence in an associated multi-laterally hydrogen bonded liquid like water is unexpected and suggestive.

The dielectric relaxation time and the structural relaxation time determined by frequency-dependent mechanical relaxation studies (e.g., ultrasonics, Brillouin scattering) are usually found to lie close to one another in the case of associated liquids.(104) If this were the case for water then the Brillouin scattering measurements conducted by Teixeira and colleagues(70,71) would be expected to show a broadening of the peaks at around -20°C where the dielectric relaxation time is found from Bertolini _et al_'s work, to be ~ω_B^{-1}, the inverse of the frequency of the 90° excited (or annihilated) phonon frequency. However, there is no indication of such broadening in the measurements reported to date, suggesting that the longitudinal relaxation time is at least an order of magnitude shorter than the dielectric relaxation time, as estimated by Slie _et al_.(104) An explanation for this difference is not yet at hand. Presumably it would be of considerable help in understanding the microscopic fluctuations which all the other measurements indicate are present in this liquid. There is particular interest in the possibility of two relaxation time scales in the low temperature liquid,(2) since the time scale for critical fluctuations in the usual critical phenomena are known to be longer than those characteristic of the 'normal' liquid. Even the dielectric relaxation data at 0°C give some suggestion of a second, very weak relaxation at a frequency about 10 times higher than the primary relaxation (R. H. Cole, private communication).

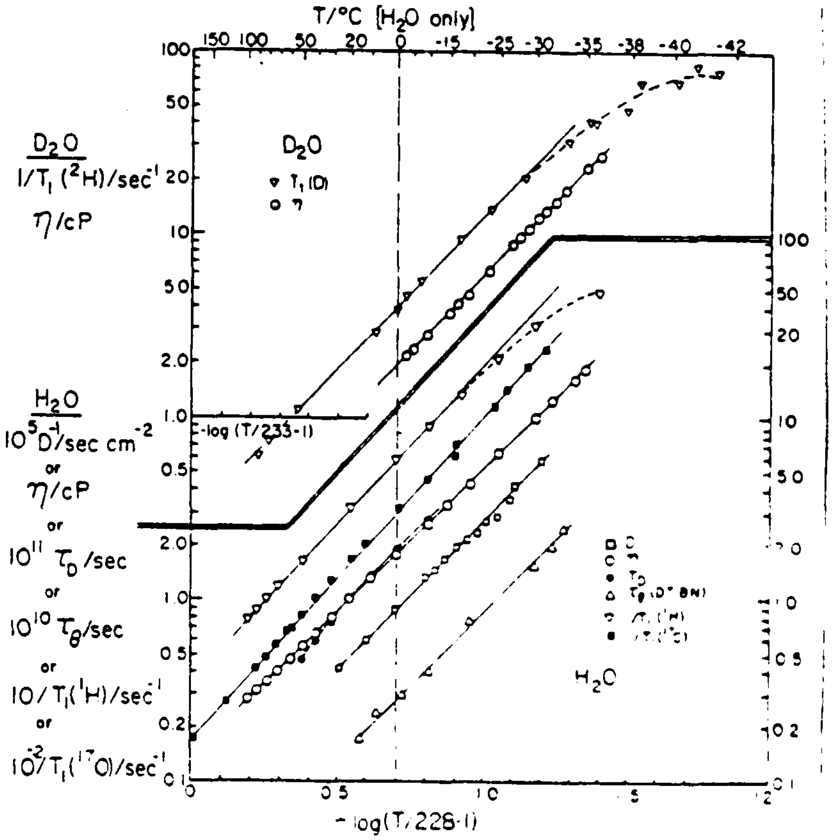

Figure 8. Tests of Eq. (2) for various transport properties and relaxation times in supercooled water and D$_2$O (from ref. 1, reproduced with permission).

The conformity of the various transport coefficients and relaxation times measured for H_2O and D_2O at normal pressure to Eq. (2) is demonstrated in Figure 8, the singular temperature favored by the data being 228 K.

The shortest time scale for a dynamic process in liquid water is that implied by a second broad Lorentzian observed in the spectrum of polarized light scattered by non-propagating refractive index fluctuations in water. This Lorentzian exhibits a half-width which at 0°C corresponds to a relaxation time for the index fluctuation of 0.3 ps. It was first described by Montrose et al(105) in 1974 and was recently studied down to -17°C by Conde and Teixeira(106) using a capillary cell.

As in the quasi-elastic neutron scattering study discussed earlier, the second Lorentzian components, in this case the narrow one, can be associated with a relatively long time constant process associated with rotational diffusion; its time constant and non-Arrhenius temperature dependence correlate well with those of dielectric(103) and NMR(98-100) studies. The short time process on the other hand has a much smaller temperature dependence, which as best can be discerned from the data to hand, follows an Arrhenius law. Furthermore its pre-exponent has a value of 5.6×10^{-15}sec corresponding $(2\pi\tau c)^{-1}$ to the broad IR librational band frequency of ~700 cm^{-1} , consistent with a process involving frequent attempts to cross a librational barrier with occasional successes in which the proton 'flicks' through the tetrahedral angle to form a 'new' H-bond at the expense of an 'old' one. This elementary restructuring process is considered to proceed incessantly and without need of cooperative involvement of other molecular motions (in fact a temporarily static environment is implicit in the model) - hence the Arrhenius behavior. It is quite likely that the same local 'switching' motion is executed and reversed several times before a structural rearrangement occurs. The diffusion of the defects in the local quasi-lattice which are created/eliminated is presumably the process which allows rotational diffusion and viscous flow to occur. The time constant obtained fom this measurement is regarded as the 'hydrogen bond lifetime.'(105,106) It is not clear, however, why this motion is not seen as a separate contribution in NMR studies.

SOLUTION STUDIES If instead of studying pure water, we examine the properties of dilute solutions in which the foreign species can serve as a probe for the dynamics of the solvent structure in which they move, we can in principle gain a considerable increase in the precision with which the transport properties may be characterized. For instance, Speedy(107) has recently obtained data precise to 1% on the electrical conductivity of solutions of KCl and HCl in water using fine capillary conductance cells which permit an extension of the data to -30°C at pressures up to 50 MPa. This study considerably extends an earlier penetration of the supercooled regime by Takisawa et al.(108) Speedy found that his low temperature data at the lowest concentrations could be fitted to Eq. (1) with the same parameters which were yielded very precisely by a fit of the more precise and accurate literature data for temperatures above 0°C. The best fit of T_s from these studies is 227.4 K at the lowest concentrations. The consistency of these results is an important indication that the supercooled water data obtained in fine capillaries is in no way influenced by contamination effects, surface effects, etc. provided excessively fine capillaries are avoided.(46)

An interesting feature of the conductivity fits is that the exponent best fitting the data is significantly lower than those characterizing the slopes of the plots in Figure 8. In the case of dilute HCl solutions, Speedy et al(109) have used the chloride ion conductivity derived from the KCl data to extract a conductivity vs. temperature relation for the proton λ_{H+}. The proton, of course, is restricted to a peculiar mode of transport which links its behavior closely to the hydrogen bonded network of the solvent. In this case, the Eq. (2) with an exponent of unity describes all the data, and yields perhaps more convincingly than in any previous study, the value of the singular temperature, $T_s = 227.4K$.

In related work, Speedy et al(91) have tested the effects on the dilute KCl conductance of ethanol additions while exploring, for transport properties, the solute effect described earlier in this review in connection with thermodynamic properties.(90) The interesting result, found also by Halfpap and Sorensen,(89) see below, emerges that although the density fluctuations, judged from the behavior of the compressibility, are rapidly damped out by such additions,(71) the anomalies in the conductivity are enhanced. There is slight evidence for an actual increase in the singular temperature. Certainly the latter is not depressed as it is by additions of ionic salts.(107) In analyzing these data Speedy et al introduced the notion of background terms in the transport equation. Choosing a VTF equation (Eq. (4) above) form for the latter, they obtained data fits to the expression

$$1/\sigma = (T/T_s - 1)A \exp[-B/(T-160)] \qquad (5)$$

in which the exponent in the singular term of Eq. (2) now has the value of unity. The implication is that exponents differing from unity in fits to Eq. (2) reflect the presence of background terms, as was the case for thermodynamic properties.(2) This would be consistent with the notion(110) that both transport and thermodynamic properties are analytical functions of temperature about the singular temperature, an assumption which yields, by a Taylor expansion, a leading term in (T/T_s-1) , i.e. $\gamma = 1.0$.

A justification for this form of background is provided by an analysis of binary solution data on the system H_2O + hydrazine performed by Oguni.(111) Following the solution extrapolation principles developed by Oguni and Angell,(87) viscosities of hydrazine + water solutions measured by capillary viscometry at temperatures ranging down to $-35^{\circ}C$ were extrapolated to zero water content to obtain a viscosity—temperature relation for 'normal' water. The 'normal' viscosity vs. temperature relation for water was found to conform to the VTF equation with best fit parameters similar to those found from the high pressure studies relaxation time in Table 1 above, viz., T_o = 143 K, B = 409 K . The fit using the parameters extrapolated from the high pressure studies, T_o = 128 K , B = 520 K is only slightly poorer, and the latter value is more consistent with an independent estimate based on a thermodynamic vanishing entropy analysis.(41)

The use of solvent effects for diagnosing the structural characteristics associated with anomalies in pure water has also been introduced by Halfpap and Sorenson,(89) who used both ordinary capillary viscometry, and light-scattering from latex spheres, to observe the effect, of ethanol on the one hand and hydrazine on the other, on the viscosity of water at low temperatures. Here the interesting observation was that the completely hydrophilic molecule hydrazine reduced the viscosity of water quite sharply, while ethanol with its hydrophobic ethyl group strongly enhanced the viscosity (as it did the resistivity). Thus, although hydrogen bonding per se is not destroyed by the addition of hydrazine, the special hydrogen bonding patterns which are associated with the anomalies in water are dismantled. By contrast, they are, if anything, enhanced by the presence of the hydrophobic group. This, like the results of Speedy _et al_,(46) strongly hints that the cage-like water molecule arrangements known to form around hydrophobic groups, are the important structural elements associated with the anomalous character of low temperature water. This is essentially the picture anticipated in the analysis of Stillinger.(85)

Finally in this section we mention some very recent results by Easteal and Woolf,(112) which although not strictly dealing with supercooled conditions, are so diagnostic for low temperature water structure that they must be included in this discussion. Easteal and Woolf introduced the pressure variable into the study of tracer diffusion of guest molecules and found striking differences in the pressure coefficients. Thus, where the self-diffusion coefficient of water increases with pressure, leading to the expectation that guest molecules would exibit a comparable dependence, Easteal and Woolf find that the diffusivity of the non-hydrogen bonding molecule acetonitrile, CH_3CN, actually decreases with increasing pressure, a direct violation of the Stokes-Einstein equation. Ethanol diffusivity, on the other hand, showed an even more rapid increase with pressure than does water itself. The only previous result comparable to the observation for acetonitrile is that reported for interstitial ions in open network liquid silicates where both computer simulation studies(113) and experimental observations on the responses of calcium diffusion and viscosity(114) to pressure increases in closely similar liquid silicates, show the interstitial ions decreasing in mobility while the liquid fluidity increases. The relationship between liquid silica (and open framework silicates) and water has recently been emphasized,(113) the Easteal-Woolf observations are presumably to be interpreted as for the liquid silicate interstitials. In other words, their observations suggest the existence in liquid water at low temperatures of cage-like structures through which non-hydrogen bonded molecules can slip at low pressures but in which the channels become constricted and inhibiting as pressure increases. The greater increase of D(ethanol), on the other hand, implies as Sorensen suggested(89,90) the location of EtOH molecules in the most open, highly structured microregions of the liquid. These are the regions that respond most rapidly, according to LeChatelier's principle, to increases in pressure, thereby releasing the guest molecules for more rapid diffusivity increases, on average, than for the host molecules.

Simulations and Theoretical Interpretations

Before discussing directly and in detail the various schemes within which the above described properties may be interpreted, it is appropriate to introduce some of the additional general observations made possible by molecular dynamics calculations. Although further reference to analyses of the output of these calculations in support of the various theoretical schemes will be made below, certain items of interest in the sense of additional data input should first be described. For the case of the deep supercooled regime, simulations are not extensive: due to the long structural equilibration times involved, the region is out of reach of all but the most powerfully funded simulationists. (To experimentalists who find themselves sometimes irked by the apparent ease with which current simulation programs can reproduce and then interpret their most painstakingly achieved results, this situation comes as a mild relief.)

Apart from one of the early runs in the classic study of Rahman and Stillinger(50,115) – a run which settled down, at constant energy, to a final temperature of $-8.2^{\circ}C$ – the only significant penetration of the supercooled regime obtained using an accurate pair potential has been that from NPT ensemble Monte Carlo calculations using the TIPS 2 potential recently reported by Jorgensen.(116) The results for $25^{\circ}C$ and $75^{\circ}C$ were in excellent accord with experiment. At $-30^{\circ}C$, the intensive thermodynamic properties C_p, α, and κ_T, proved very slow to converge and, while qualitatively maintaining a correct trend and exhibiting an expansivity zero (i.e., density maximum), failed to register the large increases observed experimentally, presumably due to the excessive equilibration time requirements. Monte Carlo calculations suffer the same ergodicity problems as molecular dynamics calculations, and since the relaxation times in experiment increase by more than an order of magnitude between 25°C and -30°C the computational difficulties can be appreciated. However, even without complete equilibration being assured, the results at -30°C were sufficient to underscore the importance of certain of the key trends as the supercooled regime is entered. To this author, the most striking feature is the rapid narrowing, and peak value increase, in the O-H...O angle, coupled with the large increase in 4-bondedness - a requirement for anomalous density decreases at low temperatures. These rsults indicate a way of distinguishing tetrahedral liquid networks with 'sharp' liquid state density maxima, from those with weak or absent maxima(117) (H_2O, 165° (sharp) SiO_2, 140°, (weak):GeO_2, 133°, (absent).

At a more qualitative, but still valuable, level the properties of a wide region of PVT space for water have been mapped out in a study by Yamamoto and co-workers,(118) who have paid considerable attention to the supercooled regime. These workers used a particularly simple potential, which permitted very fast Monte Carlo calculations without sacrificing, it would seem, the essential requirements for reproducing 'water-like' behavior. The equation of state obtained from fits to state points evaluated over wide ranges of temperature and pressure, reproduces the experimental observations of C_v maxima(69) at low pressures and constant pressure divergences in the $_T$ and α with T_s values remarkably close to those yielded by experiment.(34,40,107)

A refinement of the use of simulation which is being developed to clarify the meaning of 'structure' in water (and other liquids) is currently being described by Stillinger and Weber.(119) The principle here is to use the ability of computer simulation to quench instantaneously a typical configuration of a liquid such that it drops into the nearest minimum on the 3N+1 dimensional potential energy surface conceptualized by Goldstein for his extended discussions(120) of viscous liquids, the glassy state and the Kauzmann paradox(121) some time ago. The liquid system, especially at lower temperatures and longer relaxation times is conceived as spending most of its time vibrating anharmonically in the vicinity of such minima, the depth of the minimum depending on the temperature. Stillinger and Weber have succeeded in reducing this picture to a formal representation of the partition function in which the vibrational and configurational contributions to the configuration integral are uniquely separated. The idea behind the Stillinger-Weber configuration quench simulations is that, in this way the energies of these structures, and their characteristic geometries can be determined <u>in the absence of vibrational smearing</u>, by examining such quenched states and thus the broad features of the potential surface can be mapped and the configurational part of the partition function properly evaluated. The structures involved in the cooperative region below ~-20°C, and the origin of the cooperative effect, should become much clearer from the examination of such 'hidden structures'(119) than it can be from the instantaneous liquid configurations or even vibrationally averaged configurations on which current analyses are being conducted.

We should note, in connection with the validity of the Stillinger-Weber endeavor, that effectively instantaneous quenches are routinely performed by glass scientists when they anneal glasses to constant 'fictive' temperature over periods of days, and then cool to room temperature. Relative to the relaxation time, this cooling changes the temperature so rapidly that no structure change other than by vibrational contraction can occur. This is possible because the system near its glass transition temperature is already confined to exploring such deep minima that it has no possibility of escaping, during the final cooling to room temperature, the minimum above which it is located at the time of quenching. (At the Kauzmann temperature it would, in principle, be in the single lowest minimum on the surface - which it would in principle take an infinite time to find!) By instantaneous quenches in molecular dynamics simulations, systems which exist in palpably <u>fluid</u> states can be trapped in one of (the nearest one) the much shallower and more frequent minima characteristic of the higher levels of the potential surface. Such quenches have been carried out for hard spheres and liquid KCl to establish the 'loose random packing' limit(119(a)) and they are much needed for the case of water, particularly from supercooled states to help elucidate the 'significant structures' problem.

In the meantime we examine the various models which have been proposed to help understand the supercooled regime, recognizing that a model adequate to deal with this extreme regime will probably have much to say about the stable state of water in which the greatest interest naturally resides.

For reasons of space, our treatment cannot be comprehensive, and we will emphasize the approaches we consider most profitable and interesting.

At this time there appear to be two distinct classes of model being developed:

(1) those which focus on the statistical consequences and correlations, which develop from <u>random</u> bonding patterns subject to the geometrical restriction of a maximum of 4 bonds per molecule.

(2) those which seek to identify some cooperative principle which <u>directs</u> the course of bond pattern development.

Additionally there is some support for a 'heterophase fluctuation' interpretation of the phenomena in which increases of heat capacity, for instance, are associated with production within the liquid of ultra-micro prenucleation crystallites(9,72) with approximately the enthalpy per mole of the solid phase (ice I). However, this interpretation will not be discussed further here because the present author is unable to understand why, if this approach were correct, the phenomena approaching the homogeneous nucleation temperature are not manifested when other liquids, or even an 80% water + 20% H_2O_2 solution, are supercooled.(2)

We should note also that the 'background' liquid on which the anomalies superimpose, seems to be very well described by the Sceat-Rice random network model.(23) These authors suggest that the absence of anomalies in the temperature regime -45 to 25°C is due to the absence of ring closures in their Cayley tree-based model. This excludes the possibility of large density fluctuations since without ring closures the bulky structures characteristic of ice I and the clathrates cannot arise, and the density maximum will not appear.

Predominant among models of Class 1 is the 4-bonded molecule percolation model of Stanley and Teixeira (ST)(81) which has been much discussed recently.(54,103,118) This model examines the statistical consequences of increasing 'bond' connections - defined by an energy cut-off criterion - which form with decreasing thermal energy, and focusses attention on the adjacency of molecules which are connected to 4 other molecules. Using an ice I_h lattice and random placement of bonds, ST show how clusters of 4-bonded molecules naturally form and rapidly proliferate as the total fraction of possible bonded sites approaches unity. If, as seems reasonable (and as anyway can be established by analysis of an ST2 simulation configuration even without determination of 'hidden' structure(122)), the volume per molecule in a 4-bonded cluster is greater than for molecules outside, or on the edge of, such a cluster, then the features of water in the supercooled region can be qualitatively and (except for the lowest temperatures) almost quantitatively accounted for. The transport property temperature dependences in this model are assumed to be determined by the changing concentration of 1- and 2-bonded molecules, an approach which seems to this reviewer to be an somewhat arbitrary and simplistic treatment of what are surely complex and cooperative processes, but which has the advantage of describing the data with a minimum of input.

In a current study of ST2 water characteristics Geiger and Stanley(123) have found that the percolation exponents for the disordered continuous system are essentially the same as those known for random bond percolation on 3-dimensional ordered lattice. This tends to vindicate the original ice lattice-based formulation of the model.

The Stanley/Teixeira model represents a controlled return to the old and discredited cluster models of water with the important difference that the nature of the matrix in which the 'patches' exist is clearly described and is a continuously and variously bonded assemblage (since, as argued some time ago by Gibbs _et al_(124) and confirmed by MD configuration analysis,(125) the percolation threshold for single-bonded connectedness is well above the boiling point.) Furthermore, the bulky patches of the ST model _do_ exist in the MD configurations of ST2 water according to a recent analysis of Geiger _et al_,(122) and have the dimensions expected from the correlation length of density fluctuations measured by Bosio _et al_'s small angle X-ray scattering studies.(54)

It is a feature of the ST model that, while a percolation threshhold for 4-bonded molecules appears to be imminent in the vicinity of -45°C, no singularity in the thermodynamic properties, such as has been indicated by the various data fits reviewed in early sections of this review, is predicted by the model. Rather, a maximum in the isothermal compressibility is predicted to lie at about -60°C. This is in the vicinity of the temperature at which the growth of the 'patches' to a dimension where nucleation of ice is probable (although the 4-bonding statistics could be equally well worked out on a random network or a clathrate-hydrate lattice probably with little difference in outcome.) A reason for some concern with the ST treatment is that the distribution of 1-, 2-, 3-, and 4-bonded molecules predicted by the model, while according quantitatively with the output of the Rahman Stillinger ST2 computations, seems to accord equally well with the distributions analyzed from other simulated waters, even Yamamoto water,(118) though the calculated physical properties of the simulated waters are markedly different.

To obtain quantitative results, the ST model assigns an excess volume per mole to molecules involved in 4-bonded patches, and then uses the quantitative assessments of the fraction of the molecules in such patches in relation to temperature to predict the temperature dependence of properties such as the compressibility. This leads to the prediction of a maximum in κ_T at deep supercooling. An alternative way of producing such a result with a single parameter within a random bonding model and with a continuous relation between bonds per molecule and volume, is via a volume-cooperative bond-lattice description in which the ΔV of the simple two state equation(82) is replaced with a $\Delta V_o/N_x$ where N_x is the fraction of possible bonds broken at the temperature under consideration and ΔV_o is the volume increment per bond at high temperatures. This approach was considered briefly in ref. 40, but not developed because it did not account for the singularity apparently implied by the various water anomalies reviewed. Better correlation with spectroscopic data(2,49) would be obtained if the volume increment per bond were to change sign at intermediate extents of bonding, e.g., by writing

$$\Delta V = -\Delta V_o/N_x + 2\Delta V_o \qquad (6)$$

The problem of describing the existence of supercooling within the lattice models is briefly considered by Meijer et al(126) but no attempt is made to describe the properties of the supercooled state.

Turning to Class 2 (cooperative) models within which singularities might be sought we encounter two discussions by Stillinger.(85,127) In ref. 127 Stillinger considers the effect of system size on such properties as melting point and density maximum and develops the partition function for an N molecule system in terms of two order parameters one of which, Ψ, describes the 'ice-likeness' of the system (later simplified for discussion in terms of the concentration of (bulky) bicyclic octamers) and the other Θ the potential energy (+pV) for the molecules. He then constructs a $\Psi - \Theta$ surface, and shows how its form implies the possibility of a 'catastrophe' during supercooling of the liquid with diverging fluctuations in the parameter, Stillinger discusses the conditions under which a liquid (water) could follow this path. The essential feature is the existence of an attraction between bulky (high Ψ) elements of the structure.

In ref. 85 Stillinger discusses a variety of possible molecular configurations which could be responsible in cold water, for locally bulky microregions. He notes that typically these alternative structures, which consist of frameworks of 'good' or unstrained hydrogen bonds, will have faces which can match to one another also without strain, hence should experience, in otherwise strained surroundings, a net attraction for one another. Since they are themselves internally low in energy they will tend to both increase in number and to cluster as temperature decreases. Thus the ingredients for an accelerating cluster growth, with an eventual divergence in cluster size at a singular temperature T_s are present. The formation of the infinite ramified cluster at the singular temperature corresponds well with the notion of 'long range ordering of strong hydrogen bonds' introduced by the author and colleagues(18) to rationalize the existence of a lambda-like anomaly they felt was implied by their anomalous heat capacity and proton chemical shift studies, combined with the existence of vitreous ice.

The question to be decided is whether or not the infinite cooperative cluster of the Stillinger model (which in the ST model is the percolation threshold for randomly formed 4-bonded molecule clusters - the difference is not great) can be reached without first encountering a <u>limit of mechanical stability</u>. This alternative possibility has been the particular province of R. J. Speedy who first introduced the idea in the supercooled water context in a joint paper with the author(40) and has since developed it in a particularly interesting and provocative paper in which the properties of both supercooled and superheated water are tied together into a single overall phenomenological scheme.(110) We will elaborate on this in a concluding section below, but first will continue the discussion of cooperative principles in water since the basis for a long range correlation effect is necessary to the distinction between water and other liquids in Speedy's overall scheme.

For his cooperative effect Speedy takes inspiration from Keppler's 1611 exhortation to biologists(128) to seek the origin of the near-ubiquitous incidence of 5-sidedness in plants in the sap that runs in their structures. In a current article Speedy refines the argument for geometrical cooperativity outlined earlier,(40) and argues that <u>pentagonal</u> rings have a natural propensity for self-replication, and that the structures they form by their nature exclude much volume to other molecular centers, i.e., tend to generate low density patches in the liquid. Some support for the easy self-replication notion may be drawn from the observation that gas hydrates may be formed with many fewer incorporated guest molecules when freezing is rapid, (D. Glew, private communication, 1977) i.e., clathrate structures in the rapidly quenched liquid appear to propagate more efficiently than does Ice I_h (this leads to some concern about the conformations characteristic of water vitrified in the presence of small hydrophobic molecule cryogens(20,21,24)). In a pentagonal ring each pair of molecules finds its components in an eclipsed conformation whereas in the hexagonal rings of Ice I_h all pairs are staggered. This distinction provides a basis for ongoing (Speedy, R. J. and Mesei, K., private communication) analysis of computer-generated configurations for trends in Ice I_h-like vs. pentagonal sided clathrate structures during supercooling (Ice I_h has two eclipsed and four staggered pairs in its hexagonal ring elements).

STABILITY LIMIT CONJECTURE The basic idea here is that the large fluctuations in density and entropy encountered in the deep supercooling region reflect the approach of the system to a state of mechanical, as opposed to thermodynamic, stability. At the limit, commonly known as the spinodal, the fluctuations grow without limit carrying the system completely out of its initial phase space, the molecules reassembling in some other region which will tend to be the nearest stable phase. The best known case is the behavior of a superheated liquid at a pressure less than the critical pressure. Here a small pure droplet of water at 1 atm. presure, for instance, will spontaneously rupture at 280°C because of its close approach to the spinodal predicted, from the most accurate equations of state, to lie at 324°C (it is actually an imprecise <u>region</u> of temperature smeared by fluctuations, rather than a point, according to current theory(129)). Speedy(110) has taken the superheated liquid spinodal as a point of departure for developing a global picture for the mechanical stability boundary on water. In this view the high temperature spinodal which, at ~320°C crosses into the negative pressure region, is finally bent back towards positive pressures due to the growing importance of the cooperative 4-bonded molecule 'ordering' phenomenon.

By assuming that the pressure can be expanded along an isotherm as a Taylor series in $\rho-\rho_s$ about the spinodal at P_s,ρ_s , Speedy obtained a simple equation of state. This describes the precisely known PVT properties of water in the 0-100°C, 0.1-100 MPa region with surprising accuracy, and yields P_s,ρ_s as best fitted parameters. The variation of P_s with T is shown in Figure 9.

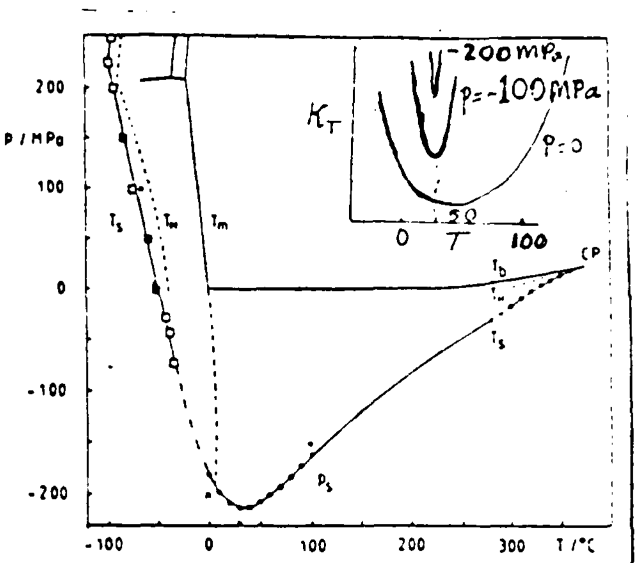

Figure 9 Estimated locus of the limit of stability for water T_s or ρ_s, shown in relation to the equilibrium phase diagram (T_m = melting line, T_b = boiling line, CP = critical point) and the experimental kinetic limits of stability T_H: (●) values of T_s and ρ_s for H_2O from Tables I–III ref 110. (□) values of T_s − 7 °C for D_2O from Table III (column 2) and Figure 4; (+) ρ_s(100 °C) calculated from ref 20; (×) ρ_s(0 °C) and ρ_s(25 °C) estimated by Yayanos; (T_H) values from Table I for superheated H_2O and Table III for supercooled water; (T_m) is extrapolated to terminate at ρ_s(5 °C) = −190 MPa as discussed in section 2.3. (After. Speedy, ref 110. Reproduced by permission)

Insert. Behavior of K_T at negative pressures.

ρ_s, the limiting low density for the liquid state turns out to be constant in the range 0-100°C at essentially the density (0.89 ρ_{iceIh}), of the empty Type I clathrate hydrate structure!

The extremum in P_s occurs at 35°C (P_s = -212.4 MPa), which is also the temperature of the density maximum extrapolated to that (negative) pressure, as thermodynamic analysis requires.(110) Similar behavior is predicted by extrapolations of the N.B.S. multiparameter equation of state for water to negative pressures (Lester Haar, private communication: see also ref. 130 for equation of state details). We would point out that water in the vicinity of the P_s extremum at 35°C is inherently schizophrenic, being unable to decide whether its density fluctuations are tending to take the system in the direction of collapse to the vapor (one large void) or collapse to a clathrate hydrate (many small <u>ordered</u> voids). The behavior of $_T$ vs. T in Figure 27 (P = 0.6 kbar) in the paper on simulated water by Yamamoto and co-workers,(118) (c.f. Figure 3 in ref. 74) - which would collapse to two vertical infinitesimally spaced lines on approach to P_s, at 35° (see Figure 9 insert) - indicates the extreme case of a thermodynamically anomalous fluid!

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